



Study of Graphene-Immobilized Metal Nanoparticles for Catalytic Hydrogen Generation

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博士論文

Study of Graphene-Immobilized Metal Nanoparticles for Catalytic Hydrogen Generation

グラフェン固定化金属ナノ粒子触媒による水素発生
に関する研究

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宋福展

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Fuzhan Song

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Abstract

This dissertation is focused on the immobilization of ultrafine metal nanopartilces (NPs) on alkalized graphene as catalysts for the hydrogen generation from liquid-phase chemical hydrogen storage materials. In the introduction part, we described the advantages of liquid-phase chemical hydrogen storage materials. In addition, we also introduced the effect of support materials on highly efficient dehydrogenation. At the subsequent parts, we successfully immobilized ultrafine noble metal (Pd), non-noble metal-based (PtNi) and non-noble bimetallic (CuCo) NPs on diamine-alkalized reduced graphene oxide, which exhibited excellent catalytic performance for the dehydrogenation of these chemical hydrides (such as formic acid, hydrous hydrazine and ammonia borane). Especially the synthesized Pd catalyst showed the best catalytic property for the dehydrogenation of formic acid compared to other heterogeneous catalysts as reported so far. The main research results of this dissertation are summarized as follows.

(i) Diamine-alkalized Reduced Graphene Oxide: Immobilization of Sub-2 nm Palladium Nanoparticles and Optimization of Catalytic Activity for Dehydrogenation of Formic Acid

An efficient strategy to downsize the metal NPs and provide basic sites located nearby for optimizing the catalytic performance of the alkalized reduced graphene oxide-supported metal catalysts has been explored, for the first time, by the potent alkalization of rGO with diamine. By virtue of the coordination effects between the metal ions and the amine groups ligated to rGO, monodispersed Pd NPs (1.5 nm) can be facilely anchored on the diamine-alkalized rGO by a simple reduction approach. The

diamine groups not only highly dispersed the GO against ordered restacking, but also provided coordinating groups to combine with Pd^{2+} ions, resulting in rich and uniform nuclei and a controlled growth process of Pd on rGO. The turnover frequency (TOF) for heterogeneously catalyzed decomposition of formic acid reached 3810 h^{-1} at 50°C , the highest value ever reported for heterogeneously catalyzed FA decomposition, comparable to the most active homogeneous catalysts.

(ii) Monodispersed PtNi Nanoparticles Deposited on Diamine-alkalized Graphene for Highly Efficient Dehydrogenation of Hydrous Hydrazine at Room Temperature

The strategy has been further explored to immobilize the PtNi NPs on diamine-alkalized reduced graphene oxide. By the virtue of the alkalization of rGO with diamine, monodispersed PtNi NPs (2.5 nm) can be facilely deposited on the alkalized rGO. The resultant $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ showed an excellent catalytic activity with 100 % H_2 selectivity for the dehydrogenation of hydrous hydrazine under mild conditions, with a TOF value of 903 h^{-1} at 30°C and 2056 h^{-1} at 50°C , respectively. The excellent performance on catalytic activity could arise from the synergic interactions between Pt and Ni. In addition, the diamine-alkalized graphene also promoted electron transfer to form the electron-rich NPs, which could efficiently facilitate the cleavage of the N-H bonds and thus improve the catalytic property.

(iii) Monodispersed CuCo Nanoparticles Supported on Diamine-Alkalized Graphene as a Non-noble Metal Catalyst for Dehydrogenation of Ammonia Borane

Non-noble bimetallic CuCo NPs were successfully supported on diamine-alkalized

reduced graphene oxide. Compared to other supports materials, the catalyst synthesized with the alkalized rGO displays remarkably enhanced catalytic performance for dehydrogenation of ammonia borane with TOF of $163 \text{ mol}_{\text{H}_2}\text{mol}_{\text{cat}}^{-1}\text{min}^{-1}$ at 50 °C. The synergic effect between ultrafine Cu and Co NPs played an important role on improvement in dehydrogenation of ammonia borane. As an effective strategy, it provided an opportunity to immobilize ultrafine non-noble metal NPs on GO, which had tremendous application prospect in various catalytic fields.

In summary, this dissertation is focused on the fabrication of ultrafine metal NPs by taking the advantages of the alkalization of rGO and the discussion of their catalytic applications for highly efficient hydrogen generation from liquid-phase chemical hydrogen storage materials (such as hydrous hydrazine, formic acid and ammonia borane).

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Chapter 1

Introduction

The dramatic climate changes caused by greenhouse gas emission and ever-increasing need for energy have spurred international interest in developing renewable energy technologies.¹ Essentially, how to supply sufficient and sustainable energy has become one of the most important challenges of this century. Among many energy carriers, hydrogen (H_2) has attracted increasing attentions and been considered as the promising candidate for satisfying the growing demand for the sustainable and clean energy supply.²

Hydrogen, as one of the most abundant element on Earth, has high energy density, three times as much as that of petroleum: heating values are 47.2 MJ kg^{-1} (11.1 kWh kg^{-1}) for petroleum and 123 MJ kg^{-1} (33.3 kWh kg^{-1}) for hydrogen.³ For example, when a modern, commercially available car runs 400 km, it could burn about 24 kg of petrol in a combustion engine; to the same range, 4 kg of hydrogen is needed for the electric car with a fuel cell. In addition, the only product of the fuel cell process is water, which could effectively reduce the greenhouse gases emission.^{2a} Therefore, the U.S. Department of Energy (DOE) has established the targets for on-board H_2 storage systems (fuel-cell power) in future vehicles. Until to 2017, the H_2 storage aims in gravimetric capacity and volumetric capacity are 5.5 wt% and 40 g L^{-1} , respectively, at 50°C under 100 atm delivery pressure. The DOE targets are for a full system, which contains materials, insulation, balance-of-plant components and so on.⁴ However, there is no any candidate material to satisfy the DOE target yet.

1.1 Physical hydrogen storage

As a simplest way, storage hydrogen in a cylinder with high pressure has low energy density and therefore could not meet the demand of fuel cell application. Many investigations are focused on storage hydrogen on porous materials with large surface area (such as carbon, metal organic framework, silica, polymer and so on).⁵

Nikamp *et al.* discussed the hydrogen storage capacity for some carbonaceous adsorbents with a large volume of micropores by physical absorption at 77 K and 1 bar.⁶ They also discussed the relation between hydrogen storage amount and surface area. It was found that the carbonaceous adsorbents (e.g. activated carbon) have a more optimistic enhancement than other materials due to stronger intrinsic interaction with hydrogen. Hydrogen adsorption amount could be achieved at 560 ml STP g⁻¹ by tuning the pore diameter and storage pressure. Rosi *et al.* reported the hydrogen physical adsorption by metal-organic framework-5 (MOF-5) with a composition of Zn₄O(BDC)₃ (BDC is 1,4-benzendicarboxylate). The MOF-5 has a cubic three-dimensional structure, which has high surface area of 3000 m² g⁻¹. They found that the hydrogen uptake amount of MOF-5 could achieve at 17.2 hydrogen molecules per formula unit (4.5 wt %) at 77 K, which is attributed that hydrogen could be bound to zinc and the BDC linker. Even at room temperature, the hydrogen uptake amount of MOF-5 also increases with pressure, achieving 1 % at 20 bar.^{7,8} However, hydrogen physical absorption on porous materials still suffers a low hydrogen absorption capacity at ambient conditions.

1.2 Chemical hydrogen storage

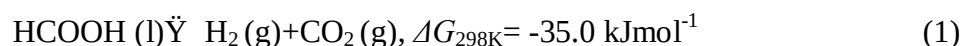
Compared with the physical adsorption, the chemical hydrogen storage is considered as a more promising strategy for the application of hydrogen fuel cells, which could efficiently store hydrogen in the form of chemical bonds and safely release a large

amount of hydrogen gas.⁹ The liquid-phase chemical storage materials have attracted much attention due to their low reaction temperature, high catalytic kinetics and stability. In addition, they also provide the possibility to use the existing infrastructures for gasoline. Among the chemical hydrogen storage materials, formic acid, hydrous hydrazine and ammonia borane have become the most promising candidates due to their high hydrogen contents, stability and safe handling under ambient conditions.¹⁰

1.2.1 Chemical hydrogen storage materials

1.2.1.1 Formic acid

Formic acid (FA, HCOOH) as a non-toxicity and stable liquid under ambient conditions has high hydrogen content (4.4 wt%) and volumetric hydrogen density (53 g L⁻¹). In addition, the only products of CO₂ and H₂ can be catalytically reduced to FA on a large scale, achieving the sustainable and reversible energy storage. Therefore, FA, as an ideal hydrogen carrier, has tremendous research interests.¹¹ The decomposition of FA can follow two possible pathways:

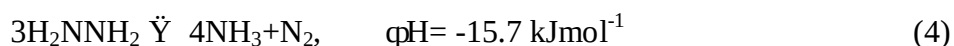
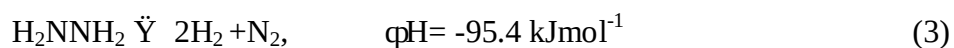


The latter dehydration is undesired and should be strictly controlled because the CO impurity is toxic to fuel cell catalysts.¹² Up to now, various catalytic systems have been examined and rapid dehydrogenation from FA has been achieved. Recently, Beller and co-workers prepared a series of Ru-based homogeneous catalysts such as RuCl₃·xH₂O, RuBr₃·xH₂O, [RuCl₂(benzene)]₂, [RuCl₂(p-cymene)]₂ and [RuCl₂(PPh₃)]₃.¹³ They investigated their catalytic properties in the presence of amine additives at 40 °C and found that the kind of amine additive and its ratio to FA played an important role in the

improvement of FA dehydrogenation. The 2NEt₃-5HCOOH system showed excellent catalytic property. More recently, Laurenczy, Beller and co-workers have synthesized an iron catalyst system with excellent catalytic activity using Fe(BF₄)₂·6H₂O and tris[(2-diphenylphosphino)ethyl]phosphine [P(CH₂CH₂PPH₂)₃, PP₃]. Without any additives or base, the iron catalyst system exhibited excellent catalytic performance with a turn number of 92000 at 80 °C.¹⁴

1.2.1.2 Hydrous hydrazine

Hydrous hydrazine, such as hydrazine monohydrate (N₂H₄·H₂O), has been considered as a promising hydrogen carrier for storage and transportation owing to its high hydrogen content (8.0 wt%), easy recharging, relatively low cost and the only production of nitrogen in addition to hydrogen via a complete decomposition.¹⁵ Moreover, as a liquid-phase material, the hydrous hydrazine has advantages of using the existing liquid-based distribution infrastructure, which is more competitive than the solid chemical hydrogen storage materials.¹⁶ However, the decomposition to ammonia (NH₃) (eqn 4) should be avoided, because the presence of NH₃ could decrease the yield of hydrogen. In addition, the NH₃ impurities could also damage the Nafion membrane and poison the catalysts. Therefore, it is very important to develop efficient catalysts with 100 % H₂ selectivity for the dehydrogenation of hydrous hydrazine

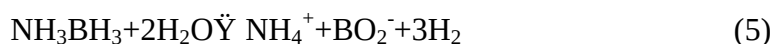


Recently, many mono- and bimetallic catalysts for the dehydrogenation of hydrous hydrazine have been synthesized. The Ni-based bimetallic catalysts especially showed good catalytic performance with high H₂ selectivity at room temperature. The iridium

catalyst supported on alumina is the first report on the dehydrogenation of hydrous hydrazine.¹⁷ From 2009, Xu and co-workers has done a lot of work on the decomposition of hydrous hydrazine and synthesized various mono- and bimetallic catalysts.¹⁸ It was found that the catalytic performance was determined by metal ratio and the dehydrogenation of hydrous hydrazine with 100 % H₂ selectivity was achieved by the surfactant-stabilized Ni-based bimetallic catalysts. In addition, the addition of NaOH could also play an important role in the improvement of catalytic property. In the presence of NaOH, the hydrogen selectivity for Ni_{0.45}Pt_{0.55} catalyst obviously improved from 61 % to 86 %, which was attributed that the alkaline environment was benefited for N-H bonds cleave.¹⁹

1.2.1.3 Ammonia borane

Ammonia borane (NH₃BH₃, AB) has attracted interests due to its high gravimetric hydrogen capacity of 19.6 %, volumetric hydrogen capacities of 146 g L⁻¹ and nontoxicity.²⁰ Moreover, AB is soluble in polar solvents, such as water, N,N-Dimethylformamide, ethanol and so on, which is important for safe handling under mild conditions. According to eqn (5), one mole of AB can release three moles of hydrogen (H₂) via a complete hydrolytic reaction:



In order to achieve a complete hydrolysis of AB, various noble metal-based catalysts have been extensively investigated, where Pt, Ru and Rh exhibited the best catalytic kinetics.²¹ However, the limited resources restrict their practical applications. Alternatively, the cost-effective non-noble metals, such as Co, Fe and Ni, have attracted increasing attentions.²² Metin *et al.* prepared monodisperse nickel nanoparticles (NPs)

supported on Ketjen carbon by the reduction of nickel acetylacetonate with borane tributylamine in the presence of oleylamine and oleic acid.²³ It is interesting that the presence of borane tributylamine was benefited for the formation of uniform nickel nucleation and growth, leading to the monodispersed Ni NPs on Ketjen carbon with average size of 3.2 nm. The synthesized catalysts showed high catalytic property with a TOF of $8.8 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{min}^{-1}$ even at room temperature. Therefore, the synthesis of non-noble catalysts with excellent catalytic performance at ambient temperature is urgently important.

1.2.2 Support materials

It is known that the structure and property of support materials play an important role in improving catalytic performance. Until now, various types of support materials have been reported, such as silica, MOFs, graphene oxide and so on.

1.2.2.1 Silica

As the porous materials, mesoporous silica has attracted intense interest due to its high surface area, excellent thermal stability and proper pore size.²⁴ Up to now, there are many reports on using silica as the support materials. Especially for functional silica, it could be considered as a promising new class of supports for hosting nanoparticles.²⁵ With amine grafted silica, Zahmakiran *et al.* synthesized a series of metal nanocatalysts, which showed excellent catalytic performance for the dehydrogenation of formic acid.²⁶ Jiang *et al.* prepared the AuNi NPs of 3-4 nm embedded in silica nanospheres of 15 nm.²⁷ The synthesized catalysts showed high catalytic activity and long durability in the hydrolysis of ammonia borane.

1.2.2.2 Metal-organic frameworks

Metal-organic frameworks (MOFs), is a kind of polymers constructed by the coordination between metal ions and organic ligands.²⁸ Yaghi *et al.* has formally proposed the concept of metal-organic frameworks.²⁹ Utilization of the coordination of organic linker and inorganic vertices, their structures can be designed. The pore size can be tuned by controlling the length of organic linkers and maximum surface area could be up to $10000 \text{ m}^2 \text{ g}^{-1}$. Therefore, it is considered as a promising support material for metal NPs.³⁰

Up to now, various mono- and bimetallic NPs supported by MOFs have been synthesized. The liquid immersion of MOFs within metal salts solution may be the simplest and most-used method to introduce metal ion into MOFs. However, this impregnation method usually results into the aggregation the metal precursors on the external surface of MOFs. In 2012, through a double solvents method, we successfully introduced metal precursors into the pores of MIL-101. After the thermal reduction with H_2 , the ultrafine Pt NPs were encapsulated within the pores of MIL-101 without deposition on the external surface of MOFs. Due to the confinement effect of the pore of MIL-101, the ultrafine Pt NPs with size of 1.8 nm were obtained, which showed an excellent catalytic activity. Since then, a series of metals such as AuNi, AuCo and CoCu NPs were also successfully introduced into MIL-101.³¹

1.2.2.3 Graphene oxide

Graphene is consisted of monolayer carbon sheet with a hexagonal packed lattice structure. At 2004, Geim *et al.* at Manchester University firstly prepared the single-layer graphene from graphite by mechanical exfoliation technique, which led to an explosion of interest (see Figure 1).³² Now, graphene has emerged as one of the most active

research fields, which is attributed to their unique physical and chemical properties, such as high thermal conductivity, fast charged carrier mobility and strong Young modulus.³³ Especially as an ideal support, it has the advantages of hydrophilicity and large specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), which could anchor metal nanoparticles in the solution-based controlled reduction.³⁴ However, due to its two-dimensional basal plane structure and the negligible interactions between graphene and metals, it is still a major obstacle to obtain monodispersed metal particles with very small sizes on graphene.

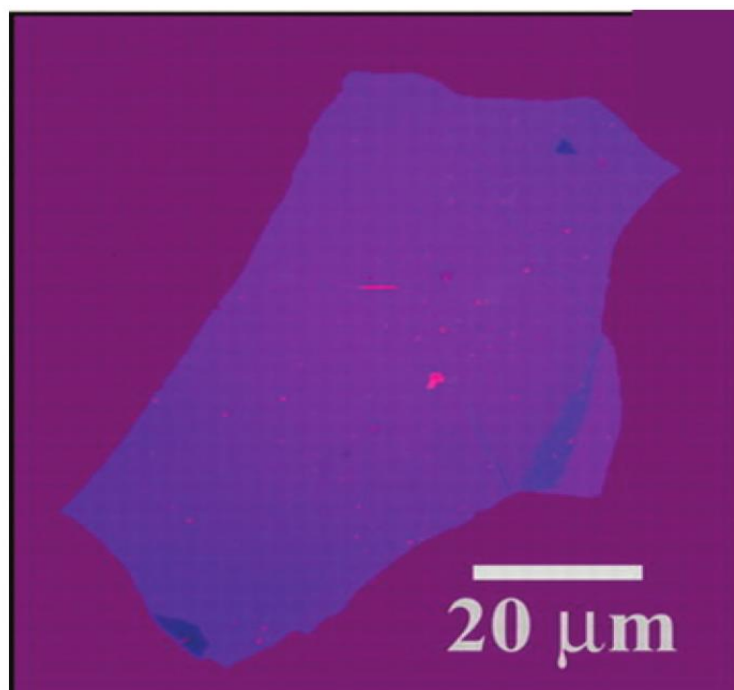


Figure 1. Single layer graphene first observed by Geim and others at Manchester University (from ref. 32).

Rational modification of the GO surfaces with electron-rich functional groups would facilitate the dispersion of the metal precursors on the support and control the size during the growth of metal NPs. Moreover, such modification may also provide an opportunity to tailor the electronic properties and alkalinity/acidity of GO, and thus optimize the catalytic performance of the resultant catalysts. Kim and co-workers has

reported that platinum clusters were successfully deposited on DNA functional GO surface.^{35a} Using GO functionalized with the DNA functional groups, the ultrafine platinum nanoclusters with size of 1.4 nm have been obtained. In addition, the platinum nanoclusters supported on DNA-GO exhibited excellent electrochemical property for oxygen reduction reaction. The long-term cyclic voltammetry (10000 cycles) and stable durability (10000 cycles) were observed due to the noncovalent 'π-π' interactions between the DNA and GO nanosheet. Moreover, the similar modification was used to improve the electrocatalytic property for formic acid.^{35b}

It is known that the modification with amine group could efficiently improve the catalytic property. Recently, there are a few reports on support functionalized with alkaline groups. In 2012, Yadav *et al.* reported that gold nanoparticles were encapsulated in amine-functionalized silica nanospheres and the catalytic performance for formic acid could efficiently improve due to the strong metal-molecular support interaction between silica and metal catalyst.^{36a} In addition, Yamashita and co-workers synthesized a basic resin bearing $\text{-N(CH}_3)_2$ functional groups as support for immobilization of Pd NPs, which also showed the excellent catalytic property for dehydrogenation of FA.^{36b} The similar improvement are also found in hydrolysis of AB.^{36c} This is because that the alkaline groups are benefited for formation of metal NPs and improvement of synergic interaction of support and metal catalyst, leading the enhancement of catalytic property. Nevertheless, a well-defined and controllable surface modification strategy of pristine GO is still lacking.

1.3 Scope of the present work

This work is focused on the immobilization of ultrafine metal NPs, such as Pd, PtNi and CuCo, on functional graphene and the discussion of catalytic application to highly

efficient hydrogen generation from liquid-phase chemical hydrogen storage materials, including formic acid, hydrous hydrazine and ammonia borane.

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(iii) Monodispersed CuCo Nanoparticles Supported on Aromatic Diamine-Alkalized Graphene as a Non-noble Metal Catalyst for Hydrogenation of Ammonia Borane

Non-noble bimetallic CuCo NPs were successfully supported on diamine-alkalized reduced graphene oxide. Compared to other supports materials, the catalyst synthesized with the alkalized rGO displays remarkably enhanced catalytic performance for dehydrogenation of ammonia borane with TOF of 163 mol_{H₂}mol_{cat}⁻¹min⁻¹ at 50 °C. The synergic effect between ultrafine Cu and Co NPs plays an important role on improvement in dehydrogenation of ammonia borane. As an effective strategy, it provides an opportunity to immobilize ultrafine non-noble metal NPs on GO, which has tremendous application prospect in various catalytic fields. This part was described in chapter 4.

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Chapter 2

Diamine-alkalized Reduced Graphene Oxide: Immobilization of Sub-2 nm Palladium Nanoparticles and Optimization of Catalytic Activity for Dehydrogenation of Formic Acid

An efficient strategy to downsize the metal nanoparticles (NPs) and provide basic sites located nearby for optimizing the catalytic performance of the reduced graphene oxide (rGO)-supported metal catalysts has been explored, for the first time, by the potent alkalization of rGO with diamine. By virtue of the coordination effects between the metal ions and the amine groups ligated to rGO, monodispersed Pd nanoparticles (diameter ≈ 1.5 nm) can be facilely anchored on the diamine-alkalized rGO by a simple reduction approach. The turnover frequency (TOF) for heterogeneously catalyzed decomposition of formic acid reaches 3810 h^{-1} at 323 K, the highest value ever reported under ambient conditions compared to the other heterogeneous catalysts.

2.1 Introduction

Supported metal NPs, as a class of very promising nanocatalysts, have received great interest. Nevertheless, the syntheses of well-dispersed ultrafine metal NPs remain a great challenge. The structure and property of support materials are crucial for controlling the growth of metal NPs and thus improving the catalytic performance.¹ Reduced graphene oxide consisting of chemically converted monolayer carbon atoms has emerged as one of the most promising supports for metal NPs because the unique

advantage of hydrophilicity and large specific surface area of its precursor, graphene oxide (GO), makes it possible to anchor metal NPs in the solution-based controlled reduction.² However, due to its two-dimensional basal plane structure and the negligible interactions between GO and metals, it is still a major obstacle to obtain monodispersed metal particles with very small sizes on GO, where it is difficult to perfectly overcome the aggregation of NPs.³ Rational modification of the GO surfaces with electron-rich functional groups would facilitate the dispersion of the metal precursors on the support and control the size during the growth of metal NPs. Moreover, such modification may also provide an opportunity to tailor the electronic properties and alkalinity/acidity of GO, and thus optimize the catalytic performance of the resultant catalysts. Nevertheless, a well-defined and controllable surface modification strategy of pristine GO is still lacking.

