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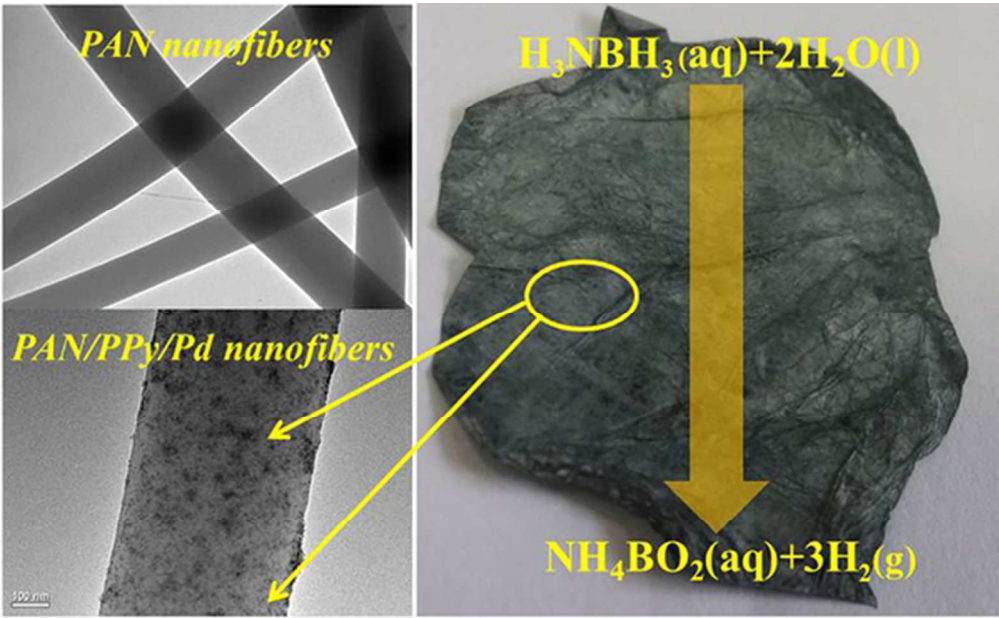


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Text: one sentence, of maximum 20 words, highlighting the novelty of the work:

Palladium/polypyrrole/polyacrylonitrile nanofiber membrane was fabricated by a one-pot synthetic method and exhibited good catalytic performance toward the dehydrogenation of AB.

ARTICLE

A one-pot synthesis of highly dispersed palladium/polypyrrole/polyacrylonitrile nanofiber membrane and their recyclable catalysis in hydrogen generation from ammonia borane

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In this report, palladium/polypyrrole/polyacrylonitrile (Pd/PPy/PAN) composite nanofiber membrane was synthesized by a one-pot redox polymerization process between pyrrole monomer and Na_2PdCl_4 in the presence of electrospun PAN nanofibers without the introducing of any other surfactants or reductants. The as-prepared Pd/PPy/PAN nanofiber membrane exhibited good catalytic performance toward the hydrogen generation from the hydrolysis of ammonia borane (AB). The apparent activation energy (E_a) was calculated to be about 33.5 kJ mol⁻¹. In addition, the Pd nanoparticles (Pd NPs) were encapsulated in PPy layers on the surface of PAN nanofibers, enabling the catalysts stable against poisoning and easily separated from the suspension system. The catalytic activity does not weaken after five cycles. This study indicated that the obtained Pd/PPy/PAN composite nanofiber membrane could be applied as an alternative in exploring new catalyst for hydrogen generation, which is an important fuel as a clean power source.

Introduction

Hydrogen (H_2) has attracted more and more attention as a clean and renewable energy carrier because water is the only byproduct after its reaction with oxygen^{1, 2}. The main problem for the widespread application of hydrogen is the storage and delivery because the density of hydrogen is very low and difficult to be transferred under gas state. Thus, searching for new solid chemical materials with high hydrogen storage/generation capability is one of the most important matters to be solved. Recently, ammonia borane ($\text{NH}_3\text{--BH}_3$, AB) was found to be a promising candidate for hydrogen generation with hydrogen capacity of 19.6 wt% and good stability in aqueous solution³. There are mainly three ways toward the release of hydrogen from AB: solid phase thermolysis, catalytic hydrolysis and catalytic dehydrogenation in nonaqueous solvent⁴. As the temperature for thermolysis is very high (over 100 °C)⁵, hydrolysis in the presence of proper

catalyst in aqueous media seems to be the most efficient and convenient path to the decomposition of AB. Recent studies show that there are numerous catalysts that could enhance the dehydrogenation of AB, such as: metal complexes with cooperative ligands⁶⁻⁸, metal oxide^{9, 10}, noble metal^{11, 12}, non-noble metal¹³⁻¹⁵ and multi-component metallic systems^{16, 17}.

