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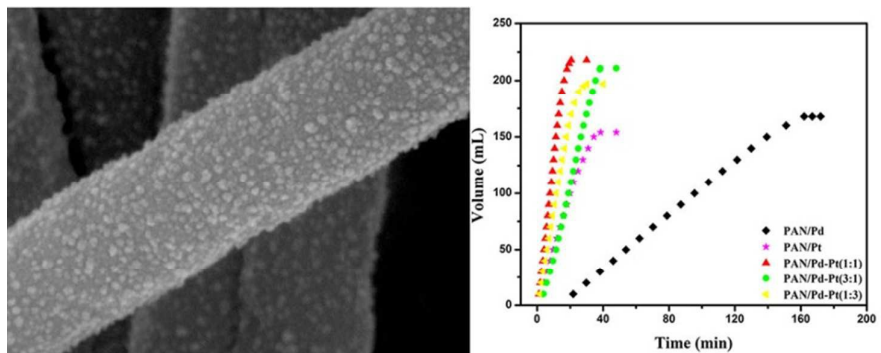
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Electrospun polyacrylonitrile nanofibers supported alloyed Pd-Pt nanoparticles were synthesized as recyclable catalysts for hydrogen generation from the hydrolysis of ammonia borane.





Journal Name

ARTICLE

Electrospun Polyacrylonitrile Nanofibers Supported Alloyed Pd-Pt Nanoparticles as Recyclable Catalysts for Hydrogen Generation from the Hydrolysis of Ammonia Borane

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Herein, we report the fabrication of polyacrylonitrile(PAN) nanofibers supported Pd-Pt alloy nanoparticles (PAN/Pd-Pt) through a simple and reliable approach by combining an electrospinning technique and in situ reduction process. The resulting PAN/Pd-Pt membranes are composed of well-defined fiber-like structure with uniform sizes. Pd-Pt alloy nanoparticles are well dispersed on the surface of PAN nanofibers and the composition of alloy nanoparticles can be regulated through adjusting the feed molar ratio of Na₂PdCl₄ and K₂PtCl₆. The obtained products are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) measurements. The as-prepared PAN/Pd-Pt composite exhibits a remarkable catalytic performance towards the hydrogen generation from the hydrolysis of ammonia borane (NH₃BH₃, AB). By tuning the composition of the alloy nanoparticles of the nanocatalyst, a turnover frequency (TOF) of 51.9 mol H₂ min⁻¹ (mol Pd-Pt alloy)⁻¹ was achieved, much higher than Pd and Pt-based nanocatalysts. In addition, the as-prepared PAN/Pd-Pt composite nanofibers show good recycle stability, as the catalyst can be easily separated from the suspension system. The electrospun nanofiber membrane supported noble metal nanoalloy catalysts show high potential to find their application for the hydrogen generation for clean energy development.

Introduction

In recent decades, many countries have initiated a great deal of scientific research and development programs in renewable and clean energy that can be regarded as the candidate of fossil fuel which causes severe environmental pollution.¹ On account of high energy density, extreme abundance, and environmental sustainability, hydrogen has emerged as an ideal synthetic clean, sustainable fuel.^{2,3} However, the wide range of application of hydrogen has been restricted by its storage and transportation problem, due to the very low density of hydrogen and the danger of explosion in the gas state. Thus, it is one of the greatest challenges to search for innovative materials with high hydrogen-storage/generation capacity. Ammonia borane (NH₃BH₃, AB) appears to be one of the most promising solid hydrogen carriers,^{4,5} owing to its high hydrogen capacity of 19.6 wt% and excellent stability,⁶ which shows potential application in fuel cells for portable electronics. Considering the thermolysis temperature (without any catalyst) of AB is a bit high,⁷ it is a key point to find proper catalyst to completely release hydrogen from AB through