Hydrogen is considered as a promising candidate for satisfying the increasing demand for the sustainable and clean energy supply. Formic acid (FA) has attracted tremendous research interest for hydrogen storage.⁴ Recently, selective and efficient decomposition of FA has been achieved with homogeneous organometallic catalysts.⁵ Compared to homogeneous catalysts, in general, heterogeneous catalysts are easily separated, controlled and recycled.⁶ For practical application, the development of heterogeneous catalysts with high performance for hydrogen generation from FA is urgently desired. Herein, for the first time, we report the immobilization of ultrafine Pd NPs on diamine-alkalized reduced graphene oxide, PDA-rGO (PDA = 1,4-phenylenediamine), which exhibits the highest TOF value (3810 h^{-1} , 323 K), for FA decomposition to H_2 , and illustrate that the alkaline diamine on reduced graphene oxide

(rGO) benefits dispersion of ultrafine Pd NPs and facilitates the decomposition of FA via the amine-assisted formate pathway.

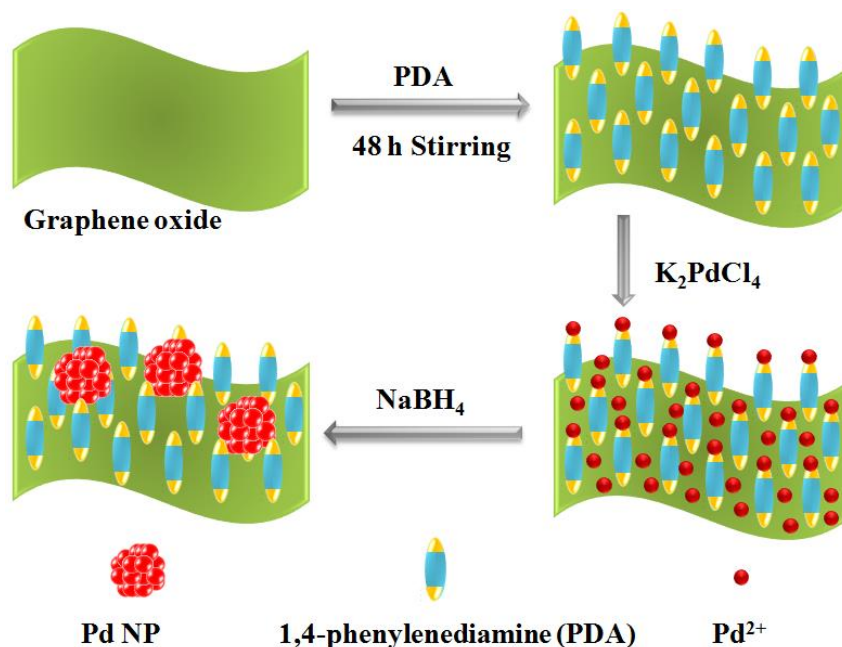


Figure 1. Schematic Illustration for Pd/PDA-rGO Nanocatalyst Preparation

The immobilization of Pd NPs to PDA-rGO is illustrated in Figure 1. Addition of PDA into the aqueous solution of GO and stirring for 48 h resulted in the formation of a black precipitation (PDA-GO) (see Figure 2). The resultant PDA-GO precipitation was separated by centrifugation and washed with water, and subsequently dispersed in water, followed by addition of an aqueous solution of K_2PdCl_4 . Finally, addition of $NaBH_4$ to the suspension and stirring for 45 minutes at room temperature resulted in the formation of ultrafine Pd NPs on the diamine-alkalized rGO, giving the Pd/PDA-rGO catalyst. For comparison, Pd/rGO was also synthesized using GO instead of PDA-GO.

2.2 Experimental section

2.2.1 Materials and general methods

All chemicals were commercial and used without further purification. Graphite (C,

Sigma-Aldrich, >99.8%), sulfuric acid (H_2SO_4 , Kishida Chem. Co., 98%), phosphoric Acid (H_3PO_4 , Tokyo Chemical Industry Co., 89%), hydrogen peroxide (H_2O_2 , Kishida Chem. Co., 30%), potassium permanganate (KMnO_4 , Kishida Chem. Co., 99.3%), 1,4-phenylenediamine ($\text{C}_6\text{H}_8\text{N}_2$, Tokyo Chemical Industry Co., 98%), 4-(aminomethyl) aniline ($\text{C}_7\text{H}_{10}\text{N}_2$, Sigma-Aldrich, 99%), 1,6-diaminohexane ($\text{C}_6\text{H}_{16}\text{N}_2$, Tokyo Chemical Industry Co., 99%), N,N-dimethyl-1,4-phenylenediamine ($\text{C}_8\text{H}_{12}\text{N}_2$, Tokyo Chemical Industry Co., 98%), aniline ($\text{C}_6\text{H}_6\text{N}$, Tokyo Chemical Industry Co., 99%), potassium tetrachloropalladate (K_2PdCl_4 , Wako Pure Chemical Industries, Ltd., >35%), sodium borohydride (NaBH_4 , Aldrich, 99%), formic acid (FA, HCOOH , Kishida Chem. Co., >98%), sodium formate dehydrate (SF, HCOONa , Sigma-Aldrich, >99.5%), hydrochloric acid (HCl , Tokyo Chemical Industry Co., >35%), acetone ($\text{C}_3\text{H}_6\text{O}$, Kishida Chem. Co., >99.5%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, Kishida Chem. Co., >99.8%) were used as received.

Powder X-ray diffraction patterns were collected for synthesized catalysts on a Rigaku Ultima IV X-ray diffractometer with Cu-K α source (40 kV, 40 mA). X-ray photoelectron spectroscopic (XPS) measurements were conducted on a JEOL JPS-9010MX X-ray photoelectron spectrometer using an Mg K α source (10 kV, 30 mA). The TEM and HAADF-STEM images and EDX spectra were recorded on Transmission electron microscope (TEM, TECNAI G² F20) with operating voltage at 200 kV equipped with energy-dispersive X-ray detector (EDX). Scanning electron microscopic (SEM) analyses were carried with a Hitachi S5000 field emission scanning electron microscope. After purging the reactor with argon three times, the decomposition of formic acid was carried out, and the generated gas was collected, which was analyzed by GC-8A (molecular sieve 5A, Ar as carrier gas) and GC-8A (Porapack N, He as

carrier gas) analyzers (Shimadzu). IR spectra were measured using a Bruker spectrometer IFS 66v/s. Raman spectra were recorded with a charge-coupled device (CCD) camera mounted on the spectrograph (Princeton Instruments Industry, SpectraPro 2500i).

2.2.2 Synthesis of graphene oxide: GO was synthesized according to the reported procedure.⁷ Firstly, a concentrated H₂SO₄/H₃PO₄ solution (180:20 mL) was added to the mixture of graphite flakes (1.5 g) and KMnO₄ (9 g) and then the solution was kept at 323 K with a water bath for 12 hours. The solution was cooled to room temperature and poured into a flask containing ice (200 g) and H₂O₂ (30%, 1.5 mL). The solid material was separated by centrifugation and washed with water (100 mL), HCl (100 mL), and ethanol (100 mL) (for 2 times). Finally, the obtained solid was dried in vacuum oven at room temperature for 12 h.

2.2.3 Syntheses of Pd nanoparticle/diamine-alkalized graphene catalysts (Pd/PDA-rGO, PDA = 1,4-phenylenediamine): GO (50 mg) was dispersed in water (50 mL) under sonication for 2.5 h. PDA (270 mg) was dissolved in acetone (4 mL) and then added dropwise into the GO solution, and stirred for 48 h, resulting in the formation of a black precipitation (PDA-GO) (Figure 2).

The resultant PDA-GO precipitation was separated by centrifugation and washed with water. Subsequently, the prepared PDA-GO was dispersed in water (25 mL), to which an aqueous solution of K₂PdCl₄ (0.09 mmol) was added, followed by an immediate addition of NaBH₄ (30 mg) dissolved in water (0.50 mL), resulting in the formation of ultrafine Pd NPs on the diamine-alkalized rGO. Finally, the Pd/PDA-rGO catalyst was collected by centrifugation, washed with water and dried under vacuum at

room temperature for 12 h, giving the Pd/PDA-rGO catalyst. To study the effect of the amount of PDA on the catalytic performance of the resultant catalysts, the catalysts have been prepared using different amounts of PDA (17, 68 and 340 mg for PDA-GO_a, PDA-GO_b and PDA-GO_c, respectively) by the similar procedure.

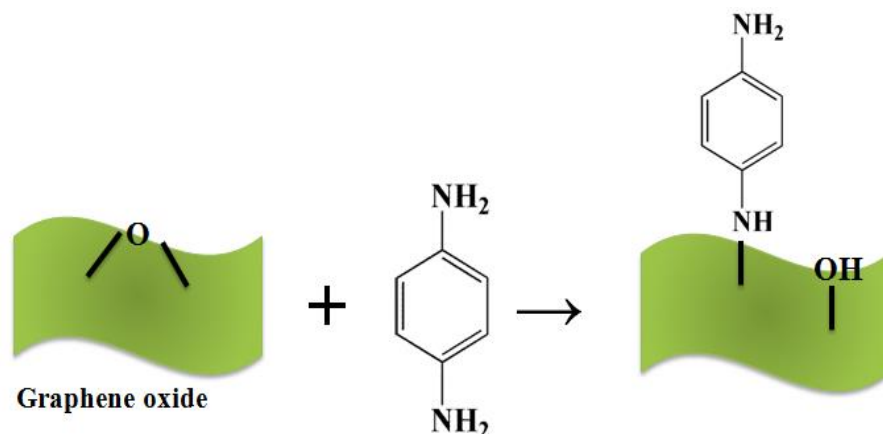


Figure 2. Schematic illustration for the synthesis of PDA-GO.

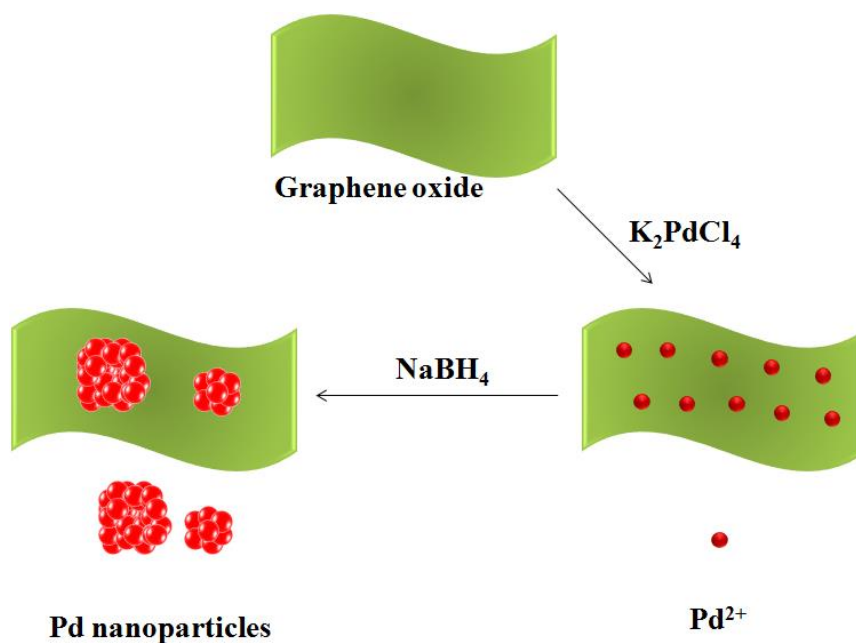


Figure 3. Schematic illustration for the synthesis of Pd/rGO.

An analogous synthetic procedure was used to prepare the Pd/AMA-rGO,

Pd/DAH-rGO, Pd/DMPDA-rGO and Pd/A-rGO catalysts using 4-(aminomethyl) aniline (AMA), 1,6-diaminohexane (DAH), N,N-dimethyl-1,4-phenylenediamine (DMPDA) and aniline (A) instead of PDA, respectively.

For comparison, the Pd/rGO catalyst was also prepared by the similar synthetic procedure using GO instead of diamine-alkalized GO. The schematic diagram for the synthesis of Pd/rGO was shown in Figure 3.

2.2.3 Catalytic activity characterization

Reaction apparatus for measuring the H₂/CO₂ evolution from the FA/SF system is the same as previously reported.^{3e} In general, a mixture of as-synthesized catalyst and water (2 mL) was placed in a two-necked round-bottom flask (30 mL), which was placed in a water bath at a preset temperature (298-323 K). A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (temperature kept constant at 298 K during measurements). The reaction started when 1.0 mL of the mixed aqueous solution containing FA (6.0 M) and SF with different molar ratios was injected into the mixture using a syringe. The molar ratios of Pd/FA were theoretically fixed at 0.015 for all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

For testing the durability of Pd/PDA-GO, 6.0 mmol of pure FA was subsequently added into the reaction flask after the completion of the first-run decomposition of FA. Such test cycles of the catalyst for the decomposition of FA were carried out for 5 runs at 323 K by adding aliquots of pure FA.

After the reaction, Pd/PDA-GO was separated from the reaction solution by centrifugation and dried under vacuum at room temperature for XRD and TEM analyses.

2.2.4 Calculation methods

The turnover frequency (TOF) reported here is an apparent TOF value based on the number of Pd atoms in catalyst, which is calculated from the equation as follow:

$$TOF = P_0 V / (2RT n_{Pd} t)$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of H_2/CO_2 gas, R is the universal gas constant ($8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$), T is the room temperature (298 K), n_{Pd} is the total mole number of Pd atoms in catalyst and t is the completion time of the reaction in hour.

2.3 Results and discussion

2.3.1 Characterization

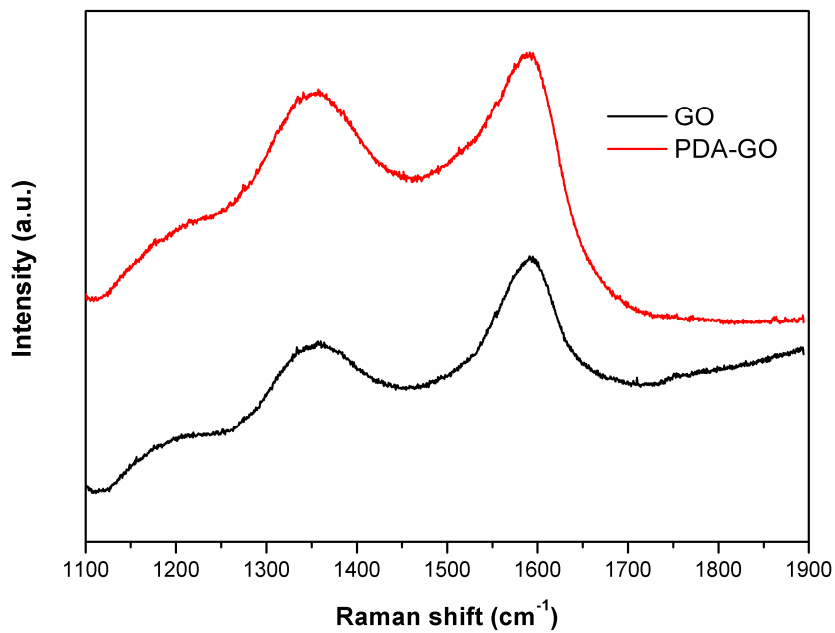


Figure 4. Raman spectra of GO and PDA-GO.

The Raman spectroscopy show the binding behavior of GO and PDA-GO (Figure 4). There are two characterized peaks in Raman spectrum of GO and PDA-GO. The peak at

1600 cm^{-1} (G band) arise from the vibration of sp^2 -bonded carbon atoms in a 2D hexagonal lattice, namely, the stretching modes of C=C bonds, while the peak at 1350 cm^{-1} (D band) is attributed to the vibrations of carbon atoms with dangling bonds in plane terminations and defects.⁸

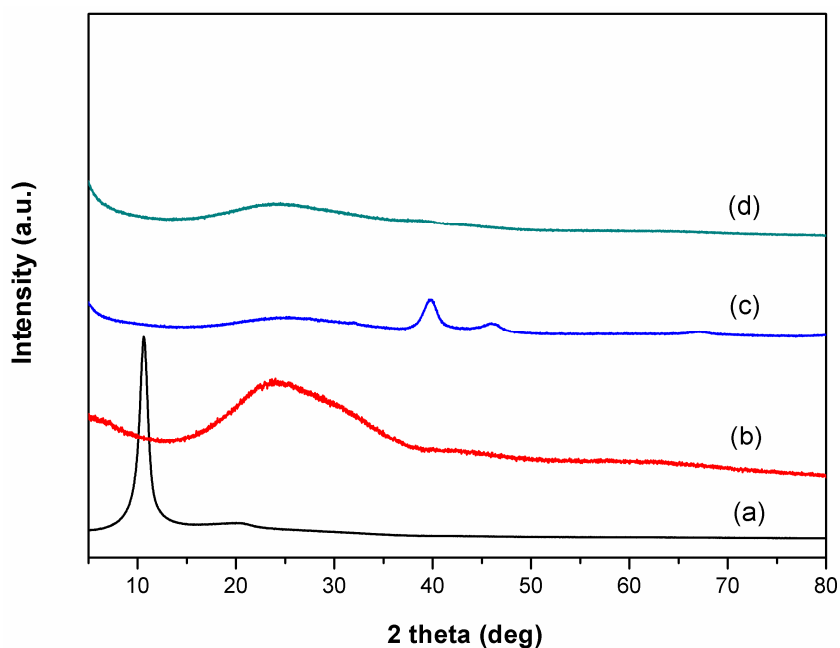


Figure 5. XRD patterns of (a) GO, (b) PDA-GO, (c) Pd/rGO and (d) Pd/PDA-rGO.

The characteristic X-Ray diffraction (XRD) for GO ($2\theta = 10.6^\circ$) is not observed for PDA-GO, suggesting disordered restacking of the PDA-GO layers (Figure 5). The diffractions at 39.8° (111) and 45.9° (200) for Pd (JCPDS: 46-1043)^{2a} are observed for Pd/rGO but not for Pd/PDA-rGO, indicating the formation of very small Pd NPs on the diamine-functionalized rGO (Figure 5).

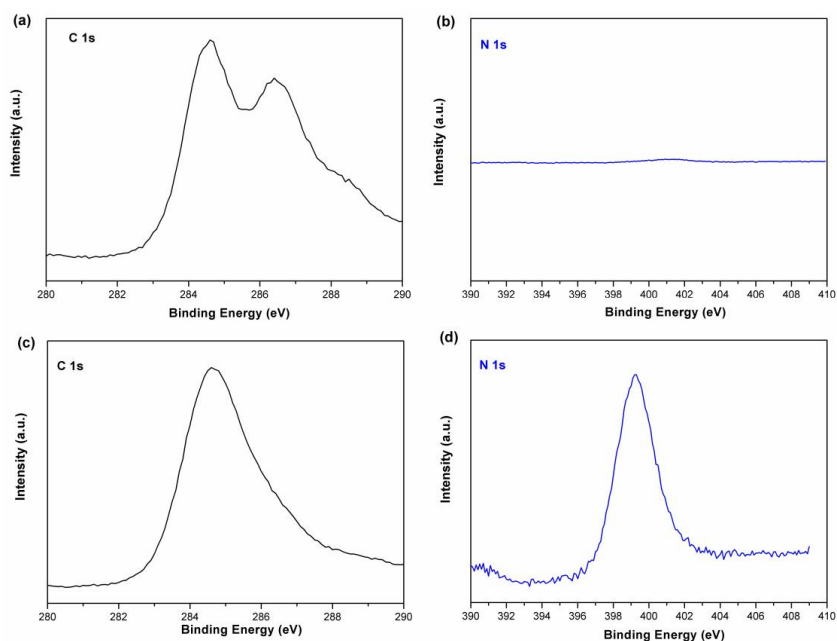


Figure 6. XPS spectra of C 1s and N 1s for (a,b) GO and (c,d) PDA-GO.

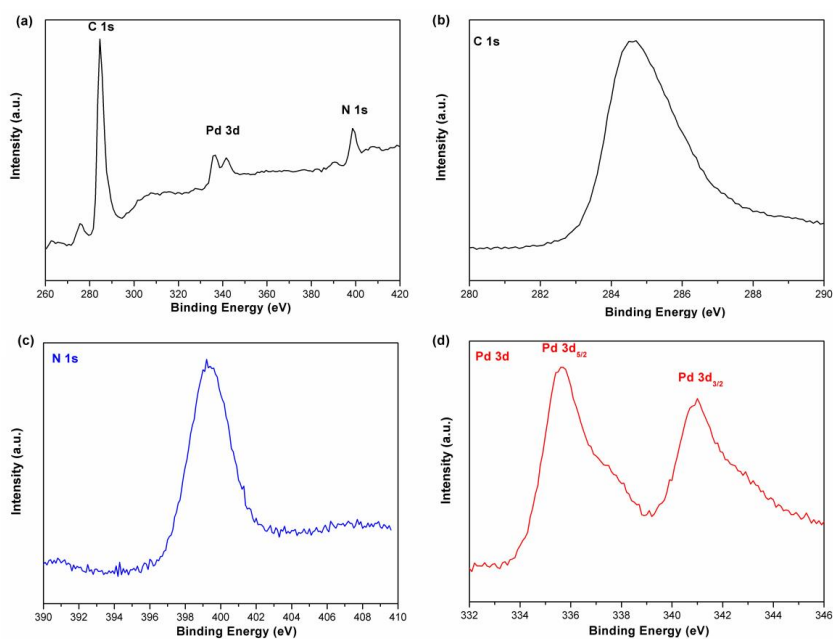


Figure 7. (a) XPS survey spectrum and high-resolution XPS spectra of (b) C 1s, (c) N 1s and (d) Pd 3d for Pd/PDA-rGO.

The X-ray photoelectron spectroscopic (XPS) investigation further confirms the anchoring of amine groups to rGO, of which the signal is observed at 399.2 eV at the N

1s level. For Pd/rGO and Pd/PDA-rGO, the same binding energies (BEs) for Pd are observed at 335.6 and 340.9 eV, corresponding to Pd⁰, at the Pd 3d_{5/2} and Pd 3d_{3/2} levels, respectively (Figures 7 and 8). The corresponding energy dispersive X-ray (EDX) pattern confirms the existence of Pd (Figure 9d).