In the past few years, Pd NPs were found to be one of the most efficient and stable catalysts for various kinds of important catalytic reactions including the electrochemical oxidation of alcohol¹⁸, hydrogenation of alkynes¹⁹, and the dehydrogenation of AB²⁰, and so on. However, such NPs always aggregate during the reaction and the catalytic performance is significantly reduced. Many approaches have been adopted to avoid the aggregation of the Pd NPs, such as immobilizing them onto some supports like metal oxides²¹, carbon^{22, 23} and polymers^{24, 25}. For example, Yuan and co-workers reported that carbon nanofiber-supported Pd NPs could be used as excellent catalyst toward Heck reaction²⁶. A basic resin has also been performed as a polymer support for the Pd NPs for the catalytic decomposition of formic acid to produce high-quality H_2 ²⁷. The polymer support process the advantage of its abundant functional groups, which efficiently prevent the leaching and aggregation of the Pd NPs. As a typical type of polymer support, electrospun polymer nanofiber membranes have attracted more and more attention because they showed large surface area and high porosity²⁸⁻³⁰. Moreover, the

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characteristic of the membrane enable the supported catalysts easily separated from the reaction system. Therefore, developing an efficient route to deposit small Pd NPs on the surface of electrospun nanofibers is a meaningful object.

In the previous reports, there are many methods for the preparation of novel metal/conducting polymer nanocomposites^{31, 32}, which could be mainly summarized as multistep and one-step methods. Among them, one-step route to prepare metal/conducting polymer nanocomposites seems to be the simplest. For example, our group has reported that hollow palladium/polypyrrole nanocapsules could be produced in one-step polymerization technique in the presence of Rhodamine B³³. A novel one-pot synthesis of free standing Pd–PPy films was also described in presence of the surface-active dopant, dodecylbenzene sulphonic acid sodium salt (NaDBSA)³⁴. In this study, we have presented a simple one-pot approach to decorate Pd NPs on the surface of electrospun polyacrylonitrile (PAN) nanofiber membrane through a redox polymerization reaction between Na_2PdCl_4 and pyrrole monomer without any other surfactants or reductants. After the polymerization, the generation of Pd NPs was accompanied with the formation of PPy, which were well deposited on the surface of PAN nanofibers. It is noted that Pd NPs were enveloped with PPy layer on the surface of PAN nanofibers, which enhanced the stability of the Pd NPs. We have investigated the catalytic performance of Pd/PPy/PAN composite nanofiber membrane for hydrogen generation from AB. The results demonstrated that Pd/PPy/PAN composite nanofiber membrane possess high catalytic activity and excellent reusability toward the hydrolysis of AB.

Experimental

Materials

Polyacrylonitrile ($M_w = 80,000$) fibril constitutive of acrylonitrile (91%), acrylamide (8.5%), and itaconic acid (0.5%) was purchased from Jilin Chemical Plant. N, N-dimethylformamide (DMF), ethylene glycol (EG) and ethanol were obtained from Beijing Chemical Corporation. AB (technical grade, 90%) and Na_2PdCl_4 were bought from Aldrich. Pyrrole was provided by Aladdin. All the chemicals were of analytical grade and used as received without further purification.

Characterization

The morphology of the nanofibers was observed by scanning electron microscopy (SEM, HITACHI SU8000) and transmission electron microscopy (TEM, JEOL JEM-1200 EX). HRTEM imaging analysis was done with a FEI Tecnai G2 F20 high resolution transmission electron microscope operated at 200 kV accelerating voltage. Energy dispersive X-ray (EDX) analysis was carried out on the HRTEM. X-ray data were collected by using an X-ray diffractionmeter (Empyrean, PANalytical B.V.) based on Cu-K α radiation. Analysis of the

X-ray photoelectron spectra (XPS) was performed on a thermo ESCALAB 250 spectrometer. FTIR spectra were obtained on a Fourier transform infrared spectrometer (FT-IR, BRUKER VECTOR 22). The amount of Pd in Pd/PPy/PAN composite nanofibers was determined using an inductive coupled plasma emission spectrometer (ICP, PerkinElmer OPTIMA 3300DV).

Preparation of electrospun PAN nanofibers

PAN nanofiber membrane was prepared through an electrospinning technique as follows: 0.9 g of PAN was dissolved in 9.1 g of DMF under vigorous stirring at 60 °C for 4 h and yellow homogeneous solution was obtained. Then, the as-prepared solution was electrospun using a glass syringe with tip inner diameter of approximately 1 mm at an applied voltage of 13 kV over a collection distance of 15 cm. The nanofibers were collected on aluminum foil and then removed for the following experiment.