hydrolysis process at ambient temperature. Recently, various kinds of nanocatalysts including inexpensive transition metals,⁸⁻¹⁰ noble metals,¹¹⁻¹⁴ metal oxides¹⁵⁻¹⁷ have been investigated for hydrogen generation from the hydrolysis of AB. Among these nanocatalysts, noble metals especially platinum (Pt) and palladium (Pd) exhibit extraordinary catalytic properties in the area of hydrogen generation.^{18,19} For example Xu and co-workers have reported that Pt nanocatalysts exhibited the highest catalytic activity toward the hydrolysis of AB at room temperature compared with other noble and transition metals.¹⁸ However, most of the individual metal nanocatalysts with a nano-size are difficult separated from the reaction system for reusability. In addition, these naked metal nanocatalysts are easily aggregated, leading to the reduction of the catalytic activity. To avoid this issue, noble metal nanoparticles are usually supported on the carbon,^{20,21} metal oxide²² and polymer matrix,²³ generating an enhanced catalytic activity and stability due to the synergistic effect.

Recently, bimetallic nanoparticles have been emerging as a new kind of important catalyst, which have been used in catalytic and electrocatalytic reactions. Especially, metallic nanoalloys have been demonstrated to show enhanced catalytic activity and stability compared with the individual metallic components owing to the synergistic effect and electronic effect.^{24,25} There have been several reports of efficient metallic nanoalloys catalyzed hydrolysis of AB for hydrogen generation at ambient temperature.^{26,27} In this study, we have prepared Pd-Pt alloy nanoparticles supported on the surface of

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electrospun PAN nanofibers for catalyzing the hydrolysis of AB. It is well known that electrospun polymeric nanofiber membrane is a good candidate as the support for the nanocatalysts due to their large surface area, flexibility and porosity.²⁸ Thus the PAN nanofiber membrane supported Pd-Pt nanoalloys provide the catalyst high catalytic activity, and easily separating from the reaction system, enhancing their recycle performance.

Herein, glutaral-functionalized PAN nanofiber membrane was fabricated through an electrospinning process and the post-treatment reaction firstly. Then the glutaral-functionalized electrospun PAN nanofiber membrane was used as a reducing agent for in situ reducing Na₂PdCl₄ and K₂PtCl₄ to form Pd-Pt alloy nanoparticles on the surface of PAN nanofibers. The composition of the Pd-Pt alloy nanoparticles can be easily regulated by adjusting the feeding molar ratio of Pd and Pt precursors. The results of the hydrogen generation and recycle experiment demonstrate that the as-prepared PAN/Pd-Pt composite nanofiber membrane exhibits high catalytic activity and good recyclability towards the hydrolysis of AB at room temperature.

Experimental

Reagents and apparatus

Polyacrylonitrile (Mw= 80,000) fibrils composed of acrylonitrile (91%), acrylamide (8.5%) and itaconic acid (0.5%) was purchased from Jilin Chemical Plant. N,N-Dimethylformamide (DMF) and ethanol were obtained from Beijing Chemical Corporation. AB (technical grade, 90%) was bought from Aldrich. Disodium tetrachloropalladate (Na₂PdCl₄) and potassium tetrachloroplatinate (K₂PtCl₄) were purchased from Aladdin. Glutaraldehyde (50%) and hydrazine hydrate (80%) were provided by Tianjing Guangfu fine chemical research institute. Sodium dihydrogen phosphate dehydrate and disodium hydrogen phosphate dodecahydrate were obtained from Sinopharm Chemical Reagent Co., Ltd. The distilled water was used throughout the experiment.

The morphology of the as-prepared PAN/Pd-Pt nanofibers was observed by scanning electron microscopy (SEM, FEI Nova NanoSEM) and transmission electron microscopy (TEM, JEOL-2000 EX). HRTEM imaging and energy dispersive X-ray (EDX) analysis were performed on a FEI Tecnai G2 F20 high-resolution transmission electron microscope operating at a 200 kV accelerating voltage. X-ray data were collected by using an X-ray diffractometer (Empyrean, PANalytical B.V.) based on Cu-K α radiation. Analysis of the X-ray photoelectron spectra (XPS) was performed on a Thermo Scientific ESCALAB250 measurement. The weight percentages of Pd and Pt in the nanofiber membrane were determined by inductively coupled plasma (ICP) atomic emission spectrometric analysis (PerkinElmer OPTIMA 3300DV).