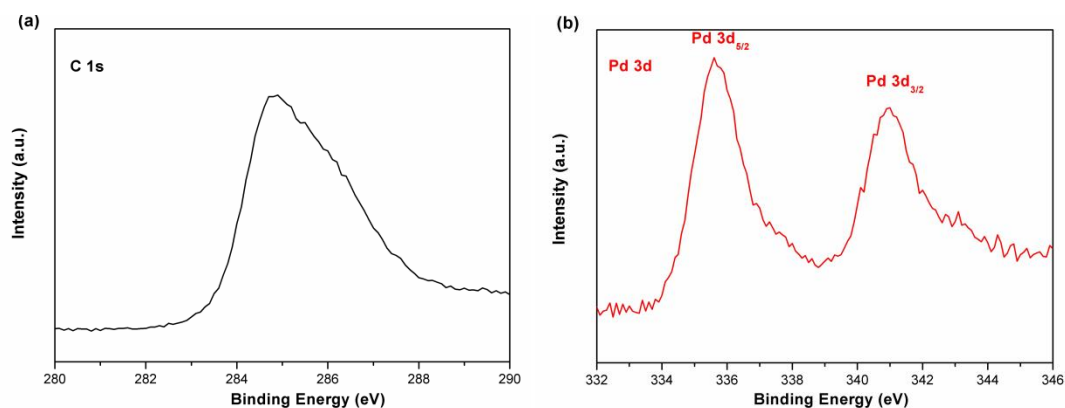


Figure 8. XPS spectra of (a) C 1s and (b) Pd 3d for Pd/rGO.

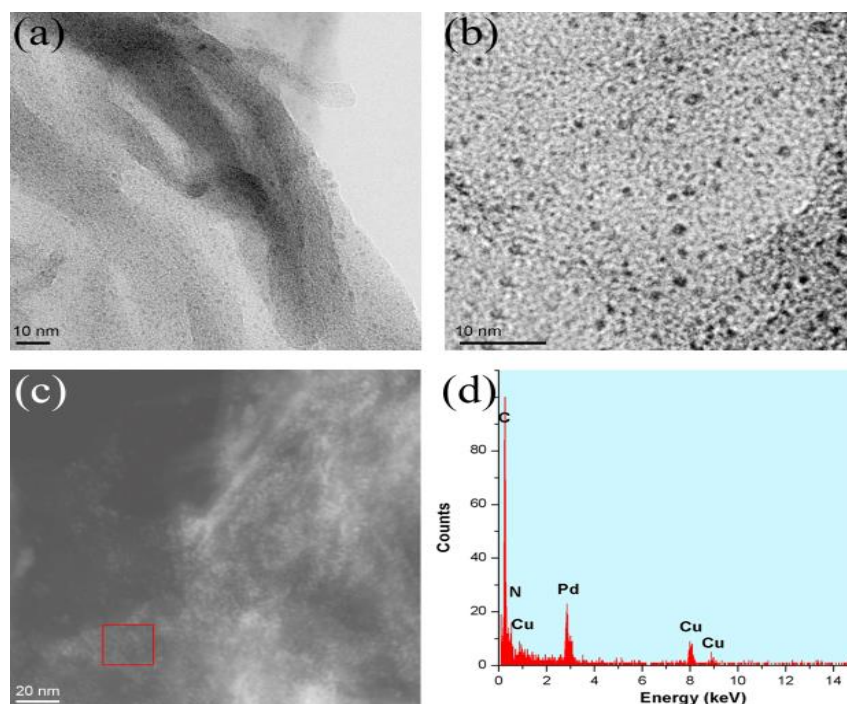


Figure 9. (a,b) TEM and (c) HAADF-STEM images of Pd/PDA-rGO, and (d) EDX pattern of the selected area in (c). The copper signals originate from the TEM grid.

The transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images of Pd/PDA-rGO show that discrete Pd NPs are homogenously dispersed on rGO with an average size of 1.5 nm, ranging from 1.0 to 2.0 nm (Figures 9a-c and 11a). In contrast, when Pd NPs are directly supported on rGO, the NPs are severely aggregated with a much larger average particle size (10 nm) (Figures 10 and 11b). The diamine groups not only highly disperse the GO against ordered restacking, but also provide coordinating groups to combine with Pd²⁺ ions, resulting in rich and uniform nuclei and a controlled growth process of Pd on rGO.

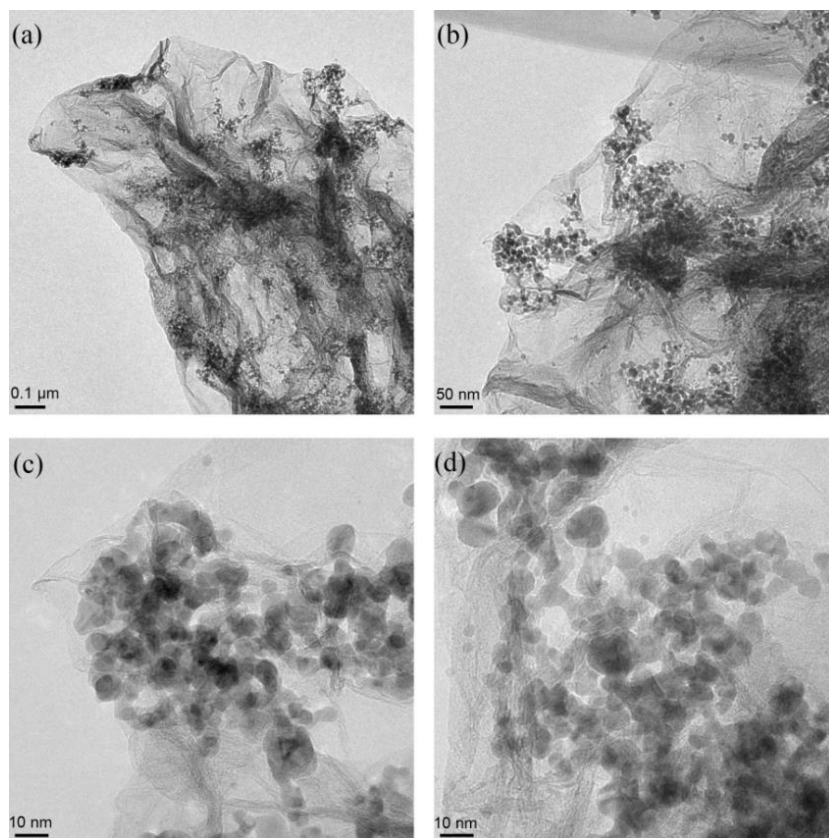


Figure 10. TEM images of Pd/rGO.

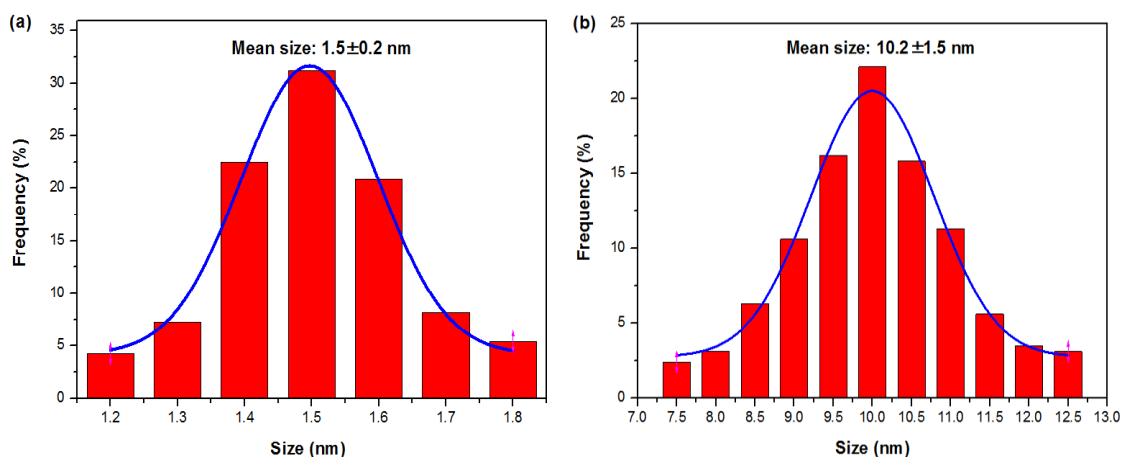


Figure 11. Particle size distribution histograms of (a) Pd/PDA-rGO and (b) Pd/rGO.

2.3.2 Catalytic activity and durability

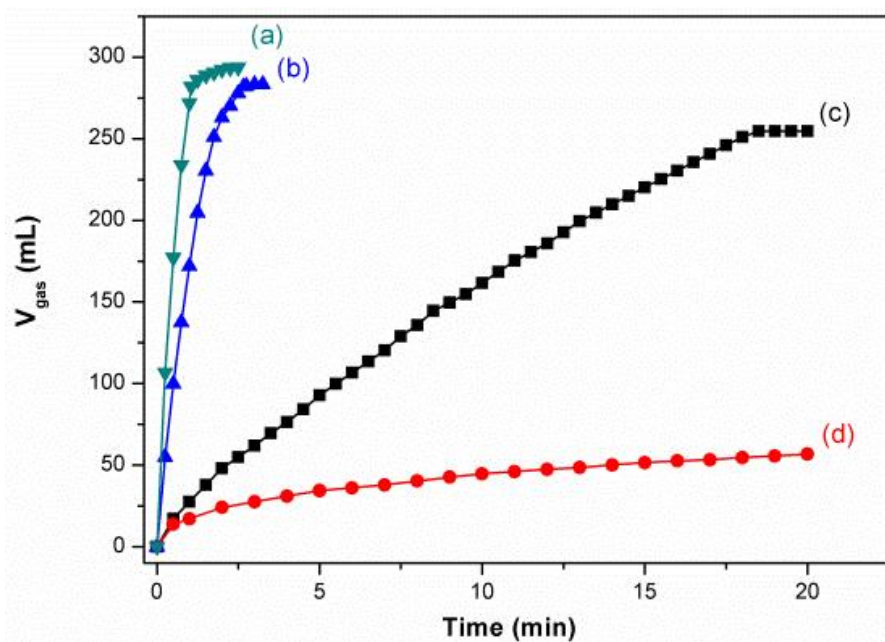


Figure 12. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of (a) FA/SF (1:1) at 323 K and (b,c) pure FA at 323 K and 298 K, respectively, over Pd/PDA-rGO, and (d) the dehydrogenation of FA/SF (1:1) at 323 K over Pd/rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$).

Figure 12a shows the volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA over Pd/PDA-rGO, which exhibits complete and selective decomposition of FA with an exceedingly fast kinetics. Within 1.05 min, 282 mL of gas can be generated from the FA/sodium formate (SF) system at 323 K ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, FA/SF = 1:1) (Figure 12a). The generated gas is identified by gas chromatography (GC) to be CO_2 and H_2 , and no CO is detected at the level of detection limit (Figures 13 and 14). It is noteworthy that the Pd/PDA-rGO gave an exceptional turnover frequency (TOF) of 3810 h^{-1} , the highest value ever reported for heterogeneously catalyzed FA decomposition, comparable to the most active homogeneous catalysts (Table 1). Even without any additive, the decomposition of pure FA can be completed in 2.67 and 18.5 min ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$), corresponding to TOF values as high as 1500 and 216 h^{-1} , at 323 and 298 K, respectively (Figures 12b and 12c).

Table 1. Catalytic activities for dehydrogenation of formic acid catalyzed by heterogeneous and homogeneous catalysts.

Catalyst	Solvent/medium	Temp. (K)	CO evolution	TOF (h^{-1}) ^a	Ref.
<i>Heterogeneous</i>					
Pd/PDA-rGO	Aqueous HCOONa	323	No	3810	This work
	Aqueous	323	No	1500	This work
	Aqueous	298	No	216	This work
(Co_6) $\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$	Aqueous HCOONa	323	No	2739	3e
Pd/MS-30	Aqueous HCOONa	323	No	2623	6e
Au/ZrO ₂ NCs	5HCOOH/2NEt ₃	323	No	1593 ^b	9
Ag ₄₂ Pd ₅₈	Aqueous	323	No	382 ^b	10

Ag@Pd/C	Aqueous	293	No	192	11
Co _{0.30} Au _{0.35} Pd _{0.35}	Aqueous	298	No	80 ^b	6b
Pd/C with citric acid	Aqueous HCOONa	298	No	64	12
PdAu/C-CeO ₂	Aqueous HCOONa	365	145 ppm	113.5	13
PdAu@Au/C	Aqueous HCOONa	365	30 ppm	21.4	14
Pd-S-SiO ₂	Aqueous	358	No	719	15
AuPd@ED-MIL-101	Aqueous HCOONa	363	Yes	106	6a
<i>Homogeneous</i>					
RuBr ₃ ·xH ₂ O, 3 equiv. PPh ₃ ^c	5HCOOH/2NEt ₃	313		3630 ^b	16
RuCl ₂ (PPh ₃) ₃	5HCOOH/2NEt ₃	313		2688 ^b	5a
[Fe(BF ₄) ₂]·6H ₂ O, 2 equiv. PP ₃ ^d	Propylene Carbonate	313	≤10 ppm	1942	4d
		353	≤20 ppm	5390	
[Ir(Cp*)(dhbp)] ^e	Aqueous	323	No	1240 ^b	5b
		363	No	14000 ^b	
[RuCl ₂ (benzene)] ₂ , 6 equiv. dppe ^f	<i>N,N</i> -dimethyl- <i>n</i> -hexylamine	313		900	17
[Ir ^{III} (Cp*)(H ₂ O)(bpm)Ru ^{II} (bpy) ₂] ^{4+g}	Aqueous HCOONa		No	426 ^b	16

^a TOF values were calculated using the amount of released gas and the completion time of reaction in hour, ^b Initial TOF values calculated at the initial stages of the catalytic reactions, ^c PPh₃ = triphenylphosphine, ^d PP₃ = tris[2-diphenylphosphino)ethyl]phosphine, ^e Cp* = *η*⁵-pentamethylcyclopentadienyl, dhbp = 4,4'-dihydroxy-2,2'-bipyridine, ^f dppe = 1,2-bis(diphenylphosphino)ethane, ^g bpm = 2,2'-bipyrimidine, bpy = 2,2'-bipyridine.

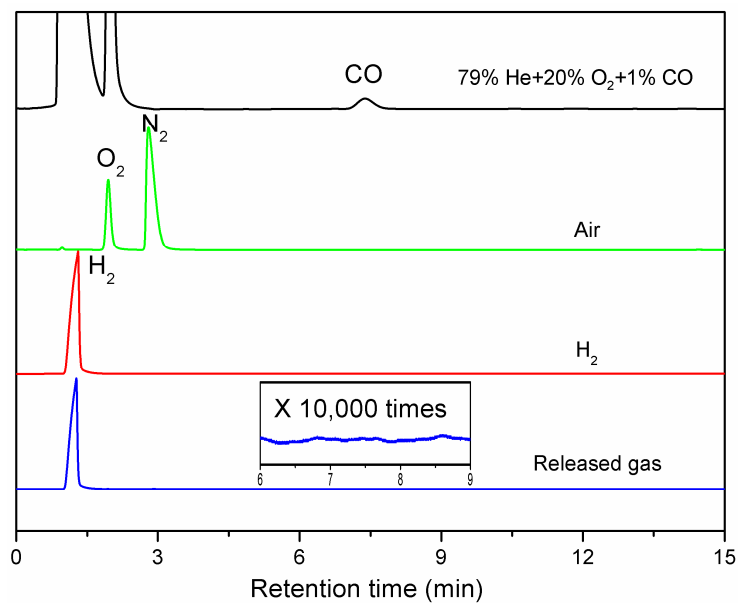


Figure 13. Gas chromatograms of CO, air and H₂ as reference gases and the released gas from the decomposition of FA/SF in the presence of Pd/PDA-rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, FA/SF = 1:1, 323 K).

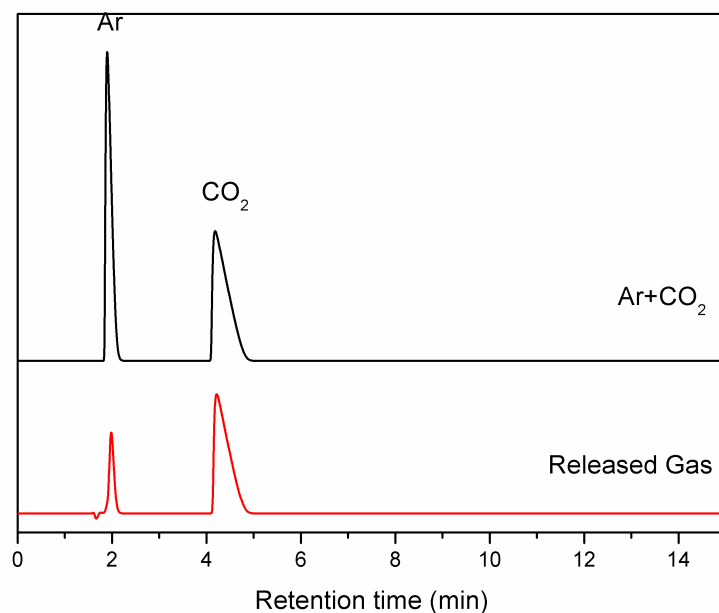


Figure 14. Gas chromatograms of CO₂ as reference gas and the released gas from the decomposition of FA/SF in the presence of Pd/PDA-rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, FA/SF = 1:1, 323 K).

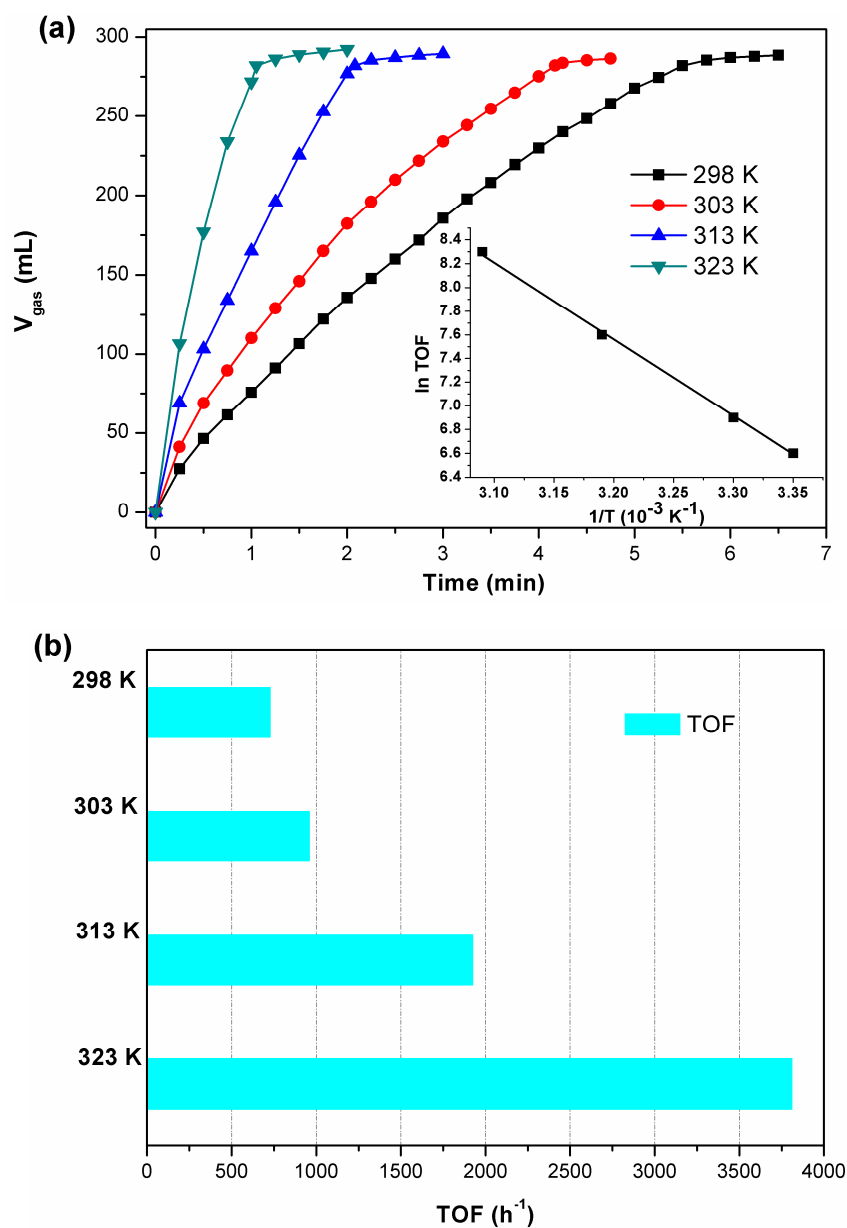


Figure 15. (a) Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time and (b) corresponding TOF values of H_2 generation for the dehydrogenation of FA/SF (1:1) at different temperatures over Pd/PDA-rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, FA/SF = 1:1). Inset of (a): Arrhenius plot ($\ln(\text{TOF})$ vs. $1/T$).

The gas generation rate over Pd/PDA-rGO catalyst greatly depends on the reaction temperature. The catalytic reactions are completed in 5.5, 4.17, 2.08, and 1.05 min at

298, 303, 313, and 323 K ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, FA/SF = 1:1) (Figure 15a), respectively, corresponding to TOF values of 727, 959, 1923, and 3810 h^{-1} (Figure 15b). The Arrhenius plot fitted on the basis of the TOF values for the decomposition of FA at different reaction temperatures gives an activation energy (E_a) of 54.3 kJ mol^{-1} . In addition, it is noteworthy that the molar ratio of FA to SF has an obvious effect on the performance of the synthesized Pd/PDA-rGO catalyst. With the increase of the molar percentage of SF in aqueous FA-SF solution, the catalytic activity increases initially and then decreases, with the best performance at the molar ratio of 1:1 (Figure 16).