Preparation of Pd/PPy/PAN composite nanofibers

17 mg of PAN nanofiber membrane was immersed in 20 ml of EG solvent. Then, 60 μL of pyrrole monomer was added to the solution under shaking for 30 min before 450 μL of Na_2PdCl_4 (0.1 M) was added into the above solution to start polymerization. The Pd/PPy/PAN composite nanofiber membrane was washed with water and ethanol for several times after the reaction was shaken for 24 h. Finally, the as-prepared nanofiber membrane was dried under 60 °C.

Catalytic hydrolysis of ammonia borane

Hydrogen gas was collected by drainage method until no more gas was observed. The reaction was carried out in a conical flask. First, 0.05 g of AB was dissolved in 10 mL water and 21 mg of Pd/PPy/PAN composite nanofiber membrane was added to start the reaction. Then, a three-necked round-bottom flask filled with water was connected to the conical flask quickly. The three-necked round-bottom flask filled with water was connected to an empty burette. The gas produced was measured by the volume of water in the burette at different time. The reaction medium was performed on a shake with the shaking rate of 100 rpm. The concentrations of the catalyst and temperature were varied to explore the kinetics of the hydrolysis of AB catalyzed by Pd/PPy/PAN composite nanofiber membrane. The Pd/PPy/PAN composite nanofiber membrane after the hydrolysis of AB was dried to study the recycling property.

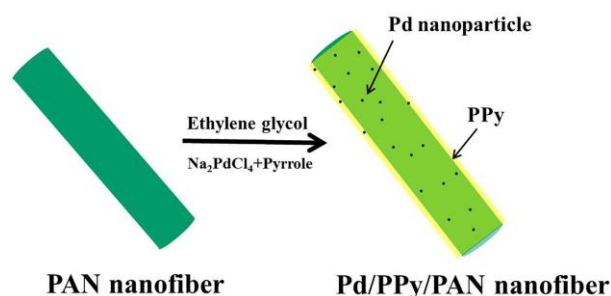


Fig. 1 Schematic illustration of the preparation of the Pd/PPy/PAN composite nanofibers.

Results and discussion

In this study, Pd/PPy/PAN composite nanofiber membrane was prepared through a simple one-pot redox chemical polymerization route. Fig. 1 is a schematic illustration about the fabrication process of Pd/PPy/PAN composite nanofibers. As the standard reduction potential of $\text{PdCl}_4^{2-}/\text{Pd}$ 0.591 V³⁵, while the oxidation potential of pyrrole monomer is 0.2 V³⁶, so PdCl_4^{2-} could react with pyrrole to produce PPy and Pd NPs.

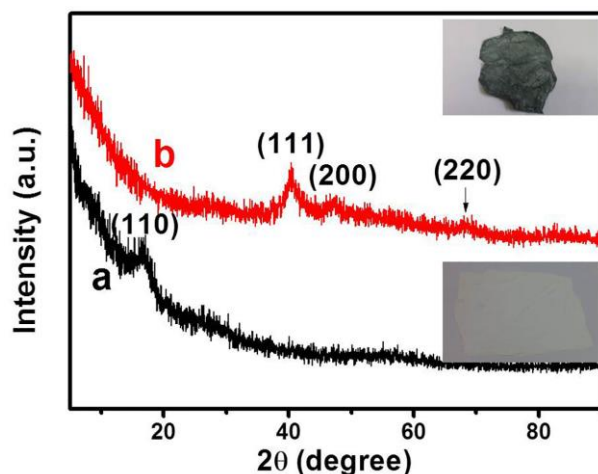


Fig. 2 XRD of (a) PAN and (b) Pd/PPy/PAN nanofibers. (The insets show the optical images of PAN (white) and Pd/PPy/PAN (greenblack) composite nanofibers.)

PPy tends to polymerize on the surface of the support³⁷, so the Pd/PPy/PAN composite nanofiber membrane was obtained. The formation of the PPy layer on the surface of PAN nanofiber membrane could be clearly observed by the change of the membrane color. The electrospun PAN nanofibers show a white color while it turns to greenblack after the polymerization, which indicates that PPy was in situ polymerized on the surface of PAN nanofibers membrane. The formation and the crystal structure of the Pd NPs were proved by the XRD pattern. As shown in Fig. 2, it can be seen that pure PAN nanofibers show a peak at about 16.9°, which corresponds to the orthorhombic PAN (110) Bragg reflection³⁸. However, this peak disappears after the formation of Pd NPs and PPy. Another three peaks at $2\theta = 39.9^\circ$, 47.1° and 68.2° corresponding to the characteristic of Pd (111), (200) and (220) crystalline planes appear³⁹, which demonstrate the formation and the good crystallinity of the supported Pd NPs.