Preparation of electrospun PAN nanofibers

In a typical experiment, PAN nanofibers were prepared via a typical electrospinning process. During this process, 1.2 g of

PAN was dissolved in 13.8 g of DMF under vigorous stirring at 90 °C for 4 h to form a homogeneous solution. Then, the polymer solution was electrospun using a glass syringe with a tip inner diameter of approximately 1 mm at an applied voltage of 15 kV over a collection distance of 15 cm. The PAN nanofibers were collected on aluminum foil and then removed for the following experiment.

Fabrication of glutaral-functional PAN nanofiber membrane

Briefly, 50 mg of PAN nanofiber membrane was immersed in 30 mL of hydrazine hydrate (80%) in a flask and refluxed at 95 °C for 3 h. After cooling down to the room temperature, the amine-functional nanofiber membrane was washed with water and ethanol for several times. Then, the membrane was immersed in 50 mL of glutaraldehyde solution (5%, diluted with 0.01 M phosphate buffer (PB)) in a conical flask with shaking at room temperature for 3 h. The resulting glutaral-functional PAN nanofiber membrane was washed with ethanol several times and dried in air for further using.

Fabrication of PAN-Pd-Pt composite nanofiber membrane

The PAN/Pd-Pt composite nanofiber membrane was synthesized through an in situ reduction process. In a typical procedure, an aqueous solution of 5 mL of Na₂PdCl₄ (8.5 mM) and K₂PtCl₄ (8.5 mM) with a Pd-to-Pt feeding molar ratio of 1:1 was added in a test tube with stirring for 5 min so that they were mixed thoroughly. Subsequently, 15 mg of glutaral-functional PAN nanofibers were placed in the test tube with water-bath heating at 50 °C for 1 h. The obtained product was washed by distilled water and ethanol for several times and dried in air for the further test. The obtained sample from this reduction step is denoted PAN/Pd-Pt (1:1). For comparison, PAN/Pd, PAN/Pt, PAN/Pd-Pt (1:3), PAN/Pd-Pt (3:1) catalysts were also prepared via the similar procedure. The amount-of-substance concentration of (Pd + Pt) is always 17 mM.

Catalytic hydrolysis of AB for H₂ generation

The reaction of hydrogen generation was carried out at room temperature and normal atmospheric pressure. During the process, a certain amount of the PAN/Pd-Pt composite nanofiber membrane was placed in the conical flask which contained 100 mg of AB dissolved in 10 mL water and the weight ratio of metal/AB is 0.0095. Drainage method was used to measure the volume of hydrogen. After the hydrolysis of AB, the PAN/Pd-Pt composite nanofiber membrane was washed and dried to study the recycle stability.

Results and discussion

Preparation and characterization of the electrospun PAN/Pd-Pt composite nanofiber membrane