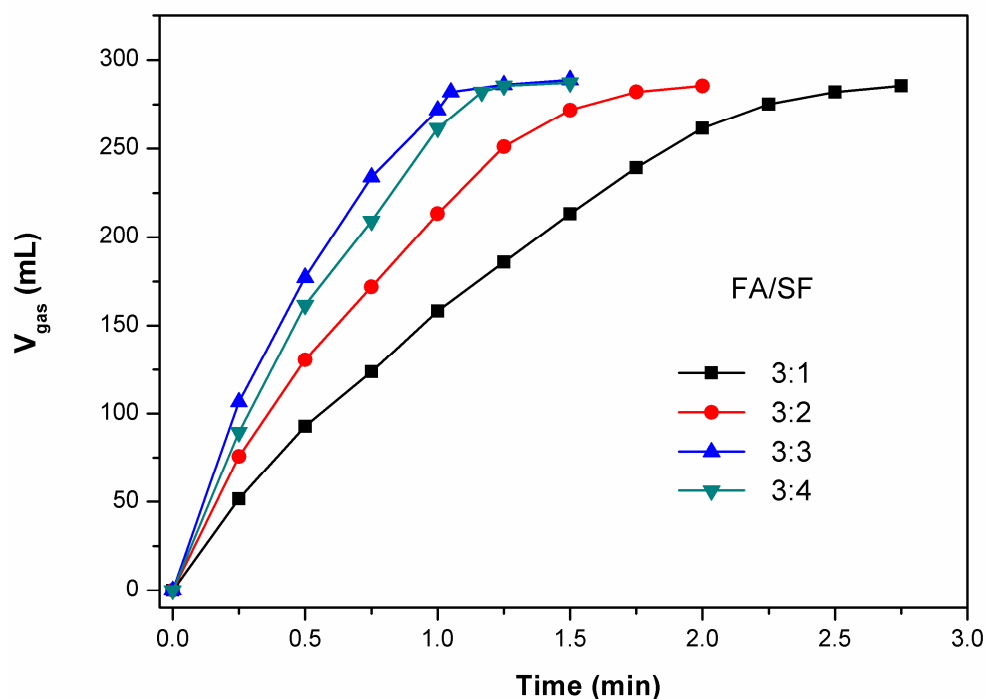


Figure 16. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA with different FA/SF molar ratios over Pd/PDA-rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, 323 K).

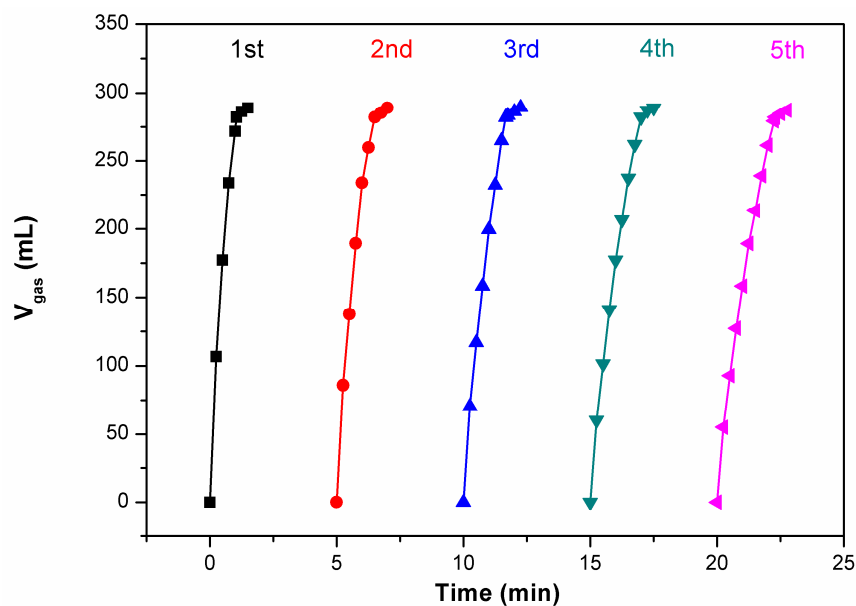


Figure 17. Durability test for the dehydrogenation of FA over Pd/PDA-rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, FA/SF = 1:1, 323 K). The stability of Pd/PDA-rGO was examined by successively adding aliquots of FA (6 mmol) into the reactor after the completion of last run.

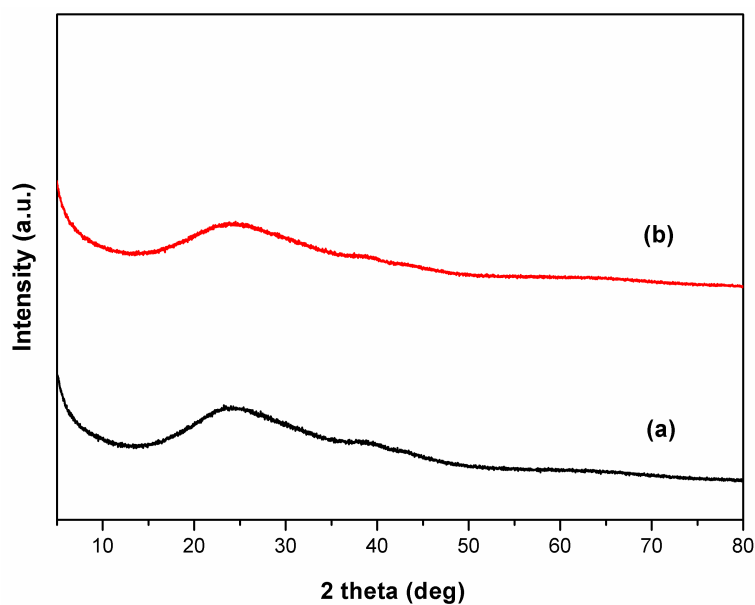


Figure 18. PXRD patterns of Pd/PDA-rGO catalyst (a) before and (b) after catalysis

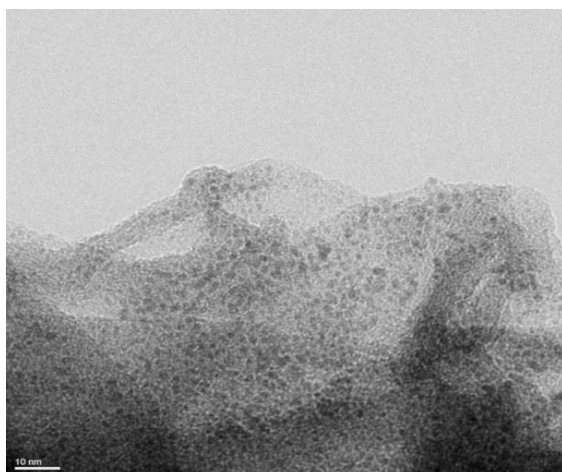


Figure 19. TEM image of Pd/PDA-rGO catalyst after catalysis

We further examine briefly the stability of Pd/PDA-rGO catalyst by adding aliquots of FA (0.23 ml, 6.0 mmol) into the reactor after the reaction completion of last run. No significant loss in activity and selectivity is observed over 5 cycles (Figure 17). TEM and XRD measurements of the recovered catalyst show no obvious change in the Pd particle size (Figures 18 and 19), indicating that the Pd/PDA-rGO catalyst has high durability and stability under the current FA dehydrogenation condition.

In contrast to the excellent catalytic performance of Pd/PDA-rGO, the Pd/rGO catalyst shows a very low activity for the decomposition of FA under the same condition, over which only 52 mL gas is released in 20 mins (Figure 12) ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, 323 K). It is well-known that the catalytic activity generally increases with the decrease in metal NP size, as smaller particles possess higher surface areas available for reactants. Reasonably, the decrease in the particle size of Pd NPs supported by PDA-rGO should be one of the most important factors that are responsible for the drastic enhancement in the catalytic activity. On the other hand, the alkalization of GO with diamine plays another important role in promoting the catalytic performance.

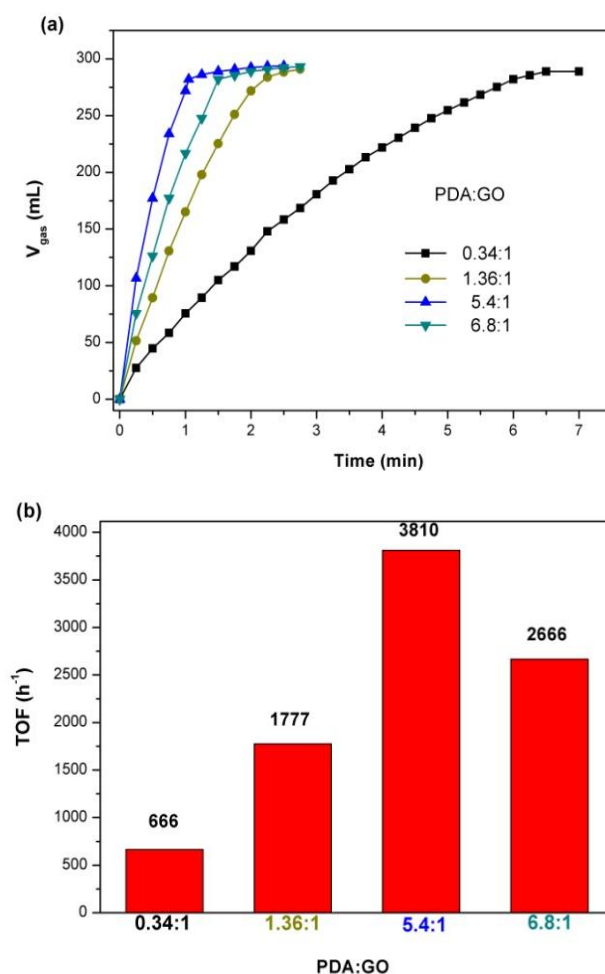


Figure 20. (a) Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time and (b) corresponding TOF values of H_2 generation for the dehydrogenation of FA over Pd/PDA-rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, $\text{FA}/\text{SF} = 1:1$, 323 K) prepared with different mass ratios of PDA:GO (0.3:1, 1.4:1, 5.4:1 and 6.8:1; GO, 0.05 g).

To determine the effect of the amount of immobilized PDA on catalytic activity, the GO supports with various mass ratios of PDA:GO have been synthesized for depositing Pd NPs (Figure 20 and Table 2). With increasing the mass ratio of PDA:GO to 5.4:1, the TOF value initially increases, while after reaching a maximum value of 3810 h^{-1} a further increase in the amount of PDA shows a negative effect on the dehydrogenation of FA.

Table 2. Elemental analysis results of PDA-GO samples prepared using different amounts of PDA.

Sample	Nitrogen (%)	Carbon (%)	Hydrogen (%)	PDA: GO (mass ratio) ^a
PDA-GO_a	4.4806	52.3689	3.0359	0.21:1
PDA-GO_b	7.499	56.0167	3.2675	0.41:1
PDA-GO	8.9087	58.2483	3.5499	0.52:1
PDA-GO_c	9.8028	58.7997	3.7538	0.54:1

^a Calculated from the mass ratios of nitrogen.

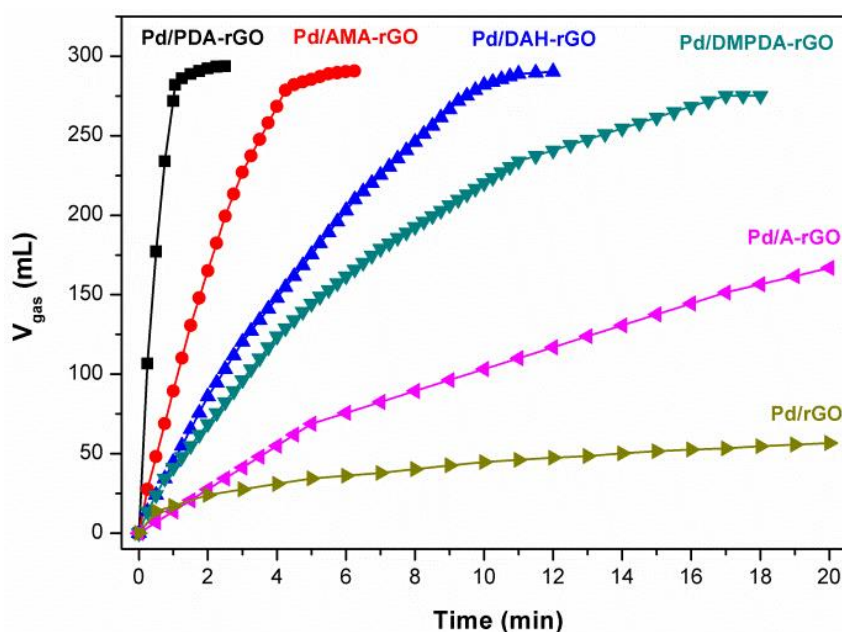


Figure 21. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA over Pd/PDA-rGO, Pd/AMA-rGO, Pd/DAH-rGO, Pd/DMPDA-rGO and Pd/rGO ($n_{\text{Pd}}/n_{\text{FA}} = 0.015$, $\text{FA}/\text{SF} = 1:1$, 323 K).

The alkaline $-\text{NH}_2$ group, as a proton scavenger, benefits the antisymmetric cleavage of O-H bond in the FA molecule, resulting in the formation of an intermediate Pd-formate complex along with $-\text{[H}_2\text{NH]}^+$ group during the initial step of the reaction. Subsequently, the Pd-formate species could undergo β -hydride elimination to produce

CO₂ and a palladium hydride species. The final hydrogen desorption step is combined with $-\text{[H}_2\text{NH]}^+$ group and a palladium hydride species, which is irreversible and also kinetically relevant, highlighting the feasibility of renewable FA as a convenient in situ hydrogen source instead of molecular H₂ for sustainable and green organic synthesis.¹⁸

To demonstrate the universality of this synthetic strategy for introducing alkalinity to GO and supporting ultrafine metal NPs, different amine-rGO systems, including PDA-rGO (PDA = 1,4-phenylenediamine), AMA-rGO (AMA = 4-(aminomethyl)aniline), DAH-rGO (DAH = 1,6-diaminohexane), DMPDA-rGO (DMPDA = N,N-dimethyl-1,4-phenylenediamine) and A-rGO (A = aniline), have been prepared and subsequently used to immobilize Pd NPs. Figure 21 shows the catalytic performance of Pd NPs immobilized by these amine-alkalized rGO supports. Compared to Pd/rGO, all the catalysts exhibit exceedingly enhanced catalytic activities for hydrogen generation from FA. However, only a moderate enhancement is found for Pd/A-rGO, which may be due to the fact that in aniline, a monoamine molecule, the only -NH_2 group is covalently bound to rGO and thereby leads to the lack of the interactions with Pd, further indicating the unique role of the diamines in this system.

2.4 Conclusion

In summary, for the first time, the alkalization of GO with diamine in this work provides a powerful method to prepare ultrafine metal NPs and modifies the alkalinity of the support for optimizing the catalytic performance. By using the alkalized GO, well-dispersed ultrafine Pd NPs with the diameter below 1.5 nm can be readily obtained. Moreover, the diamine-alkalized rGO surface benefits the formation of unique amine-associated formate, the important intermediate for formic acid dehydrogenation. Owing to both of the effects from the high Pd dispersion and amine-formic acid

interaction, the resultant Pd/PDA-rGO nanocatalysts exhibit significantly enhanced catalytic activity for dehydrogenation from FA under mild conditions, achieving the highest TOF value, with 100% H₂ selectivity, among those of heterogeneous catalysts. The present work provides an effective strategy to immobilize ultrafine metal NPs on GO, which have tremendous application prospect in various catalytic fields.

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Chapter 3

Monodispersed PtNi Nanoparticles Deposited on Diamine-alkalized Graphene for Highly Efficient Dehydrogenation of Hydrous Hydrazine at Room Temperature

An efficient strategy has been explored to immobilize the PtNi nanoparticles (NPs) on diamine-alkalized reduced graphene oxide (rGO). By the virtue of the alkalization of rGO with diamine, monodispersed PtNi NPs can be facilely anchored on the alkalized rGO, which shows excellent catalytic activity with 100% H₂ selectivity for dehydrogenation of hydrous hydrazine.

3.1 Introduction

The growing demand to meet the ever-increasing energy consumption needs without causing further damage to the environment has encouraged extensive research on the development of safe and effective hydrogen storage materials.¹ Among the various hydrogen storage materials, hydrous hydrazine, such as hydrazine monohydrate (N₂H₄·H₂O), has been considered as a promising candidate owing to its high hydrogen content (8.0wt%), easy recharging, relatively low cost and the only production of nitrogen in addition to hydrogen via a complete decomposition: $\text{H}_2\text{NNH}_2 \rightarrow \text{N}_2 + 2\text{H}_2$.² Moreover, as a liquid-phase material, the hydrous hydrazine has the potential to take advantage of the existing liquid-based distribution infrastructure, more competitive than solid chemical hydrogen-storage materials such as sodium borohydride (NaBH₄) and ammonia borane (NH₃BH₃) derivatives.³ However, the undesired decomposition to

ammonia (NH_3) $3\text{H}_2\text{NNH}_2 \rightarrow \text{N}_2 + 4\text{NH}_3$ must be avoided, because the presence of NH_3 not only decreases the yield of hydrogen but also complicates the separation process, due to the low poisoning resistance of Nafion membrane and the fuel-cell catalysts towards the NH_3 impurities.⁴ Up to now, there are a few reports on mon- and bimetallic catalysts for dehydrogenation of hydrous hydrazine, especially for the Ni-based bimetallic catalysts with 100% H_2 selectivity at room temperature.⁵ However, the catalytic kinetics of H_2 generation rate is still not satisfying the demands for practical applications, therefore, the syntheses of catalysts with excellent catalytic performance at ambient temperatures have become urgently important.

Besides the catalyst composition, the structure and property of support materials are crucial for improving catalytic performance. Until now, various types of support materials have been reported, such as hydrotalcite,^{2a} CeO_2 ,^{5b} carbon,^{5d} Al_2O_3 ,⁶ MOFs,⁷ MgO ,⁸ silica,⁹ LaOH ¹⁰ and so on. However, the weak synergistic coupling interactions between the support and catalyst limit catalytic activity at mild temperatures. Reduced graphene oxide (rGO) consisting of chemically converted monolayer carbon atoms has emerged as one of the most promising supports for metal NPs. The unique advantage of hydrophilicity and large specific surface area of its precursor, graphene oxide (GO), makes it possible to anchor metal NPs in the solution-based controlled reduction.¹¹ However, due to its two-dimensional basal plane structure and the negligible interactions between GO and metals, it is still a major obstacle to obtain monodispersed metal particles with very small sizes on GO.¹² Therefore, rational modification of the GO surfaces with electron-rich functional groups would facilitate the dispersion of the metal precursors on the support and control the size during the growth of metal NPs. Moreover, such modification may also provide an opportunity to tailor the electronic

properties and alkalinity/acidity of GO, and thus optimize the catalytic performance of the resultant catalysts.

Herein, we report the immobilization of monodispersed PtNi NPs on diamine-alkalized reduced graphene oxide, PDA-rGO, (PDA is 1,4-phenylenediamine), which affords the high TOF values (903 h^{-1} at 303 K and 2056 h^{-1} at 323 K) for hydrous hydrazine dehydrogenation.

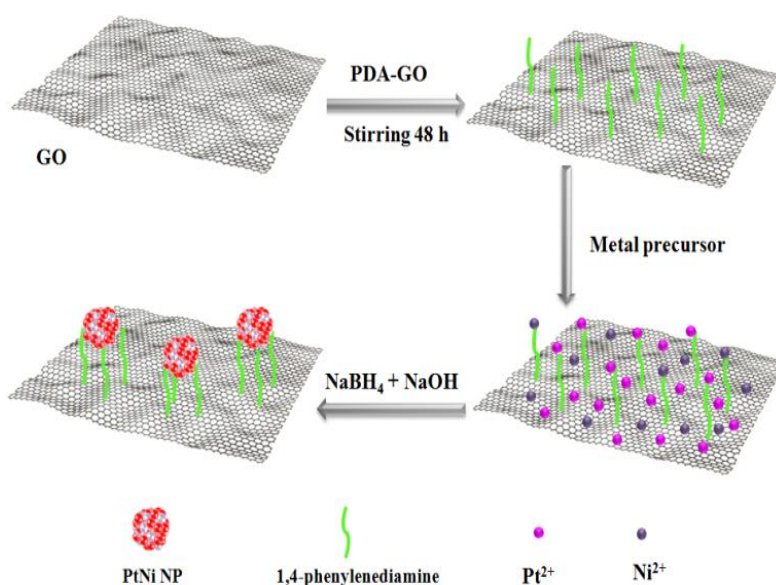


Figure 1. Schematic illustration for PdNi/PDA-rGO nanocatalyst preparation.

The addition of PDA into the aqueous solution of GO and stirring for 48 h resulted in the formation of a black precipitation, PDA-GO. The resultant PDA-GO was separated by centrifugation and washed with water, and subsequently dispersed in water, followed by the addition of an aqueous solution of K_2PtCl_4 and NiCl_2 . Finally, NaBH_4 was added into the suspension under stirring at room temperature, leading to the formation of ultrafine PtNi NPs on the diamine-alkalized rGO, denoted as PtNi/PDA-rGO (Figure 1).

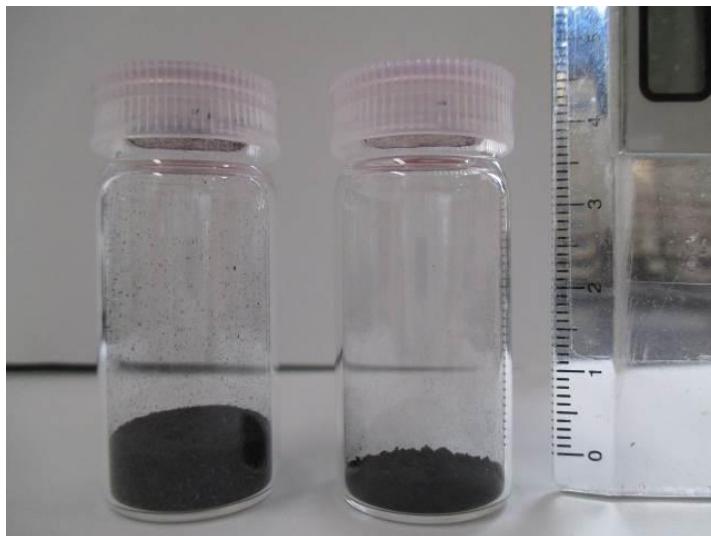


Figure 2. Photographic images of (left) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ (50 mg) and (right) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$ (50 mg).

For comparison, PtNi/rGO was also synthesized using GO instead of PDA-GO. Compared with PtNi/rGO , PtNi/PDA-rGO is much more fluffy with a larger volume, indicating its lower density (Figure 2). The diamine groups on GO layers are helpful to highly disperse the GO against ordered restacking.