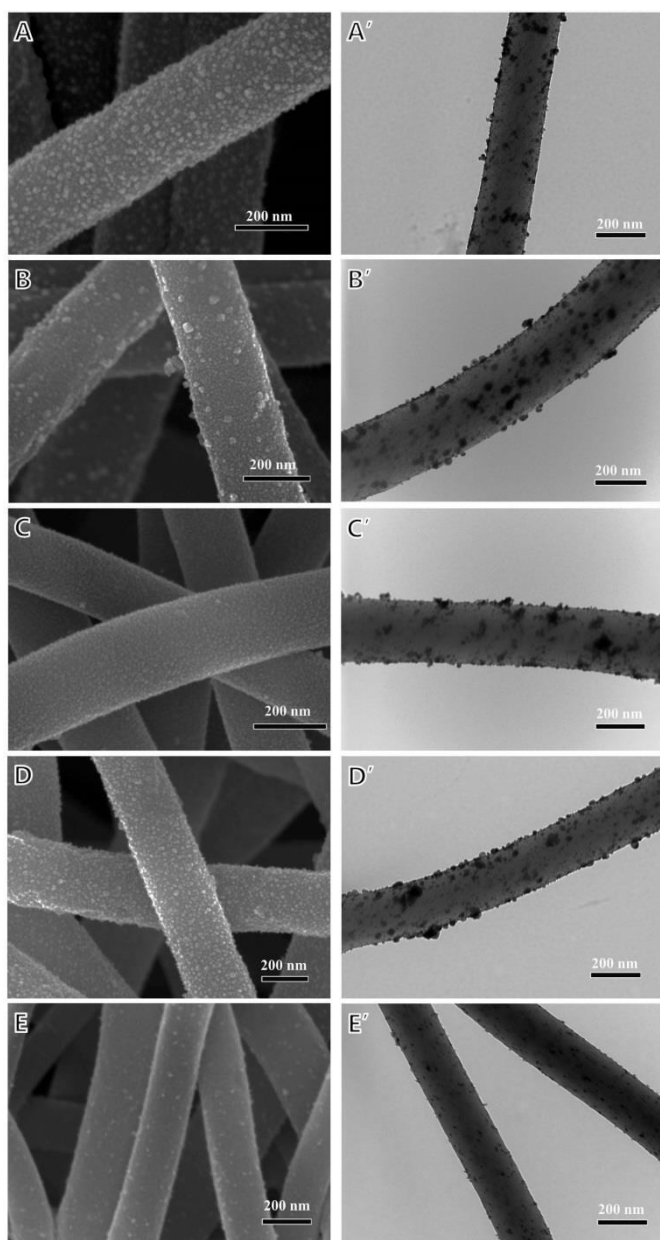


Fig. 1 SEM and TEM images of electrospun PAN nanofibers supported metallic nanoparticles: (A, A') Pd-Pt (1:1), (B, B') Pd-Pt (3:1), (C, C') Pd-Pt (1:3), (D, D') Pd and (E, E') Pt.

To study the morphologies of the as-prepared electrospun PAN nanofiber membrane supported noble metal nanoparticles, we carried out typical SEM and TEM measurements. Fig. 1A showed a typical SEM image of the PAN/Pd-Pt (1:1) composite nanofiber membrane, it was found that the nanofibers are uniform with a diameter in the range of 200-400 nm, which does not change much compared with the as-spun PAN and glutaral-functional PAN nanofibers (Fig. S1). Furthermore, a lot of bright nanoparticles have been observed on the surface of PAN nanofibers, which could be regarded as the metallic nanoparticles. The SEM images also showed that the similar morphologies were observed for other PAN supported metal nanoparticles (PAN/Pd-Pt (3:1), PAN/Pd-Pt (1:3), PAN/Pd and PAN/Pt nanofibers) (Fig. 1B-E, B'-E'). The

sizes of the metallic nanoparticles on the surface of electrospun nanofibers were determined via the TEM image. As shown in Fig. 1A', numerous Pd-Pt nanoparticles with a diameter from several to tens of nanometers were randomly distributed on the surface of PAN nanofibers with moderate density. The TEM image showed that some large Pd-Pt (1:1) nanoparticle might be due to the overgrowth and aggregation of small Pd-Pt nanoparticles. The TEM images in Fig. 1B'-E' exhibited that the sizes of other metallic nanoparticles (Pd-Pt (1:3), Pd-Pt (3:1), Pd) are similar with the Pd-Pt (1:1) nanoparticles. Different with these metallic nanoparticles, the size of Pt nanoparticles is relatively small and they are few agglomerated on the surface of PAN nanofibers. The as-prepared Pd-Pt alloy nanoparticles have been characterized by a HRTEM image. As shown in Fig. 2A and B, the resulting Pd-Pt alloy nanoparticles possess high crystalline with clear lattice structures. The lattice distance of the as-synthesized Pd-Pt alloy nanoparticles is about 0.23 nm, corresponding to the (111) lattice plane of the face-centered cubic (fcc) structure of Pd and Pt,^{29,30} indicating the formation of Pd-Pt nanoalloy. The as-fabricated PAN/Pd-Pt (1:1) composite nanofibers were also examined by energy-dispersive X-ray (EDX) spectroscopy (Fig. 2C), which showed the existence of C, N, O, Cu, Pd, Pt and no other obvious elements were observed (Cu is original from the carbon coated grid). This result demonstrates the successful formation of Pd-Pt nanoparticles on the surface of electrospun PAN nanofibers. The selected area electron diffraction (SAED) pattern of the Pd-Pt alloy nanoparticles further proved their good crystallinity (Fig. 2D). In addition, the weight percentages of Pd and Pt in the composite nanofibers