3.2 Experimental section

3.2.1 Materials and general methods

All chemicals were commercial and used without further purification. Graphite (C, Sigma-Aldrich, >99.8%), sulfuric acid (H_2SO_4 , Kishida Chem. Co., 98%), phosphoric Acid (H_3PO_4 , Tokyo Chemical Industry Co., 89%), hydrogen peroxide (H_2O_2 , Kishida Chem. Co., 30%), potassium permanganate (KMnO_4 , Kishida Chem. Co., 99.3%), potassium tetrachloroplatinate (K_2PtCl_4 , Wako Pure Chemical Industries, Ltd., >98%), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Wako Pure Chemical Industries, Ltd., 99%), sodium borohydride (NaBH_4 , Aldrich, 99%), sodium hydroxide (NaOH , Chameleon

Reagent, >98%), hydrochloric acid (HCl, Tokyo Chemical Industry Co., >35%), hydrazine monohydrate ($\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$, Sigma-Aldrich, 98%), 1,4-phenylenediamine ($\text{C}_6\text{H}_8\text{N}_2$, Tokyo Chemical Industry Co., 98%), acetone ($\text{C}_3\text{H}_6\text{O}$, Kishida Chem. Co., >99.5%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, Kishida Chem. Co., >99.8%) were used as received.

Powder X-ray diffraction patterns were collected for synthesized catalysts on a Rigaku Ultima IV X-ray diffractometer with Ni filtered Cu-K α radiation ($\lambda = 0.15406$ nm) (40 kV, 40 mA). X-ray photoelectron spectroscopic (XPS) measurements were conducted on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg K α source (10 kV, 10 mA). The argon sputtering experiments were carried out under the conditions of background vacuum of 3.2×10^{-6} Pa and sputtering acceleration voltage of 2 kV and sputtering current of 10 mA. The charging potential of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. The TEM and HAADF-STEM images and EDX spectra were recorded on Transmission electron microscope (TEM, TECNAI G² F20) with operating voltage at 200 kV equipped with energy-dispersive X-ray detector (EDX). Scanning electron microscopic (SEM) analyses were carried with a Hitachi S5000 field emission scanning electron microscope. FTIR spectra were measured by using a Bruker spectrometer IFS 66v/s. Mass analysis of the prepared gas was performed using a Balzers Prisma QMS 200 mass spectrometer.

3.2.2 Synthesis of graphene oxide: GO was synthesized according to the reported procedure.¹³ Firstly, a concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ solution (180:20 mL) was added to the mixture of graphite flakes (1.5 g) and KMnO_4 (9 g) and then the solution was kept at 323 K with a water bath for 12 hours. The solution was cooled to room temperature and poured into a flask containing ice (200 g) and H_2O_2 (30%, 1.5 mL). The solid material

was separated by centrifugation and washed with water (100 mL), HCl (100 mL), and ethanol (100 mL) (for 2 times). Finally, the obtained solid was dried in vacuum oven at room temperature for 12 h.

3.2.3 Syntheses of PtNi nanoparticle/diamine-alkalized graphene catalysts

(PtNi/PDA-rGO, PDA = 1,4-phenylenediamine): GO (50 mg) was dispersed in water (50 mL) under sonication for 2.5 h. PDA (0.27 g) was dissolved in acetone (4 mL) and then added dropwise into the GO solution. The mixture was stirred for 48 h, resulting in the formation of a black precipitation (PDA-GO). The precipitation was separated by centrifugation and washed with water. Subsequently, the prepared PDA-GO was dispersed in water (25 mL), to which an aqueous solution of K_2PtCl_4 (0.06 mmol) and $NiCl_2 \cdot 6H_2O$ (0.04 mmol) was added, followed by an immediate addition of $NaBH_4$ (30 mg) dissolved in an aqueous NaOH solution (1 mL, 5 M) with vigorous shaking, resulting in the formation of PtNi NPs on PDA-rGO. Finally, the PtNi/PDA-rGO catalyst was collected by centrifugation, washed with water and dried under vacuum at room temperature for 12 h, giving the PtNi/PDA-rGO catalyst. For comparison, the catalysts with different molar ratios of Pt^{2+}/Ni^{2+} were prepared by the same procedure using K_2PtCl_4 and $NiCl_2 \cdot 6H_2O$ as follows: 0.1 mmol (K_2PtCl_4) for Pt/PDA-rGO; 0.09 mmol (K_2PtCl_4) and 0.01 mmol ($NiCl_2$) for $Pt_{0.9}Ni_{0.1}$ /PDA-rGO; 0.08 mmol (K_2PtCl_4) and 0.02 mmol ($NiCl_2$) for $Pt_{0.8}Ni_{0.2}$ /PDA-rGO; 0.07 mmol (K_2PtCl_4) and 0.03 mmol ($NiCl_2$) for $Pt_{0.7}Ni_{0.3}$ /PDA-rGO; 0.05 mmol (K_2PtCl_4) and 0.05 mmol ($NiCl_2$) for $Pt_{0.5}Ni_{0.5}$ /PDA-rGO; 0.04 mmol (K_2PtCl_4) and 0.06 mmol ($NiCl_2$) for $Pt_{0.4}Ni_{0.6}$ /PDA-rGO; 0.03 mmol (K_2PtCl_4) and 0.07 mmol ($NiCl_2$) for $Pt_{0.3}Ni_{0.7}$ /PDA-rGO; and 0.1 mmol ($NiCl_2$) for Ni/PDA-rGO.

Additionally, the Pt_{0.6}Ni_{0.4}/rGO catalyst was also prepared using the similar synthetic procedure with GO instead of diamine-alkalized GO.

To avoid the oxidation of PtNi NPs, the catalysts were kept in an Ar-filled glove box immediately after dried under vacuum.

3.2.3 Catalytic activity characterization

In general, a mixture of as-synthesized catalyst and aqueous NaOH solution was placed in a two-necked round-bottom flask (30 mL), which was placed in a water bath at a preset temperature (298-323 K). A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (temperature kept constant at 298 K during measurements). The reaction started when hydrous hydrazine (0.1 mL) was injected into the mixture using a syringe. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generation. The molar ratios of (Pt+Ni)/hydrazine were theoretically fixed at 0.05 for all the catalytic reactions.

For testing the durability of PtNi NPs/PDA-rGO, hydrous hydrazine (0.1 mL) was subsequently added into the reaction flask after the completion of the first-run decomposition of hydrous hydrazine. Such test cycles of the catalyst for the dehydrogenation of hydrous hydrazine were carried out for 5 runs at 303 K by adding aliquots of hydrous hydrazine.

After the reaction, the Pt_{0.6}Ni_{0.4}/PDA-rGO catalyst was separated from the reaction solution by centrifugation and dried under vacuum at room temperature for TEM analyze.

Assuming all the PtNi NPs to be spherical, the specific surface area of PtNi NPs was calculated on the basis of the average particle diameter by using the equation: $S =$

$6/(d_p \times \rho)$, where S is specific surface area, d_p is the average particle diameter measured by TEM and ρ is the density, which was calculated by using the values of 21.35 g cm^{-3} for Pt and 8.91 g cm^{-3} for Ni and considering the molar ratio of Pt to Ni in the catalyst.

3.3 Results and discussion

3.3.1 Characterization

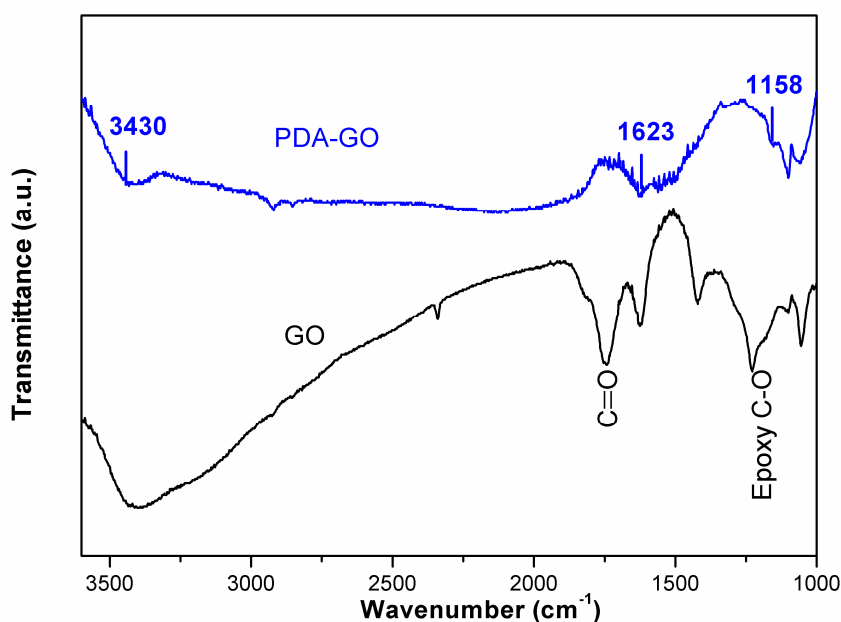


Figure 3. IR spectra of GO and PDA-GO.

Infrared spectroscopic (IR) measurements of PDA-GO show that most of the absorption bands from GO remain except for the bands assigned to the C=O and epoxy C-O (Figure 3), while new bands are observed at 1158, 1623, and 3430 cm^{-1} due to the antisymmetric C-N stretching vibration, scissoring in-plane bending mode of NH_2 groups and the N-H stretching vibrations, respectively.¹⁴ The characteristic X-Ray diffractions (XRD) at 40.5° , 46.6° , 68.8° , and 82.8° for PtNi are observed for $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$ but very weak for $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$, suggesting the formation of very small PtNi NPs on the diamine-alkalized rGO (Figure 4). With the increase of Ni

content, the diffraction peaks of $\text{Pt}_x\text{Ni}_{1-x}/\text{PDA-rGO}$ ($0 \leq x \leq 1.0$) are shifted to the higher angles, indicating the formation of PtNi alloy and no any possible segregation of Ni NPs, or Pt NPs on rGO (Figure 5).¹⁵

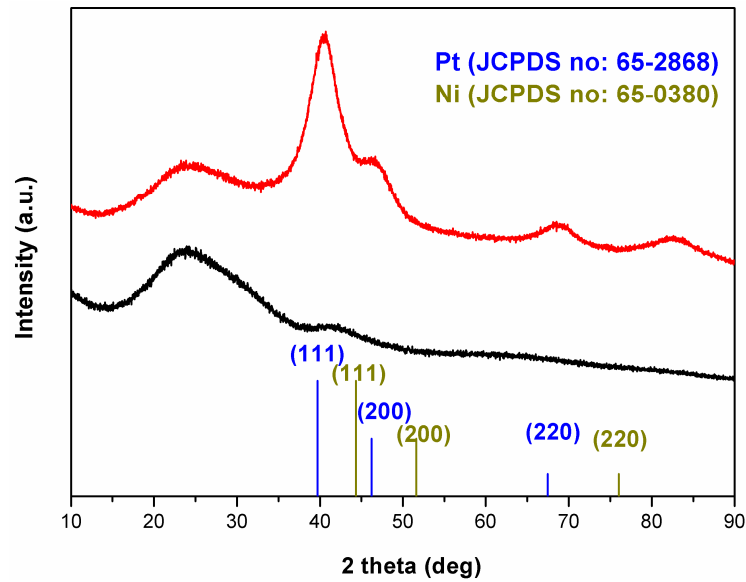


Figure 4. PXRD patterns of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ and $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$.

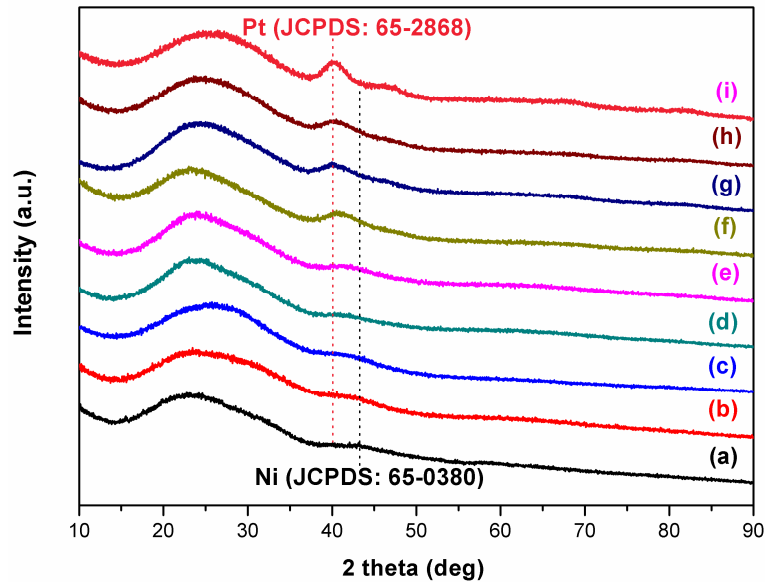


Figure 5. PXRD patterns of $\text{Pt}_x\text{Ni}_{1-x}/\text{PDA-rGO}$ ($0 \leq x \leq 1.0$): (a) Ni/PDA-rGO, (b) $\text{Pt}_{0.3}\text{Ni}_{0.7}/\text{PDA-rGO}$, (c) $\text{Pt}_{0.4}\text{Ni}_{0.6}/\text{PDA-rGO}$, (d) $\text{Pt}_{0.5}\text{Ni}_{0.5}/\text{PDA-rGO}$, (e)

Pt_{0.6}Ni_{0.4}/PDA-rGO, (f) Pt_{0.7}Ni_{0.3}/PDA-rGO, (g) Pt_{0.8}Ni_{0.2}/PDA-rGO, (h) Pt_{0.9}Ni_{0.1}/PDA-rGO and (i) Pt/PDA-rGO.

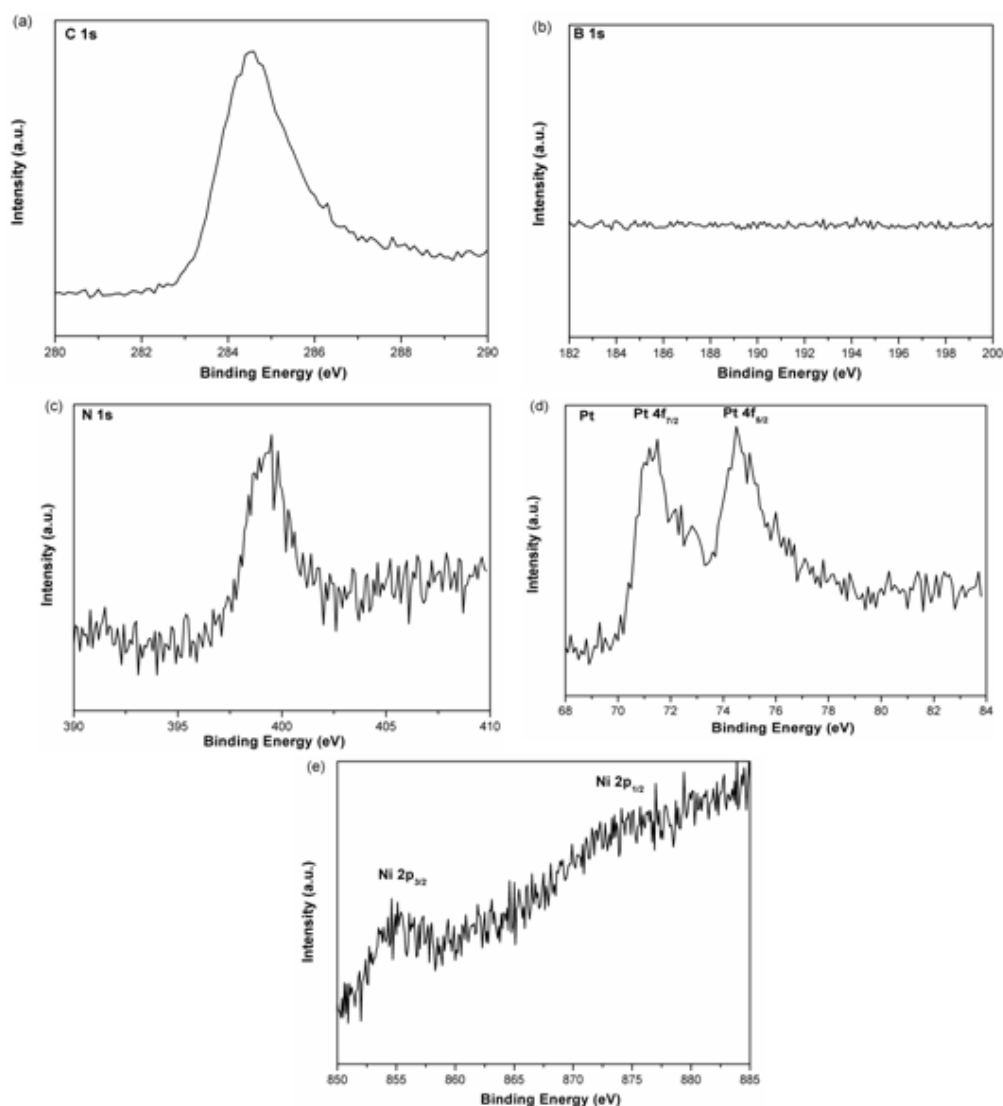


Figure 6. XPS spectra of C 1s, B 1s, N 1s, Pt 4f and Ni 2p for Pt_{0.6}Ni_{0.4}/PDA-rGO.

The X-ray photoelectron spectroscopic (XPS) measurement with Ar etching further confirms the anchoring of amine groups on GO with the signal for N 1s level at 399.5 eV. The signals at 71.5 and 74.5 eV are corresponding to Pt 4f_{7/2} and Pt 4f_{5/2} level for Pt⁰, while the signals at 854.7 and 874.1 eV are attributed to Ni 2p_{3/2} and Ni 2p_{1/2} levels for

Ni⁰ (Figure 6).

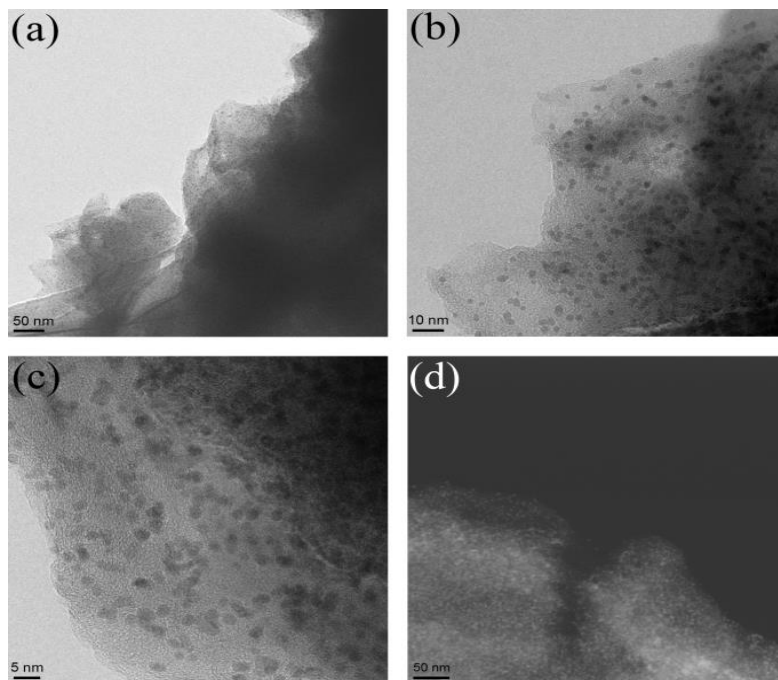


Figure 7. (a-c) TEM and (d) HAADF-STEM images of Pt_{0.6}Ni_{0.4}/PDA-rGO.

The morphologies of GO, PDA-GO and PtNi/PDA-rGO are characterized by scanning electron microscopy (SEM). In all the samples, the continuous silk wave-like morphology is observed due to the interactions between graphene layers (Figure 8).¹⁶ TEM (HAADF-STEM) images of Pt_{0.6}Ni_{0.4}/PDA-rGO show that Pt_{0.6}Ni_{0.4} NPs are homogenously dispersed on PDA-rGO with an average size of 2.5 nm (Figures 7 and 10a). According to the average size of Pt_{0.6}Ni_{0.4}, the specific surface area is calculated to be approximately 146.6 m² g⁻¹. In contrast, when Pt_{0.6}Ni_{0.4} NPs are directly supported on rGO, the NPs are aggregated with a larger average particle size (Figures 9 and 10b). In Pt_{0.6}Ni_{0.4}/PDA-rGO, the diamine groups on GO layers provide coordinating groups to combine metal ions (Pt²⁺, Ni²⁺), resulting in uniform and rich nuclei and a controlled growth process of PtNi on rGO. Without any support, according to our previous work,¹⁷

the PtNi NPs are more severely aggregated than Pt_{0.6}Ni_{0.4}/rGO.

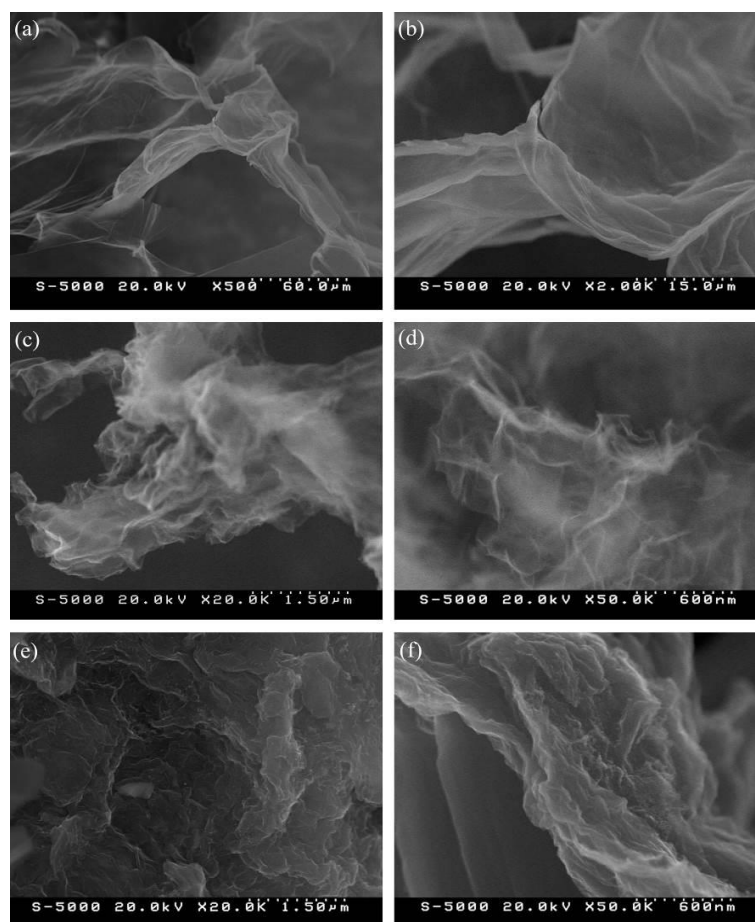


Figure 8. SEM images of (a, b) GO, (c, d) PDA-GO and (e, f) Pt_{0.6}Ni_{0.4}/PDA-rGO.

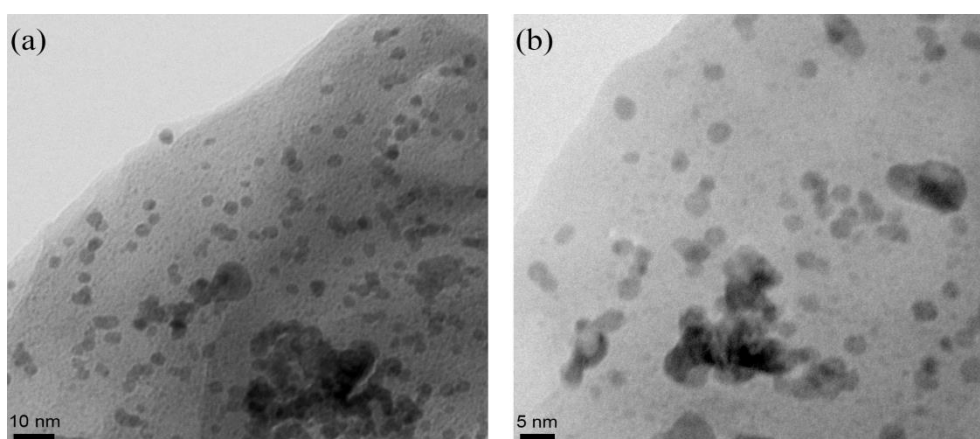


Figure 9. TEM images of Pt_{0.6}Ni_{0.4}/rGO.

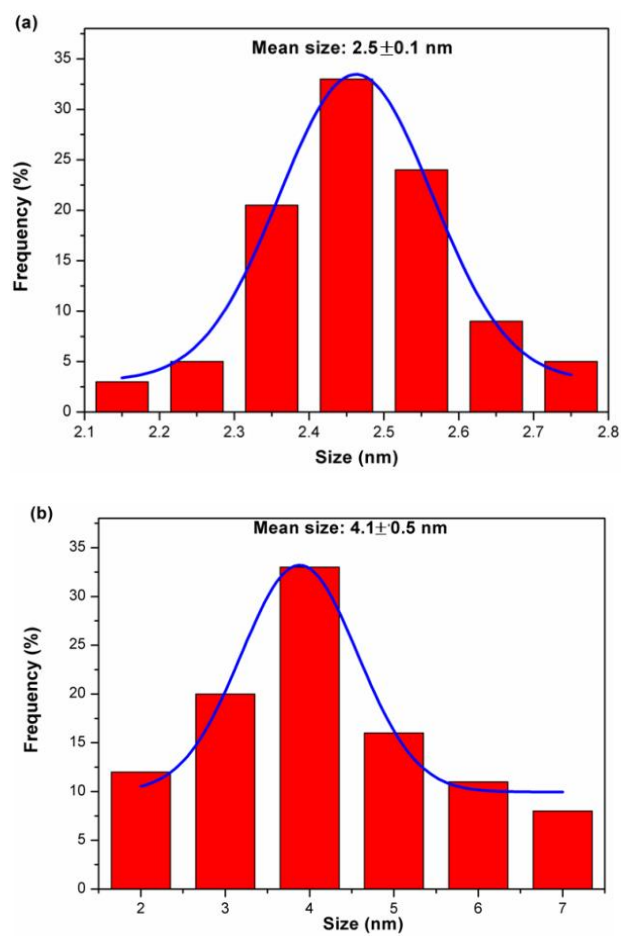


Figure 10. Particle size distribution histograms of (a) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ and (b) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$.

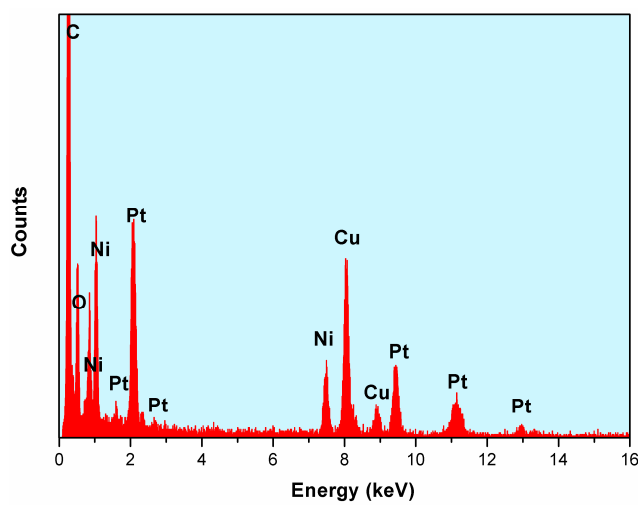


Figure 11. EDX pattern of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$.

3.3.2 Catalytic activity and durability

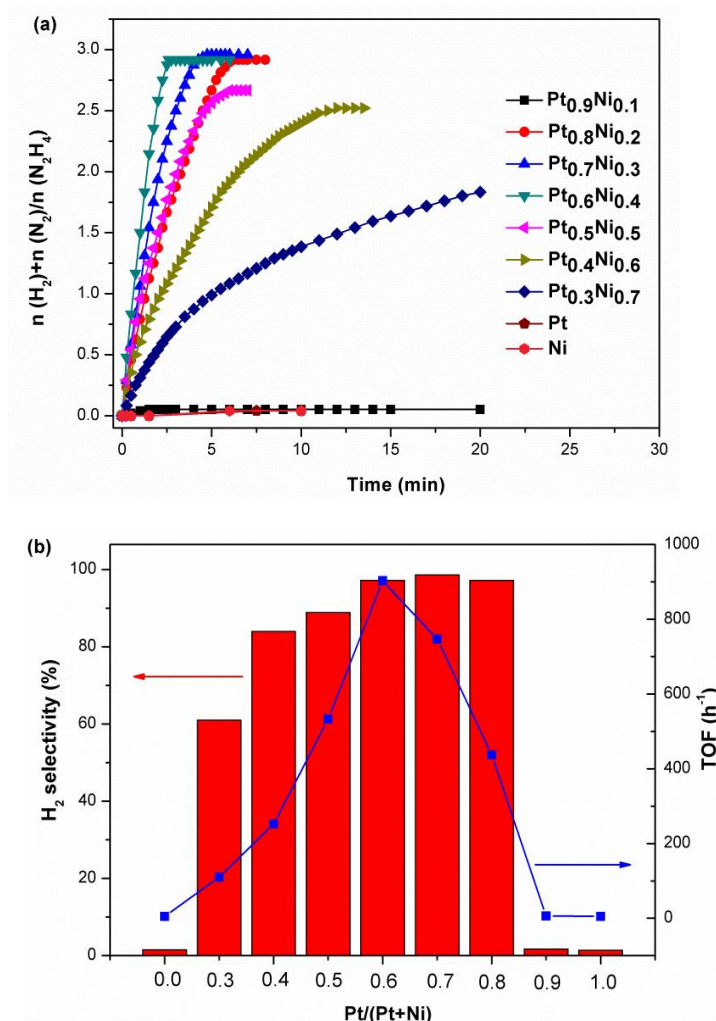


Figure 12. (a) Volume of the generated gas ($\text{H}_2 + \text{N}_2$) versus time and (b) corresponding TOF values of H_2 generation and H_2 selectivities for the dehydrogenation of hydrous hydrazine with different Pt/Ni molar ratio ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}} = 0.05$, 303 K).

The catalytic activity of $\text{Pt}_x\text{Ni}_{1-x}/\text{PDA-rGO}$ ($0 \leq x \leq 1.0$) for the dehydrogenation of hydrous hydrazine has been investigated at room temperature with a constant molar ratio of catalyst/ $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} = 0.05$. It can be seen that the catalytic activity and selectivity to hydrogen strongly depend on the Pt/Ni molar ratio (Figure 12). For monometallic Pt/PDA-rGO and Ni/PDA-rGO nanocatalysts, there is almost no gas

release from hydrous hydrazine, whereas the $\text{Pt}_x\text{Ni}_{1-x}/\text{PDA-rGO}$ nanocatalysts show high catalytic activities, exhibiting 100% H_2 selectivity with x from 0.6 to 0.8. The exceptional catalytic performances are mainly attributed to the synergistic coupling interaction between Pt and Ni. With the increasing Pt content, the catalytic activity of $\text{Pt}_x\text{Ni}_{1-x}/\text{PDA-rGO}$ initially increases, reaching an excellent catalytic activity with a TOF of 903 h^{-1} ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}} = 0.05$, 303 K) at $x = 0.6$, higher than most of those reported values (Table 1), and then decreases with a further increase of Pt amount.

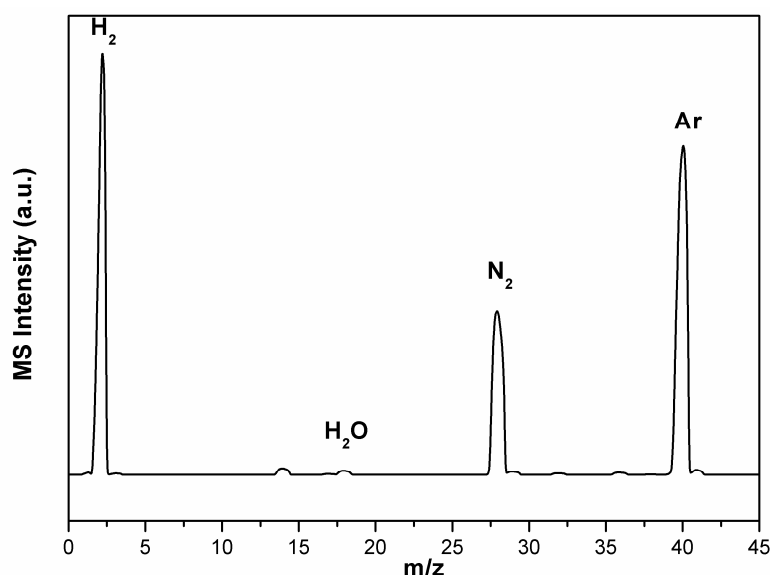


Figure 13. Mass spectrum of the released gas from the dehydrogenation of hydrous hydrazine over $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ under an argon atmosphere at room temperature, showing the absence of NH_3 in the released gas.

Mass spectroscopic (MS) results confirm the formation of H_2 and N_2 and the absence of NH_3 in the released gas (Figure 13), in agreement with the volumetric observations of 100% selectivity for hydrogen. In contrast to the excellent catalytic performance of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$, $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$ showed a very low activity for the dehydrogenation of hydrous hydrazine under the same conditions (Figure 14), over which the time for

reaction completion increased to 11 minutes, corresponding a TOF of 218 h⁻¹ ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}} = 0.05$, 303 K).

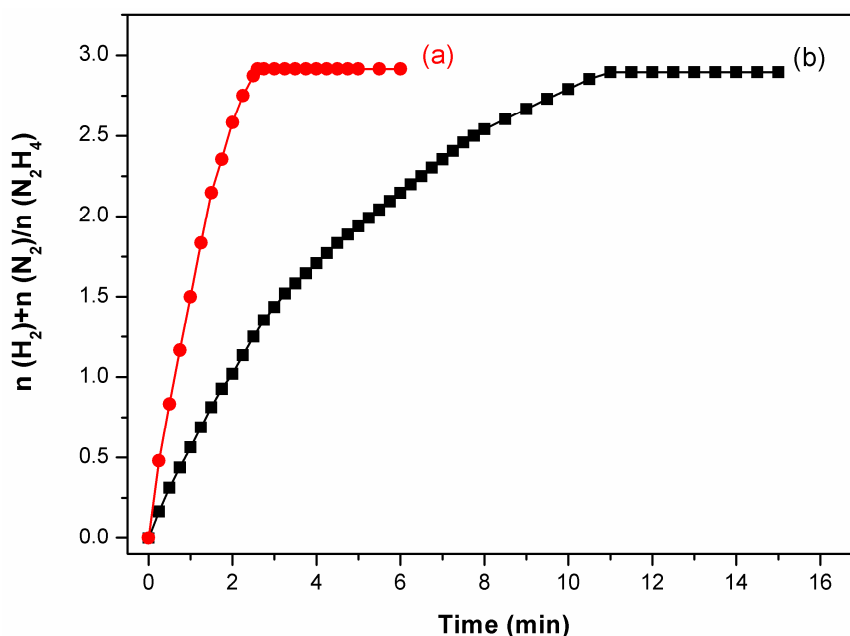


Figure 14. Volume of the generated gas ($\text{H}_2 + \text{N}_2$) versus time for the dehydrogenation of hydrous hydrazine over (a) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ and (b) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$ ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}} = 0.05$, 303 K).

Table 1. Catalytic activities of different catalysts for the dehydrogenation of hydrous hydrazine

Catalyst	Solvent/medium	Temp. (K)	Selectivity for H_2 (100 %)	TOF (h^{-1})	E_a (kJ mol^{-1})	Ref.
$\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$	Aqueous NaOH	323	100	2056	33.39	This work
	Aqueous NaOH	303	100	903		This work
$\text{Ni}_{88}\text{Pt}_{12}/\text{MIL-101}$	Aqueous NaOH	323	100	350	55.5	18
$\text{Ni}_{66}\text{Rh}_{34}/\text{ZIF-8}$	Aqueous NaOH	323	100	140	58.1	7
$\text{Ni}_{0.6}\text{Fe}_{0.4}\text{B}$	Aqueous NaOH	323	100	28.8	50.7	19
$\text{NiMoB-La}(\text{OH})_3$	Aqueous NaOH	323	100	13.3	55.1	10

Pt ₆₀ Ni ₄₀ -CNDs	Aqueous NaOH	323	100	170	43.9	5d
Co _{0.65} Pt _{0.3} (CeOx) _{0.05}	Aqueous NaOH	298	72.1	194.8		20
Ni ₆ Pt ₄ -SF	Aqueous NaOH	298	100	150		17
Ni ₃ Pt ₇ /graphene	Aqueous NaOH	298	100	68	49.4	3
Ni _{0.9} Pt _{0.1} /Ce ₂ O ₃	Aqueous NaOH	298	100	28.1	42.3	21
Rh _{4.4} Ni/graphene	Aqueous NaOH	298	100	28		22
Fe-B/multiwalled carbon nanotubes	Without additive	293	97	4032	46.7	23
Co-B-N-H	Without additive	293	100	4434	39.9	24
Ni ₃ Fe/C	Without additive	293	100	528	48.1	25
NiFe/Cu	Without additive	343	100	35	44	26
NiIr _{0.059} /Al ₂ O ₃ -HT	Without additive	303	99	12.4	49.3	6b
NiPt _{0.057} /Al ₂ O ₃ -HT	Without additive	303	97	16.5	34	6a
Ni _{1.5} Fe _{1.0} /(MgO) _{3.5}	Without additive	299	99	11		8
Rh	Without additive	298	43.8	2.5		2b
Rh ₄ Ni	Without additive	298	100	4.8		2c
Ni _{0.95} Ir _{0.05}	Without additive	298	100	2.2		27

The exceptional catalytic performance of Pt_{0.6}Ni_{0.4}/PDA-rGO, on the one hand, would be attributed to the fact that the amine groups could benefit the immobilization of the ultrafine Pt_{0.6}Ni_{0.4} NPs on rGO (Figure 8). On the other hand, the diamine-alkalized graphene promotes electron transfer to form the electron-rich Pt_{0.6}Ni_{0.4} NPs, which could efficiently facilitate the cleavage of the covalent N-H bonds and thus improve the catalytic property.^{26, 27} Moreover, as compared to Pt_{0.6}Ni_{0.4}, larger shifts of the binding energies of Pt 4f and Ni 2p were observed for Pt_{0.6}Ni_{0.4}/PDA-rGO than those for Pt_{0.6}Ni_{0.4}/rGO.

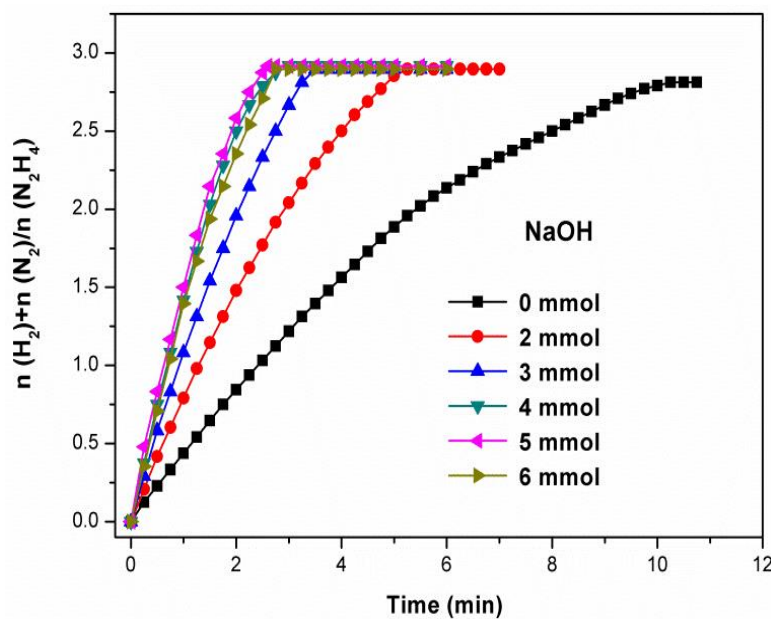


Figure 15. Volume of the generated gas ($\text{H}_2 + \text{N}_2$) versus time for the dehydrogenation of hydrous hydrazine over $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ with different amounts of NaOH ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}} = 0.05$, 303 K).

Besides the good dispersion of the ultrafine NPs and their synergistic coupling with amine groups, the presence of NaOH also plays an important role in enhancement of catalytic performance. To determine the effect of the amount of NaOH on the catalytic performance, the dehydrogenation reactions of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ with various amounts of NaOH (0-6 mmol) have been examined (Figure 15). It has been found the catalytic activity for the dehydrogenation of hydrous hydrazine increases with the amounts of NaOH until the value reaches 4 mmol, and a further increase in the amount of NaOH shows little effect on the catalytic performance. The possible reason for the effects of the NaOH additive may be explained as below: the addition of NaOH could efficiently decreases the concentration of undesirable N_2H_5^+ ($\text{N}_2\text{H}_5^+ + \text{OH}^- \rightarrow \text{N}_2\text{H}_4 + \text{H}_2\text{O}$) and promotes the rate-determining deprotonation step ($\text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3^* + \text{H}^*$), which is crucial and benefits the final elimination of N-H bonds to produce N_2 and H_2 .²⁸

However, despite of the large number of efforts that have been made from of both experimental and theoretical sides, the detailed mechanism for the decomposition of hydrazine is not yet clear, as the N-H bond cleavage in hydrazine could results in an abundance of N_xH_y ($x= 1-2$, $y=1-3$) free radicals and the subsequent activation is complicated.²⁹

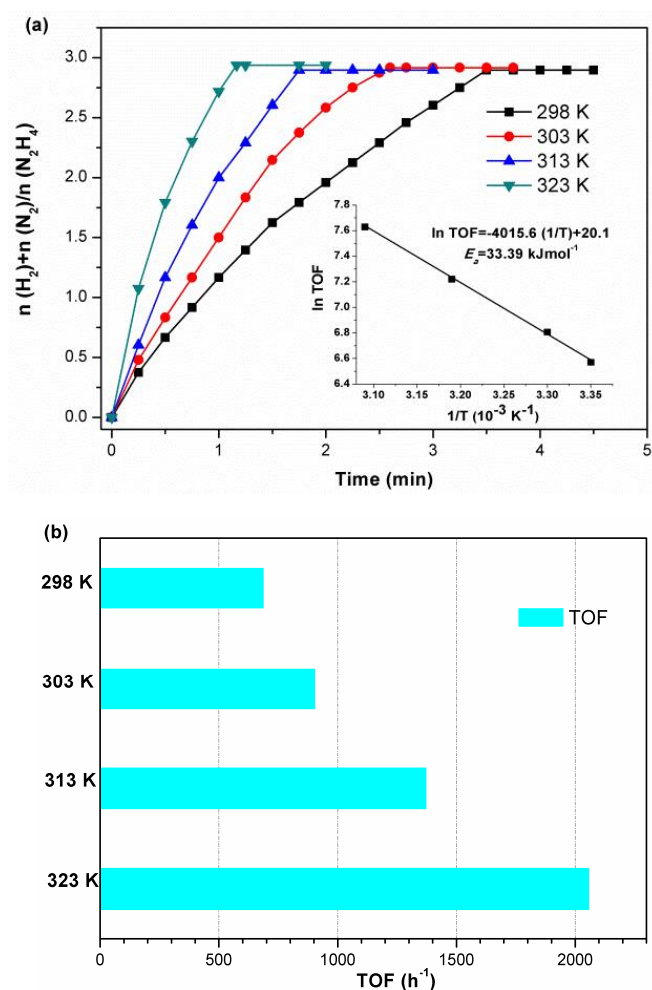


Figure 16 (a) Volume of the generated gas ($H_2 + N_2$) versus time and (b) corresponding TOF values of H_2 generation for the dehydrogenation of hydrous hydrazine at different temperatures over $Pt_{0.6}Ni_{0.4}/PDA-rGO$ ($n_{metal}/n_{N_2H_4 \cdot H_2O} = 0.05$). Inset of (a): Arrhenius plot ($\ln(TOF)$ vs. $1/T$).

The gas generation rate over $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ catalyst greatly depends on the reaction temperature. The catalytic reactions are completed in 3.5, 2.6, 1.8 and 1.2 min at 293, 303, 313 and 323 K, respectively, which corresponds to TOF values of 686, 903, 1371 and 2056 h^{-1} (Figure 16). The Arrhenius plot fitted on the basis of the TOF values for the decomposition of hydrous hydrazine at different reaction temperatures gives an activation energy (E_a) of 33.39 kJ mol^{-1} , which is lower than most of the previously reported values for hydrous hydrazine.³⁰

In addition, we further examine briefly the stability of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ catalyst by adding aqueous hydrous hydrazine (2.0 mmol) into catalyst after the reaction completion for the last run. No significant loss in activity and selectivity is observed after 5 cycles (Figure 17). TEM measurement of the recovered catalyst show no obvious change in particle size (Figure 18), indicating that the $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ catalyst has high durability and stability under the current dehydrogenation of hydrous hydrazine.