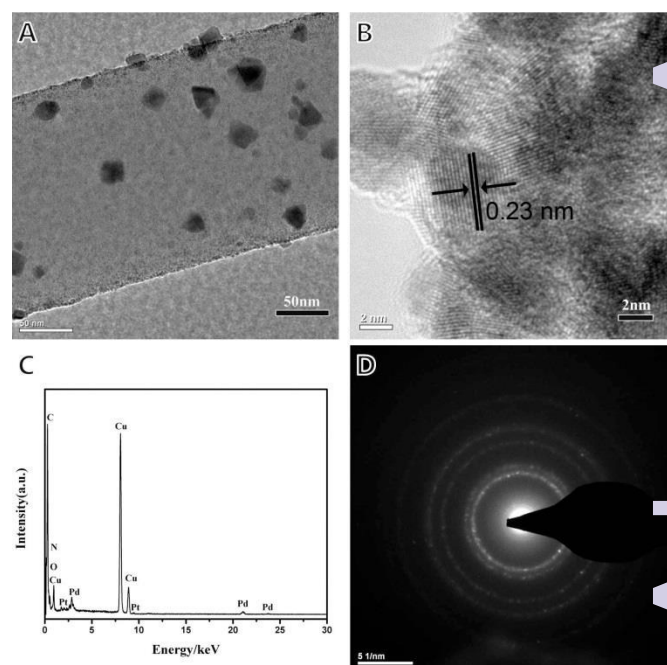


Fig. 2 (A and B) HRTEM image of the PAN/Pd-Pt (1:1) nanofibers; (C) EDX spectra of the nanofibers; (D) the corresponding SAED pattern of the Pd-Pt alloy nanoparticles on the PAN/Pd-Pt (1:1) nanofibers.

were also determined by ICP measurement, which gave a value of about 7.2% and 1.6% in PAN/Pd-Pt (1:1) nanofibers. The weight percentages of the Pd and Pt in the other composite nanofibers have also been measured, which have been shown in Table S1.

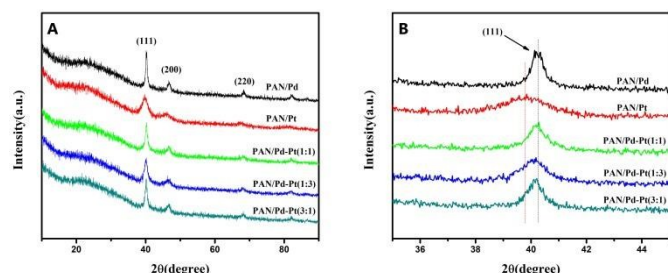


Fig. 3 (A) XRD patterns of PAN/Pd, PAN/Pt, PAN/Pd-Pt (1:1), PAN/Pd-Pt (1:3), and PAN/Pd-Pt (3:1) nanofiber membranes; (B) enlarged patterns of the (111) peaks.