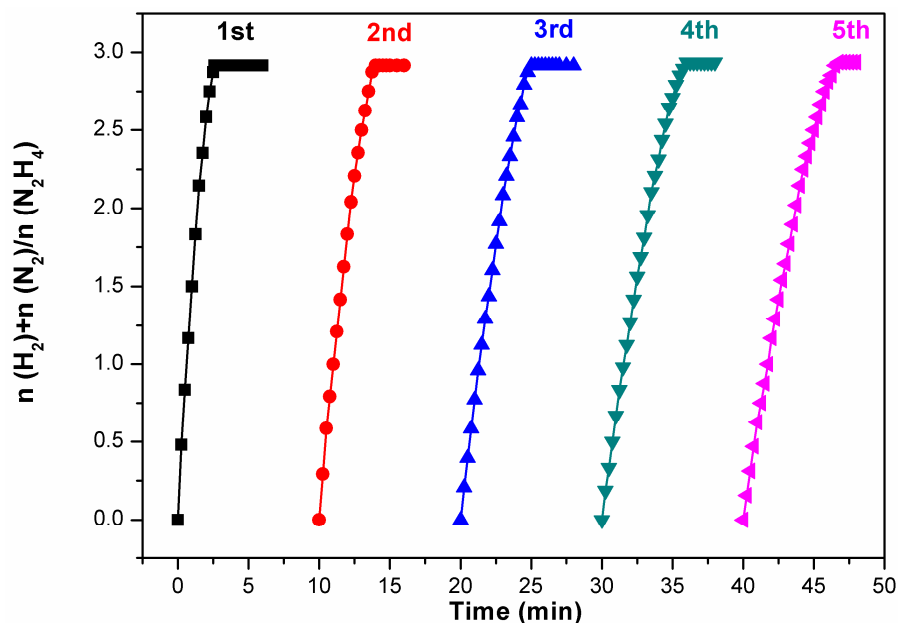


Figure 17. Durability test for the dehydrogenation of hydrous hydrazine over $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}} = 0.05$, 303 K).

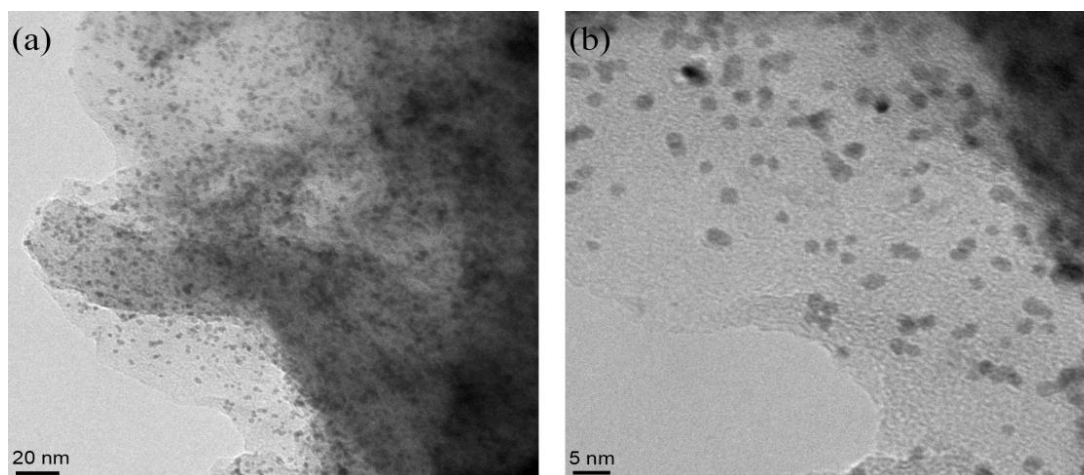


Figure 18. TEM images of Pt_{0.6}Ni_{0.4}/PDA-rGO after catalysis.

3.4 Conclusion

In summary, we have successfully immobilized the ultrafine PtNi NPs on diamine-alkalized reduced graphene oxide. By using the alkaline graphene, well-dispersed ultrafine PtNi NPs (2.5 nm) can be readily obtained. The resultant Pt_{0.6}Ni_{0.4}/PDA-rGO shows an excellent catalytic activity for the dehydrogenation of hydrous hydrazine under mild conditions, with a TOF value as high as 903 h⁻¹ at 30 °C and 2056 h⁻¹ at 50 °C. The excellent performance on catalytic activity could arise from the synergic interactions not only between Pt and Ni but also between NPs and PDA-rGO support. As an effective strategy, it provides an opportunity to immobilize ultrafine metal NPs on GO, which have tremendous application prospect in various catalytic fields.

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Chapter 4

Monodispersed CuCo Nanoparticles Supported on Aromatic Diamine-Alkalized Graphene as a Non-noble Metal Catalyst for Dehydrogenation of Ammonia Borane

Non-noble bimetallic CuCo NPs were successfully supported on diamine-alkalized reduced graphene oxide. Compared to other supports materials, the catalyst synthesized with the alkalized rGO displayed remarkably enhanced catalytic performance for dehydrogenation of ammonia borane with TOF of $163 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{min}^{-1}$ at 323 K. The synergistic effect between ultrafine Cu and Co NPs played an important role on improvement in dehydrogenation of ammonia borane.

4.1 Introduction

The dramatic climate change, limited fossil fuels and rapidly increasing need for energy have spurred internationally unprecedented interest in development of safe and effective hydrogen storage materials.¹ Due to its high hydrogen content (19.6 %), water solubility and nontoxicity, ammonia borane (NH_3BH_3 , AB) is considered a promising candidate for hydrogen storage materials.² In addition, one mole of AB can release three moles of hydrogen (H_2) via a complete decomposition: $\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2$. Thus, it is urgently important to synthesize the catalysts with excellent catalytic performance for AB as a practical H_2 storage medium.

Although rapid dehydrogenation has been achieved by using noble metals, the limited

resources restrict their practical applications.³ Alternatively, the cost-effective non-noble metals (such as Co, Fe and Ni) have attracted more and more attentions.⁴ However, the catalytic kinetics of H₂ generation rate is still not satisfying the demands for practical applications; therefore, the synthesis of non-noble catalysts with excellent catalytic performance at ambient temperature is urgently important.

Ultrafine metal nanoparticles (NPs) with particle size below 4 nm have attracted particular interest due to their increased surface area and the number of edge and corner atoms, which greatly improves their catalytic properties.⁵ In order to get well dispersed metallic NPs and restrain the agglomeration of metal NPs, organic surfactants have been widely used.⁶ However, although these organic surfactant molecules have a good dispersibility in solution, the long alkyl chains capped on the metal NPs generally hinder the direct contact between metal NPs and reactants, decreasing the catalytic activities.⁷ Recently, support effects have received considerable attention, which could not only effectively restrain the agglomeration of metal NPs, but also improve their catalytic activities.⁸ Reduced graphene oxide (rGO) consisting of chemically converted monolayer carbon atoms has been considered as one of the most promising supports for metal NPs due to its high carrier mobility, excellent thermal and electrical conductivity.⁹ Especially, the functional GO with electron-rich modified groups could coordinate metal ions in precursor solution and control the size during the growth of metal NPs. Moreover, such modification may also adjust the electronic properties and alkalinity/acidity of GO, and thus efficiently improve the catalytic performance of the resultant catalysts.

Herein, we immobilize successfully the monodispersed CuCo NPs on diamine-alkalized reduced graphene oxide, PDA-rGO, (PDA = 1,4-phenylenediamine),

which shows the high TOF values ($163 \text{ mol}_{\text{H}_2}\text{mol}_{\text{cat}}^{-1}\text{min}^{-1}$ at 323 K) for hydrolytic dehydrogenation of AB.

4.2 Experimental section

4.2.1 Materials

All chemicals were commercial and used without further purification. Graphite (C, Sigma-Aldrich, >99.8%), sulfuric acid (H_2SO_4 , Kishida Chem. Co., 98%), phosphoric Acid (H_3PO_4 , Tokyo Chemical Industry Co., 89%), hydrogen peroxide (H_2O_2 , Kishida Chem. Co., 30%), potassium permanganate (KMnO_4 , Kishida Chem. Co., 99.3%), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Wako Pure Chemical Industries, Ltd., >99%), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Wako Pure Chemical Industries, Ltd., 99%), sodium borohydride (NaBH_4 , Aldrich, 99%), hydrochloric acid (HCl , Tokyo Chemical Industry Co., >35%), ammonia borane (NH_3BH_3 , Tokyo Chemical Industry Co., >97%), 1,4-phenylenediamine ($\text{C}_6\text{H}_8\text{N}_2$, Tokyo Chemical Industry Co., 98%), acetone ($\text{C}_3\text{H}_6\text{O}$, Kishida Chem. Co., >99.5%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, Kishida Chem. Co., >99.8%), polyvinylpyrrolidone K 30 (PVP, viscosity average molecular weight is 40000, Tokyo Chemical Industry Co., >99%) and Vulcan XC-72R (carbon, specific surface area of $240 \text{ m}^2\text{g}^{-1}$, Cabot Corp.) were used as received.

4.2.2 Synthesis of graphene oxide: GO was synthesized according to the reported procedure.¹⁰ Firstly, a concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ solution (180:20 mL) was added to the mixture of graphite flakes (1.5 g) and KMnO_4 (9 g) and then the solution was kept at 323 K with a water bath for 12 hours. The solution was cooled to room temperature and poured into a flask containing ice (200 g) and H_2O_2 (30%, 1.5 mL). The solid material was separated by centrifugation and washed with water (100 mL), HCl (100 mL), and

ethanol (100 mL) (for 2 times). Finally, the obtained solid was dried in vacuum oven at room temperature for 12 h.

4.2.3 Syntheses of PtNi nanoparticle/diamine-alkalized graphene catalysts

(PtNi/PDA-rGO, PDA = 1,4-phenylenediamine): GO (50 mg) was dispersed in water (50 mL) under sonication for 2.5 h. PDA (0.27 g) was dissolved in acetone (4 mL) and then added dropwise into the GO solution. The mixture was stirred for 48 h, resulting in the formation of a black precipitation (PDA-GO). The precipitation was separated by centrifugation and dried under vacuum oven for 12 h. Subsequently, the prepared PDA-GO was dispersed in water, to which an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot (0.02 \text{ mmol})$ and $\text{CoCl}_2 \cdot (0.08 \text{ mmol})$ was added, followed by an immediate addition of NaBH_4 (30 mg), resulting in the formation of $\text{Cu}_{0.2}\text{Co}_{0.8}$ NPs on PDA-rGO.

For comparison, the catalysts with different molar ratios of $\text{Cu}^{2+}/\text{Co}^{2+}$ were prepared by the same procedure using $\text{Cu}(\text{NO}_3)_2$ and CoCl_2 as follows: 0.1 mmol CoCl_2 for Co/PDA-rGO; 0.01 mmol $\text{Cu}(\text{NO}_3)_2$ and 0.09 mmol CoCl_2 for $\text{Cu}_{0.1}\text{Co}_{0.9}$ /PDA-rGO; 0.03 mmol $\text{Cu}(\text{NO}_3)_2$ and 0.06 mmol CoCl_2 for $\text{Cu}_{0.3}\text{Co}_{0.7}$ /PDA-rGO; and 0.04 mmol $\text{Cu}(\text{NO}_3)_2$ and 0.06 mmol CoCl_2 for $\text{Cu}_{0.4}\text{Co}_{0.6}$ /PDA-rGO.

Additionally, the $\text{Cu}_{0.2}\text{Co}_{0.8}$ /rGO catalyst was also prepared using the similar synthetic procedure with GO instead of diamine-alkalized GO.

The $\text{Cu}_{0.2}\text{Co}_{0.8}$ /PVP catalyst was also prepared using the similar synthetic procedure with PVP (0.05 g) instead of diamine-alkalized GO.

The $\text{Cu}_{0.2}\text{Co}_{0.8}$ /XC-72R catalyst was also prepared using the similar synthetic procedure with XC-72R (0.05 g) instead of diamine-alkalized GO.

The $\text{Cu}_{0.2}\text{Co}_{0.8}$ -SP-Free catalyst was also prepared using the similar synthetic

procedure without diamine-alkalized GO.

4.2.4 Catalytic activity characterization

In general, a mixture of as-synthesized catalyst and aqueous solution was placed in a two-necked round-bottom flask (30 mL), which was placed in a water bath at a preset temperature (298-323 K). A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (temperature kept constant at 298 K during measurements). The reaction started when aqueous AB solution (1 mmol) was injected into the mixture using a syringe. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generation. The molar ratios of (Cu+Co)/AB were theoretically fixed at 0.1 for all the catalytic reactions.

For testing the durability of $\text{Cu}_{0.2}\text{Co}_{0.8}$ NPs/PDA-rGO, aqueous AB solution (2 mmol) was subsequently added into the reaction flask after the completion of the first-run decomposition of AB. Such test cycles of the catalyst for the dehydrogenation of AB were carried out for 5 runs at 303 K by adding aqueous AB solution (2 mmol).

After the reaction, the $\text{Cu}_{0.2}\text{Co}_{0.8}$ /PDA-rGO catalyst was separated from the reaction solution by centrifugation and dried under vacuum at room temperature for TEM and XRD analyze.

4.3 Results and discussion

4.3.1 Characterization

The X-ray photoelectron spectroscopic (XPS) measurement with Ar etching further confirms the anchoring of amine groups on GO with the signal for N 1s level at 399.2

eV. The signals at 933.2 and 953.1 eV are corresponding to Cu 2p_{3/2} and Cu 2p_{1/2} level for Cu⁰, while the signals at 778.7 and 793.9 eV are attributed to Co 2p_{3/2} and Co 2p_{1/2} levels for Co⁰ (Figure 1).

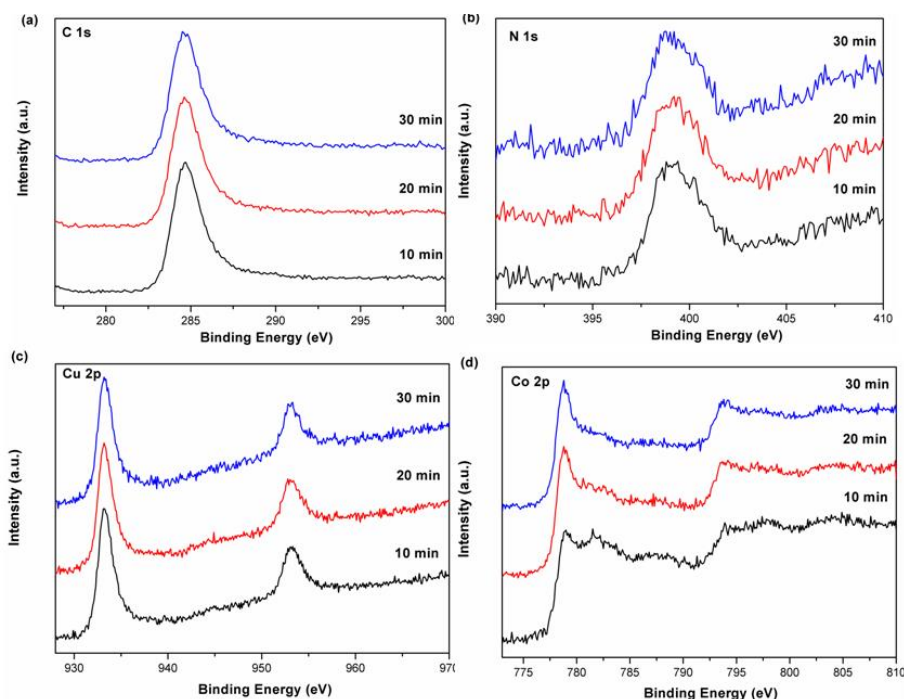


Figure 1. XPS spectra of C 1s, N 1s, Cu 2p and Co 2p for Cu_{0.2}Co_{0.8}/PDA-rGO.

The characteristic X-Ray diffractions (XRD) for CuCo are very weak for Cu_{0.2}Co_{0.8}/PDA-rGO, suggesting the formation of very small CuCo NPs on the diamine-alkalized rGO (Figure 2). The transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images of Cu_{0.2}Co_{0.8}/PDA-rGO show that discrete CuCo NPs are homogenously dispersed on rGO (Figure 3). In contrast, when Cu_{0.2}Co_{0.8} NPs are directly supported on rGO and without support, some CuCo NPs show aggregation in certain areas. For Cu_{0.2}Co_{0.8}/PVP and Cu_{0.2}Co_{0.8}/XC-72R, although the CuCo NPs are dispersed well on supports, the NPs show a larger average particle size. The formation of ultrafine CuCo NPs is attributed to

the diamine groups, which not only highly disperse the GO against ordered restacking, but also provide coordinating groups to combine with (Co^{2+} , Cu^{2+}) ions, resulting in rich and uniform nuclei and a controlled growth process of CuCo on rGO.

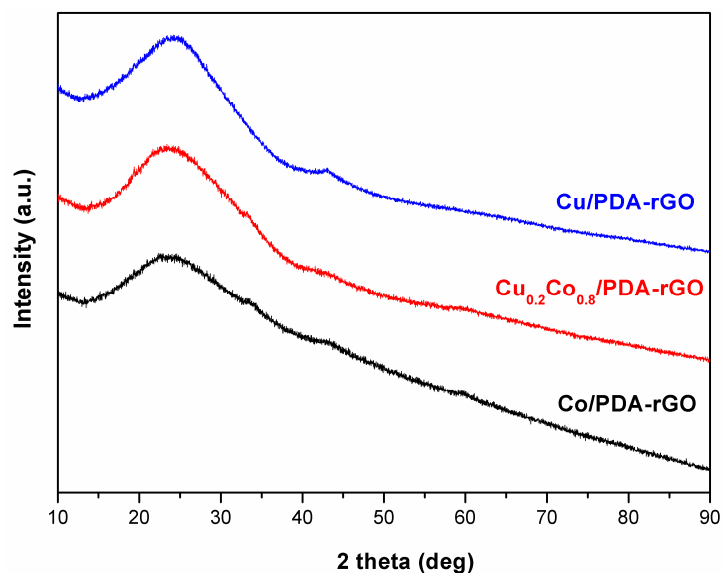


Figure 2. PXRD patterns of: Cu/PDA-rGO, $\text{Cu}_{0.2}\text{Co}_{0.8}$ /PDA-rGO and Co/PDA-rGO

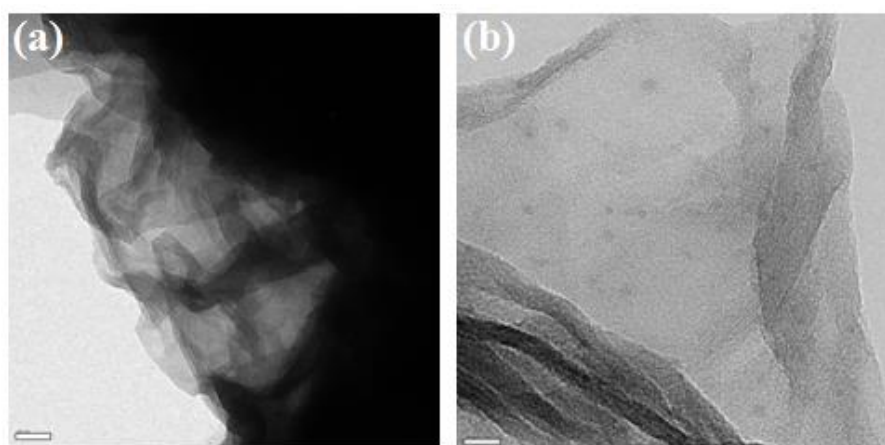


Figure 3. TEM images of $\text{Cu}_{0.2}\text{Co}_{0.8}$ /PDA-rGO (Scale bar: (a) 50 nm and (b) 10 nm).

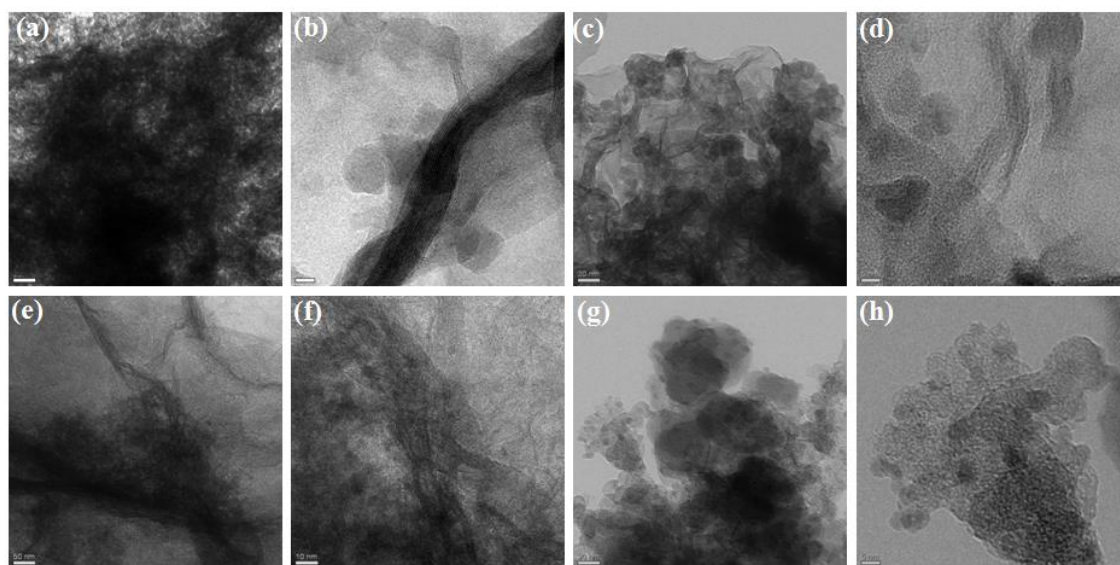


Figure 4. TEM images of: $\text{Cu}_{0.2}\text{Co}_{0.8}$ -SP-Free, $\text{Cu}_{0.2}\text{Co}_{0.8}$ /PVP, $\text{Cu}_{0.2}\text{Co}_{0.8}$ /rGO and $\text{Cu}_{0.2}\text{Co}_{0.8}$ /XC-72R (Scale bar: (e) 50 nm, (a) (c) (g) 20 nm, (g) 10 nm and (b) (d) (h) 5 nm).

4.3.2 Catalytic activity and durability

The catalytic performance of $\text{Cu}_x\text{Co}_{1-x}$ /PDA-rGO ($0 \leq x \leq 0.4$) for the dehydrogenation of AB has been investigated at room temperature with a constant molar ratio of catalyst/AB = 0.05. The Cu/Co molar ratio plays an important role in catalytic performance (Figure 5).