The crystal structures of the as-prepared PAN/Pd, PAN/Pt, PAN/Pd-Pt (1:1), PAN/Pd-Pt (1:3), and PAN/Pd-Pt (3:1) catalysts were further characterized by XRD measurement. As shown in Fig. 3A, all of the composite nanofiber membrane catalysts display a typical fcc structure. For the monometallic Pd nanoparticles on the surface of PAN nanofibers, the diffraction peaks located at the 2θ values of 40.3° , 46.9° and 68.3° are assigned to Pd (111), (200), and (220) lattice planes, respectively.³¹ In the case of monometallic Pt, the peaks at about 39.8° , 46.3° and 67.3° were attributed to the (111), (200) and (220) lattice planes of the fcc crystalline structure of Pt, respectively.³² For the alloy systems, the XRD patterns of the PAN/Pd-Pt composite nanofibers with three different feeding molar ratios of Pd/Pt (1:1, 1:3, 3:1) were similar to those of the pure Pd or Pt catalyst. For clear observation, the magnified (111) peaks of these catalysts are enlarged in Fig. 4B. The 2θ values of the (111) peak for the PAN/Pd-Pt (1:1), PAN/Pd-Pt (1:3), and PAN/Pd-Pt (3:1) catalysts, were observed at 40.2° , 40.1° and 40.3° , respectively, indicating peak positions exist between the pure metallic phases. Similar results have been also observed in other bimetallic alloy nanostructures.³³ Furthermore, the peak positions slightly shift lower with the increase in the Pt ratio, further demonstrating the successful formation of Pd-Pt alloys on the surface of electrospun PAN nanofibers.

The X-ray photoelectron spectroscopy (XPS) measurement was also used to elucidate the composition and chemical states of the as-prepared PAN/Pd-Pt composite nanofiber membrane. It was found that the peaks of C, N, O, Cl, Pd and Pt elements were obviously observed in the XPS spectra (Fig. 4A). The presence of Cl 2p should be attributed to the existence of Cl^- from Na_2PdCl_4 and K_2PtCl_4 . From Fig. 4B, it can be clearly seen that the high resolution XPS spectrum of Pd displays two prominent peaks locating at binding energies of 335.6 and 340.9 eV, corresponding to the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of metallic Pd, whereas the other two peaks at 337.2 and 342.5 eV can be assigned to the oxidized palladium(II) centers, which is in accordance with the previous report.³⁴ Fig. 4C

exhibited the XPS spectrum of Pt 4f with binding energy at around 71.1 and 74.5 eV for metallic Pt, and the bands at 72.2 and 76.0 eV were attributed to the oxidation state of Pt, which is probably the result of the oxidation of surface Pt atoms on the Pt nanoparticles with small size in air.^{35,36} These results proved that the PAN/Pd-Pt composite nanofiber membrane has been successfully prepared.

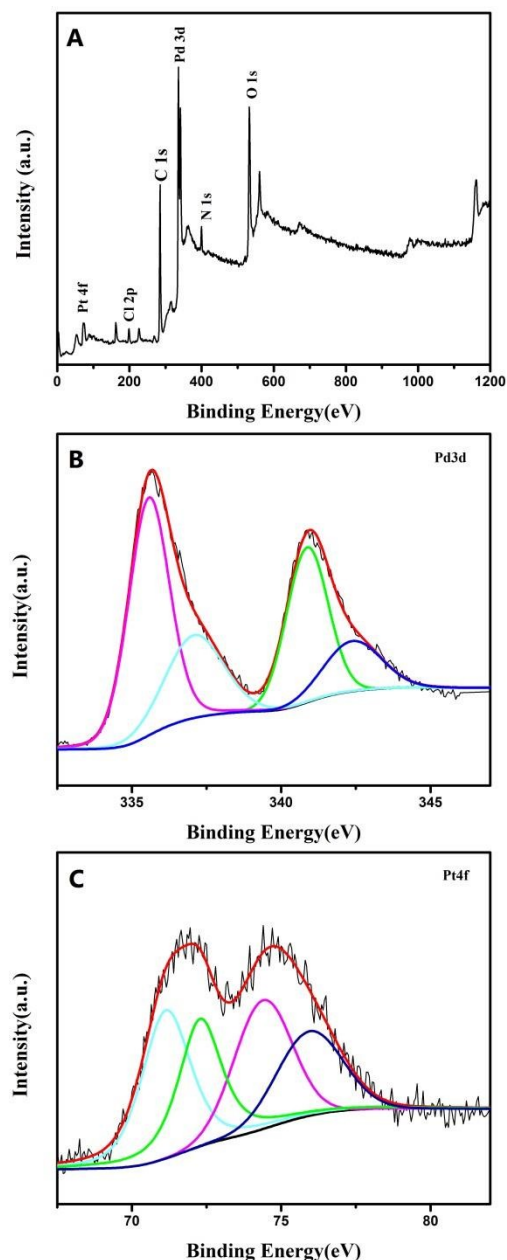


Fig. 4 XPS spectra of the as-prepared PAN/Pd-Pt (1:1) composite nanofiber membrane; (A) full spectrum; (B) Pd 3d; (C) Pt 4f.

Catalytic performance of PAN/Pd-Pt composite nanofiber membrane toward the hydrolysis of AB

The as-prepared PAN/Pd-Pt composite nanofiber membrane has been used as efficient catalysts for hydrogen generation from the hydrolytic dehydrogenation of A.

Hydrogen was produced continuously as soon as the membrane was immersed into the AB solution. The whole experimentation was carried out under ambient atmosphere at room temperature.

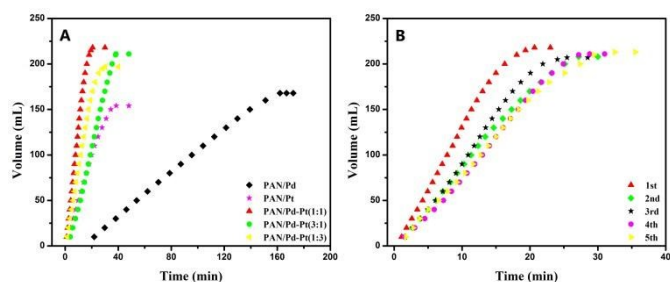


Fig. 5 (A) Hydrogen generation profiles with time in the presence of PAN/Pd, PAN/Pt, PAN/Pd-Pt (1:1), PAN/Pd-Pt (3:1) and PAN/Pd-Pt (1:3) composite nanofibers; (B) five times of recycling test of PAN/Pd-Pt (1:1) nanofibers.

nanofiber membrane toward the hydrolysis of AB might be due to the synergistic effect of the Pd-Pt alloy nanoparticles and the large surface area of electrospun nanofibers supports. During heterogeneous catalytic process, the reactants usually diffuse and then adsorb onto the surface of the catalyst from chemical bonds. After reaction, the product will desorb from the catalyst surface and diffuse away. In this study, the mechanism of the catalytic hydrolysis of AB by PAN/Pd-Pt composite nanofiber membrane was considered that there should be interactions between the AB molecules and the surface of Pd-Pt nanoparticles to form activated complex species which will be attacked by a molecule of water, then lead to the splitting of the B-N bond and hydrolysis of the BH₃ intermediate to produce the borate ion along with the H₂.⁴⁶ For Pd-Pt nanoalloys on the surface of electrospun nanofibers, there could be electronic interactions between Pd and Pt atomic orbitals, leading to electron transfer from Pd to Pt, due to the electronegativity of Pt (2.28) is higher than that of Pd (2.20).⁴⁷ The increased electron density would accelerate the electron transfer of the hydrolysis of AB, producing a better activity.

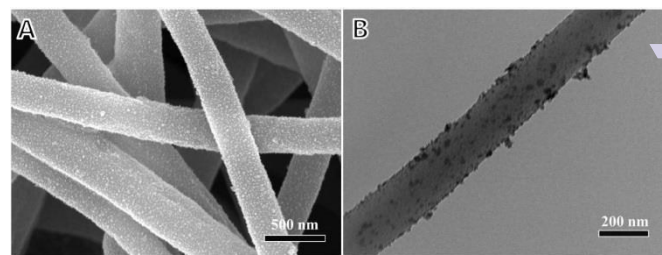


Fig. 6 (A) SEM and (B) TEM images of PAN/Pd-Pt (1:1) nanofiber membrane after the fifth catalytic reaction.