The $\text{Cu}_x\text{Co}_{1-x}$ /PDA-rGO nanocatalyst shows high catalytic activities, exhibiting 100 % H_2 selectivity with x from 0 to 0.3. The exceptional catalytic performances are mainly attributed to the synergic coupling interaction between Cu and Co. With the increasing Cu content, the catalytic activity of $\text{Cu}_x\text{Co}_{1-x}$ /PDA-rGO initially increases, reaching an excellent catalytic activity with TOF of $55 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{min}^{-1}$ ($n_{\text{metal}}/n_{\text{AB}} = 0.05$, 303 K) at $x = 0.2$, and then decreases with a further increase of Cu amount.

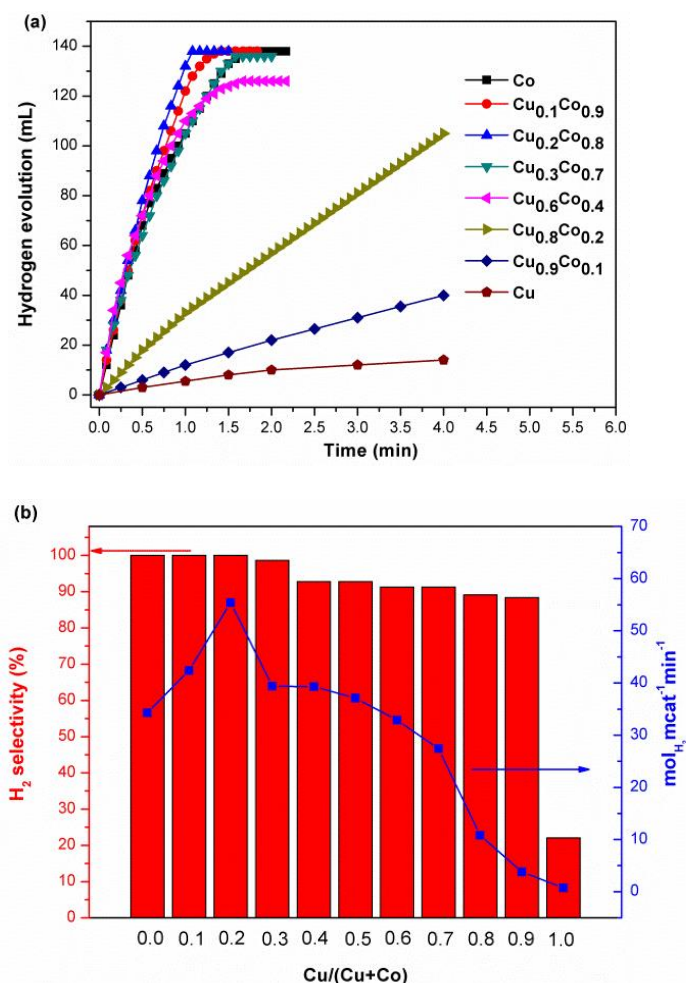


Figure 5. Volume of the generated gas (H₂) versus time for the dehydrogenation of AB with different Cu/Co molar ratio ($n_{\text{metal}}/n_{\text{AB}} = 0.05$, 303 K).

To evaluate the role of support in the promotion of catalytic performance, we prepared the Cu_{0.2}Co_{0.8}/rGO, Cu_{0.2}Co_{0.8}/XC-72R, Cu_{0.2}Co_{0.8}/PVP and Cu_{0.2}Co_{0.8}-SP-Free catalyst for comparison (Figure 6). For Cu_{0.2}Co_{0.8}/rGO and Cu_{0.2}Co_{0.8}/XC-72R, the catalytic reactions are complete in 2.9 and 3.6 min under the same condition, respectively, corresponding TOF values of 10 and 20.6 and 16.4 mol_{H2}mol_{cat}⁻¹min⁻¹ at 303 K. Without any supports, Cu_{0.2}Co_{0.8}-SP-Free showed a very low catalytic activity for hydrolytic dehydrogenation of AB under the same conditions, over which the time for reaction completion increased to 5 minutes with a TOF of 12

$\text{mol}_{\text{H}_2}\text{mol}_{\text{cat}}^{-1}\text{min}^{-1}$. When $\text{Cu}_{0.2}\text{Co}_{0.8}$ NPs were directly deposited on PVP, 126 mL of gas (91% selectivity) is released from AB in 8 min. The exceptional catalytic performance of $\text{Cu}_{0.2}\text{Co}_{0.8}$ /PDA-rGO catalyst could be attributed to the ultrafine $\text{Cu}_{0.2}\text{Co}_{0.8}$ NPs immobilized on rGO surface.

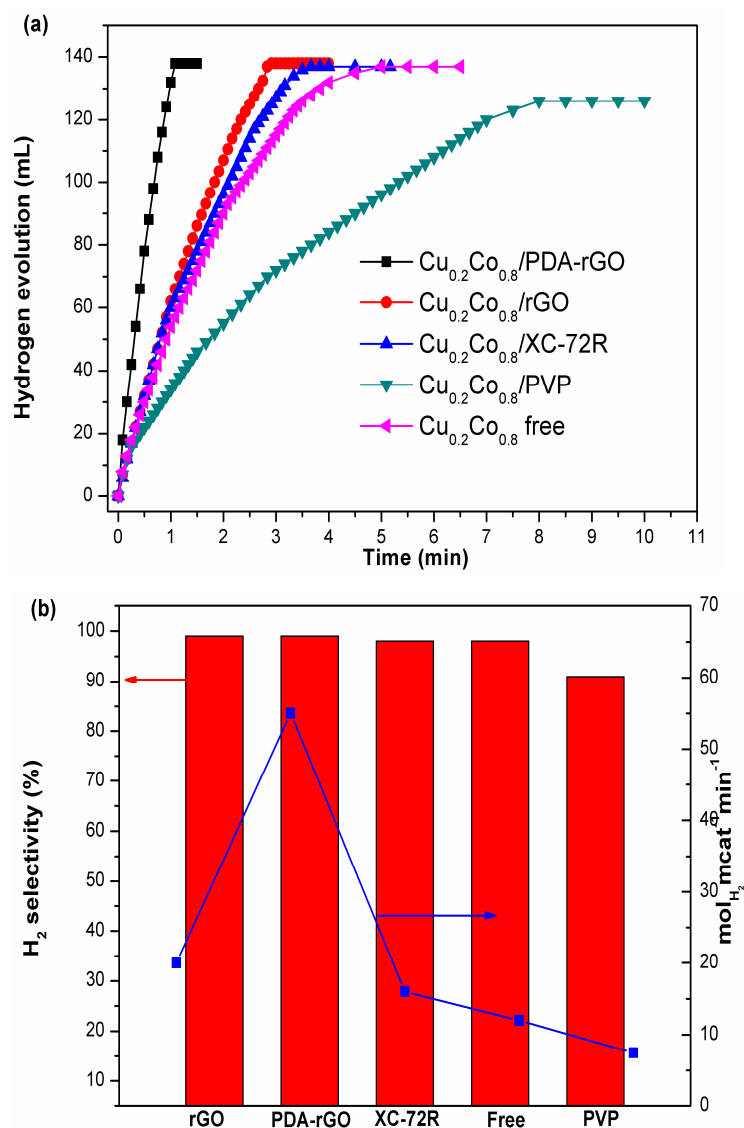


Figure 6. (a) Volume of the generated gas (H_2) versus time and (b) corresponding TOF values of H_2 generation and H_2 selectivities for the hydrolytic dehydrogenation of AB with different supports ($n_{\text{metal}}/n_{\text{AB}} = 0.05$, 303 K).

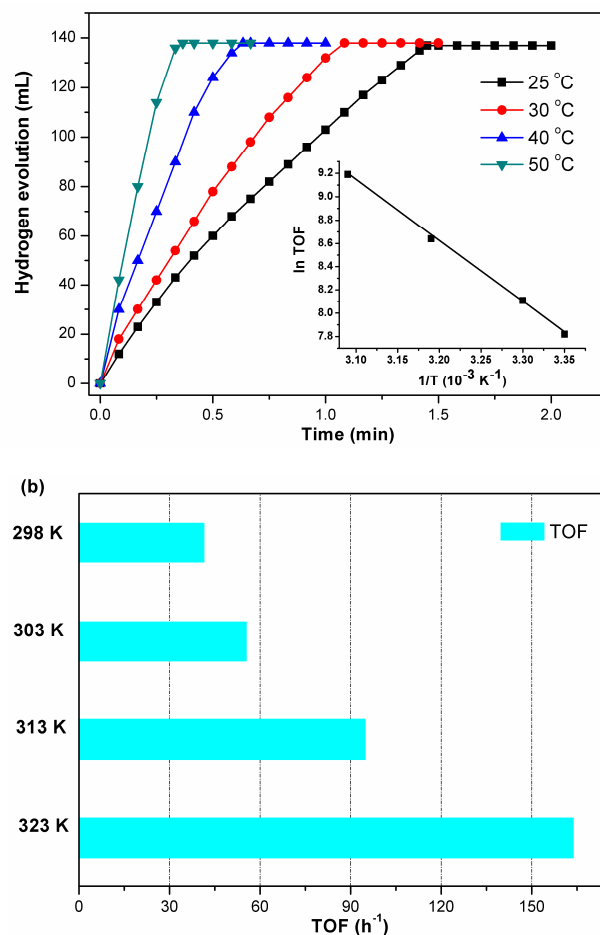


Figure 7. Volume of the generated gas (H₂) versus time for the dehydrogenation of AB at different temperatures over Cu_{0.2}Co_{0.8}/PDA-rGO ($n_{\text{metal}}/n_{\text{AB}} = 0.05$). Inset of (a): Arrhenius plot ($\ln(\text{TOF})$ vs. $1/T$).

The gas release rate over Cu_{0.2}Co_{0.8}/PDA-rGO catalyst is greatly dependent on the reaction temperature. The Cu_{0.2}Co_{0.8}/PDA-rGO catalyst exhibits the TOF values of 41, 55, 94 and 163 mol_{H₂}mol_{cat}⁻¹min⁻¹ at 293, 303, 313 and 323 K, corresponding to the reaction time of 1.45, 1.08, 0.63 and 0.36 min. The activation energy (E_a) of this process is estimated to be 25.25 kJ mol⁻¹ by the Arrhenius plot fitted on the basis of the TOF values for the dehydrogenation of AB at different reaction temperatures.

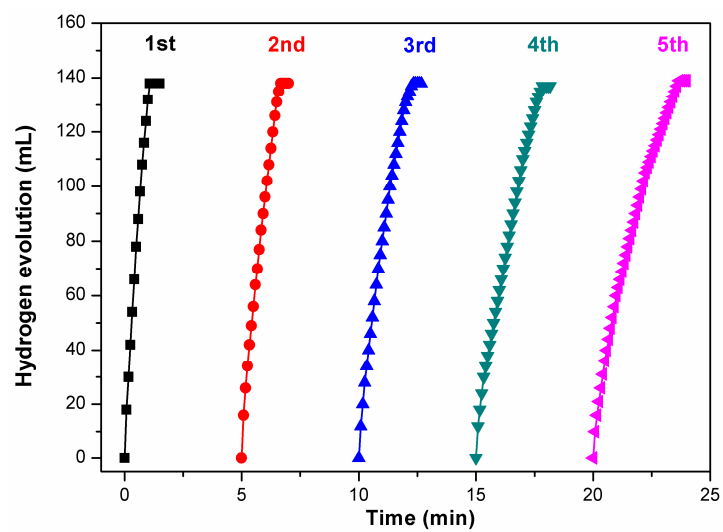


Figure 8. Durability test for the dehydrogenation of AB over $\text{Cu}_{0.2}\text{Co}_{0.8}/\text{PDA-rGO}$ ($n_{\text{metal}}/n_{\text{AB}} = 0.05$, 303 K).

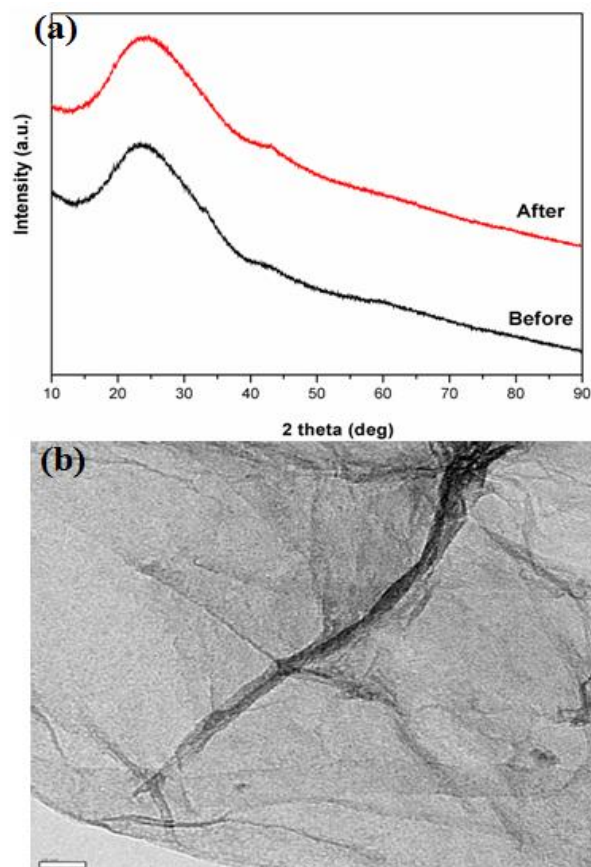


Figure 9. (a) PXRD patterns and (b) TEM image of $\text{Cu}_{0.2}\text{Co}_{0.8}/\text{PDA-rGO}$ catalyst after catalysis (Scale bar: 20 nm).

The durability of catalyst is very important for the practical application of catalysts, therefore, we further examine the durability of Cu_{0.2}Co_{0.8}/PDA-rGO catalyst by adding aliquots AB (2.0 mmol) into catalyst after the reaction completion for the last run. There is no significant loss in catalytic activity and selectivity after 5 cycles, which indicates that the prepared Cu_{0.2}Co_{0.8}/PDA-rGO catalyst has the high durability in hydrolytic dehydrogenation of AB (Figure 9).

4.4 Conclusions

In summary, the non-noble CuCo NPs have been successfully immobilized on diamine-alkalized reduced graphene oxide, which shows an excellent catalytic activity for the hydrolytic dehydrogenation of AB with a TOF value as high as 163 mol_{H₂}mol_{cat}⁻¹min⁻¹ at 323 K. This is the first example of the non-noble metal NPs supported on diamine-alkalized reduced graphene oxide for hydrolytic dehydrogenation of AB. The excellent catalytic performance could arise from the metal NPs by using the diamine alkaline groups. As an effective strategy, it provides an opportunity to immobilize ultrafine non-noble metal NPs on GO, which have tremendous application prospect in various catalytic fields.

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Chapter 5

Conclusion

The dramatic climate changes caused by greenhouse gas emission and ever-increasing need for energy have spurred international interest in developing renewable energy technologies. Essentially, how to supply sufficient and sustainable energy has become one of the most important challenges of this century. The liquid-phase chemical storage materials have attracted much attention due to their low reaction temperature, high catalytic kinetics and stability. In addition, they also provide the possibility to use the existing infrastructures for gasoline. This dissertation is focused on the immobilization of ultrafine metal nanopartilces (NPs) on alkalized reduced graphene oxide (rGO) as catalysts for the hydrogen generation from liquid-phase chemical hydrogen storage materials. Among the chemical hydrogen storage materials, formic acid, hydrous hydrazine and ammonia borane have become the most promising candidates due to their high hydrogen contents, stability and safe handling under ambient conditions. In the introduction part, we described the advantages of liquid-phase chemical hydrogen storage materials. In addition, we also introduced the effect of support materials on highly efficient dehydrogenation. At the subsequent parts, we successfully immobilized ultrafine noble metal (Pd), non-noble metal-based (PtNi) and non-noble bimetallic (CuCo) NPs on diamine-alkalized reduced graphene oxide, which exhibited excellent catalytic performance for the dehydrogenation of these chemical hydrides (formic acid, hydrous hydrazine and ammonia borane). Especially the synthesized Pd catalyst showed the best catalytic property for the dehydrogenation of formic acid compared to other heterogeneous

catalysts as reported so far. The main research results of this dissertation are summarized as follows.

(i) Diamine-alkalized Reduced Graphene Oxide: Immobilization of Sub-2 nm Palladium Nanoparticles and Optimization of Catalytic Activity for Dehydrogenation of Formic Acid

An efficient strategy to downsize the metal NPs and provide basic sites located nearby for optimizing the catalytic performance of the alkalized reduced graphene oxide-supported metal catalysts has been explored, for the first time, by the potent alkalization of rGO with diamine. By virtue of the coordination effects between the metal ions and the amine groups ligated to rGO, monodispersed Pd NPs (diameter ~ 1.5 nm) can be facilely anchored on the diamine-alkalized rGO by a simple reduction approach. The diamine groups not only highly disperse the GO against ordered restacking, but also provide coordinating groups to combine with Pd^{2+} ions, resulting in rich and uniform nuclei and a controlled growth process of Pd on rGO. Owing to both of the effects from the high Pd dispersion and amine-formic acid interaction, the resultant Pd/PDA-rGO (PDA is 1,4-phenylenediamine) nanocatalysts exhibit significantly enhanced catalytic activity for dehydrogenation of formic acid under mild conditions, achieving the highest turnover frequency (TOF) value of 3810 h^{-1} at 50°C with 100 % H_2 selectivity, among those of heterogeneous catalysts, comparable to the most active homogeneous catalysts. The amine group, as a proton scavenger, results in the formation of an intermediate Pd-formate complex along with amine group, which is benefited for final decomposition of FA. In addition, different amine-rGO systems, including PDA-rGO, AMA-rGO (AMA=4-(aminomethyl)aniline), DAH-rGO (DAH=1,6-diaminohexane), DMPDA-rGO (DMPDA=N,N-dimethyl-1,4-phenylenediamine)

and A-rGO (A=aniline), have been prepared and subsequently used to immobilize Pd NPs. Compared to Pd/rGO, all the catalysts functionalized with diamine group exhibit exceedingly enhanced catalytic activities for hydrogen generation of formic acid. However, only a moderate enhancement is found for Pd/A-rGO, which may be due to the fact that in aniline, a monoamine molecule, the only amine group is covalently bound to rGO and thereby leads to the lack of the interactions with Pd.

(ii) Monodispersed PtNi Nanoparticles Deposited on Diamine-alkalized Graphene for Highly Efficient Dehydrogenation of Hydrous Hydrazine at Room Temperature

The strategy has been further explored to immobilize the PtNi NPs on diamine-alkalized reduced graphene oxide (PtNi/PDA-rGO). By the virtue of the alkalization of rGO with diamine, monodispersed PtNi NPs (2.5 nm) can be facilely deposited on the alkalized rGO. The resultant Pt_{0.6}Ni_{0.4}/PDA-rGO shows an excellent catalytic activity with 100 % H₂ selectivity for the dehydrogenation of hydrous hydrazine under mild conditions, with a TOF value as high as 903 h⁻¹ at 30 °C and 2056 h⁻¹ at 50 °C, higher than most of those reported. The exceptional catalytic performance of Pt_{0.6}Ni_{0.4}/PDA-rGO, on the one hand, would be attributed to the fact that the amine groups could benefit the immobilization of the ultrafine Pt_{0.6}Ni_{0.4} NPs on rGO. On the other hand, the synergic interactions not only between Pt and Ni but also between NPs and support could also efficiently improve the catalytic property. The diamine-alkalized graphene could promote electron transfer to form the electron-rich NPs, which could efficiently facilitate the cleavage of the covalent N-H bonds and thus improve the catalytic property. In addition, the presence of NaOH also plays an important role in enhancement of catalytic performance. The addition of NaOH could efficiently

promotes the rate-determining deprotonation step ($\text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3^* + \text{H}^*$), which is crucial and benefits the final elimination of N-H bonds to produce N_2 and H_2 .

(iii) Monodispersed CuCo Nanoparticles Supported on Diamine-Alkalized Graphene as a Non-noble Metal Catalyst for Dehydrogenation of Ammonia Borane

Although rapid dehydrogenation of ammonia borane has been achieved by using noble metals, the limited resources restrict their practical applications. Alternatively, the cost-effective non-noble metals (such as Co, Fe and Ni) have attracted more and more attentions. However, the catalytic kinetics of H_2 generation rate is still not satisfying the demands for practical applications; therefore, the synthesis of non-noble catalysts with excellent catalytic performance at ambient temperature is urgently important. Non-noble bimetallic CuCo NPs were successfully supported on diamine-alkalized reduced graphene oxide (CuCo/PDA-rGO). Compared to other supports materials (rGO, Carbon and Polyvinylpyrrolidone), the catalyst synthesized with the alkalized rGO displays remarkably enhanced catalytic performance for dehydrogenation of ammonia borane with TOF of $163 \text{ mol}_{\text{H}_2}\text{mol}_{\text{cat}}^{-1}\text{min}^{-1}$ at 50°C . The amine groups benefit for the dispersion of ultrafine CuCo NPs on rGO, which efficiently enhances the catalytic hydrolysis of ammonia borane. Moreover, the synergic effect between ultrafine Cu and Co NPs also plays an important role on improvement in dehydrogenation of ammonia borane. There is no significant loss in catalytic activity and selectivity after 5 cycles, which indicates that the prepared $\text{Cu}_{0.2}\text{Co}_{0.8}/\text{PDA-rGO}$ catalyst has the high durability in dehydrogenation of ammonia borane. As an effective strategy, it provides an opportunity to immobilize ultrafine non-noble metal NPs on GO, which has tremendous application prospect in various catalytic fields.

In summary, this dissertation is focused on the fabrication of ultrafine metal NPs by taking the advantages of the alkalization of rGO and the discussion of their catalytic applications for highly efficient hydrogen generation from liquid-phase chemical hydrogen storage materials (such as formic acid, hydrous hydrazine and ammonia borane).

List of Publications

Journal Publications

1. Diamine-alkalized reduced graphene oxide: immobilization of sub-2 nm palladium nanoparticles and optimization of catalytic activity for dehydrogenation of formic acid.

Fu-zhan Song, Qi-Long Zhu, Nobuko, Tsumori and Qiang Xu*

ACS Catal., **2015**, 5, 5141-5144.

2. Monodispersed PtNi nanoparticles deposited on diamine-alkalized graphene for highly efficient dehydrogenation of hydrous hydrazine at room temperature.

Fu-zhan Song, Qi-Long Zhu and Qiang Xu*

J. Mater. Chem. A, **2015**, 3, 23090-23094.

3. Monodispersed CuCo nanoparticles supported on diamine-alkalized graphene as a non-noble metal catalyst for dehydrogenation of ammonia borane.

Fu-zhan Song, Qi-Long Zhu and Qiang Xu*

In preparation.