It is well known that the recyclability is also an important aspect for every catalyst in practical application. The most significant advantage of the PAN/Pd-Pt composite nanofiber membrane as catalyst for the hydrolytic dehydrogenation of AB was that it did not exhibit an obvious loss of catalytic activity even after five times of recycling (Fig. 5B). The PAN/Pd-Pt nanofiber membrane could be separated from the solution easily with just a tweezer. After washing with water and ethanol several times, the membrane was dried for the next cycles. From Fig. 5B, it was clearly seen that the reaction could be finished based on the as-prepared PAN/Pd-Pt (1:1) composite nanofibers catalyst in 21 min for the first time. Then the next four times recycling reaction exhibited approximate time but a little slower than the first time. Nevertheless, the rate of hydrogen generation was still considerable. The morphology of the PAN/Pd-Pt (1:1) composite nanofiber membrane after the fifth catalytic reaction was shown in Fig. 6. The network of the composite nanofibers was generally kept intact and the size of most of the Pd-Pt alloy nanoparticles immobilized on the surface of PAN nanofibers did not significantly change.

Conclusions

Entry	Catalyst	TOF(min ⁻¹)	Reference
1	PAN/PPy/Pd	3.9	13
2	PAN/Pd/Ag	6.29	14
3	Pd@MIL-101	45	37
4	RGO-Pd	26.3	38
5	SiO ₂ -Pd (0)	10	39
6	RGO-Ni ₃₀ Pd ₇₀	28.7	40
7	C-Co ₃₅ Pd ₆₅	22.7	41
8	RGO-Cu ₇₅ Pd ₂₅	29.9	42
9	Pd-Pt Nanocubes	50.1	43
10	Pt/CeO ₂ /RGO	48	44
11	Pt _{0.65} Ni _{0.35}	28.82	45
12	PAN/Pd-Pt (1:1)	51.9	This study

Table 1 Various Pd and Pt based catalyst systems tested in the hydrolysis of ammonia borane. TOF values were taken directly from the related articles or calculated from the data presented in the article.

Fig. 5A showed the hydrogen generation profiles with time for the reactions of the hydrolysis of AB (1.0 wt%) in the presence of PAN/Pd, PAN/Pt, PAN/Pd-Pt (1:1), PAN/Pd-Pt (1:3) and PAN/Pd-Pt (3:1) composite nanofiber membranes. It can be obviously seen that the PAN/Pd-Pt nanofibers catalysts showed a significant enhancement of hydrogen generation activity in this experiment. Especially, the PAN/Pd-Pt (1:1) composite nanofiber membrane catalyst exhibits a much better activity than those of mono- and bi-metallic catalysts synthesized with the same approach, which produced about 218 mL of H₂ in only about 21 min. The turnover frequency (TOF) of the obtained PAN/Pd-Pt (1:1) composite nanofiber membrane was calculated to be about 51.9 mol H₂ min⁻¹ (mol Pd-Pt alloy)⁻¹. This value is much higher than that of Pd and Pt based nanocatalysts that reported previously (Table 1).^{13,14,37-45} The high catalytic activity of the PAN/Pd-Pt composite

In summary, we have developed a facile and effective method for synthesizing PAN/Pd-Pt alloy composite nanofiber membrane with different Pd/Pt weight ratios through an electrospinning technique and subsequent in situ reduction process. The as-prepared PAN/Pd-Pt composite nanofiber membrane possessed high catalytic activity and excellent recycling property for the hydrogen generation from the hydrolysis of AB under ambient atmosphere at room temperature. The present study is important because it can be readily extended to the fabrication of other alloy nanoparticles supported on the surface of electrospun polymeric nanofibers for circulating application especially in aqueous solution. Furthermore, the present PAN/Pd-Pt composite nanofiber membrane nanocatalyst, with a high hydrogen generation rate under mild reaction conditions represent a promising step toward the development of AB as a practical on-board hydrogen-storage and supply material.

Conclusions

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Conclusions

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