Fig. 3a and b depict typical SEM images of the electrospun PAN nanofibers, revealing their smooth surface with an average diameter of around 252 nm. This is also proved by TEM image (Fig. S1). In contrast, the morphology of the as-prepared Pd/PPy/PAN composite nanofibers after the polymerization became much coarser and many particles were immobilized on the surface of PAN nanofibers. Accordingly, the average diameter of the composite nanofibers increased to be about 353 nm (Figure 3c and d). This result indicates that PPy and Pd NPs have been deposited on the surface of the electrospun PAN nanofibers. To further evaluate the dispersion

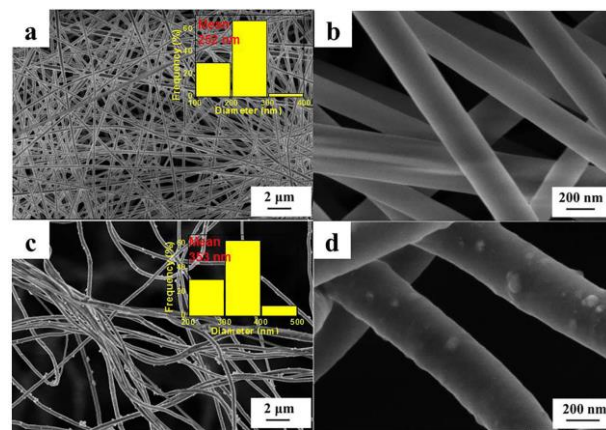


Fig. 3 (a and b) SEM of the PAN nanofibers. (c and d) SEM of the as-prepared Pd/PPy/PAN composite nanofibers. (The insets show the diameter distribution of PAN and Pd/PPy/PAN composite nanofibers.)

state of the Pd NPs in the PPy matrix on the surface of PAN nanofibers, TEM images were performed. From Fig. 4a, it can be seen that large amounts of NPs are dispersed on the surface of the PAN nanofibers. A higher magnification (Fig. 4b) shows numerous Pd NPs are immobilized on the surface of PAN nanofibers. The size of the obtained Pd NPs was about 5 nm. The lattice spacing of 0.23 nm was calculated from Figure 4c, which should be corresponding to Pd (111) crystal planes⁴⁰. The as-synthesized Pd/PPy/PAN composite nanofibers were also examined by energy-dispersive X-ray (EDX) spectroscopy (Figure 4d), which showed the existence of C, N, O, Cu, Si, Cl and Pd (Cu element is ascribed to the carbon grid and Si is ascribed to the probe of the instrument). This result indicated the formation of Pd NPs and PPy layer on the surface of PAN nanofibers. Moreover, the overall weight percentage of Pd in the Pd/PPy/PAN composite nanofiber membrane was determined to be about 8.0% by ICP measurement.

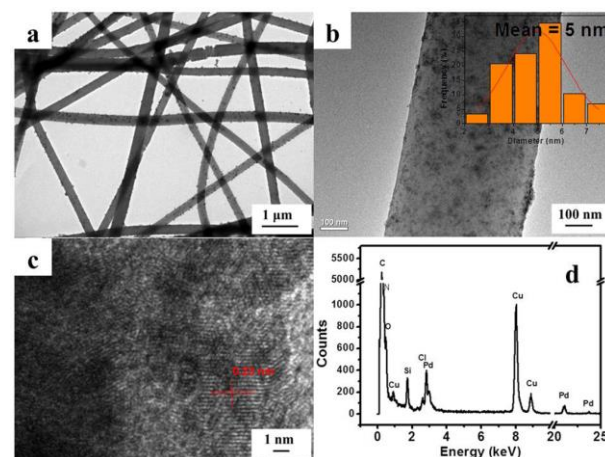


Fig. 4 (a and b) TEM of the Pd/PPy/PAN composite nanofibers. (c and d) HRTEM image and EDX of the Pd/PPy/PAN composite nanofibers. (The insets show the diameter distribution of Pd NPs on Pd/PPy/PAN composite nanofibers)

Fig. 5 shows the FTIR spectra of the as-electrospun PAN and Pd/PPy/PAN composite nanofibers. For PAN nanofiber membrane, the peaks at 2937 cm^{-1} and 2851 cm^{-1} are assigned to antisymmetrical and symmetrical C–H stretching. Besides, the peaks at 2246 cm^{-1} , 1730 cm^{-1} and 1450 cm^{-1} are related to the C≡N stretching vibration, C=O stretching vibrations of the acrylamide exist in PAN nanofibers⁴¹ and C–H bending deformation. In the curve of Pd/PPy/PAN composite nanofibers, the main peaks ascribed to the PAN were all observed. In addition, some other characteristic bands of PPy at 1560 cm^{-1} , 1205 cm^{-1} , 1048 cm^{-1} and 930 cm^{-1} appear indicating the formation of PPy on the surface of PAN nanofibers⁴².

The formation of Pd/PPy/PAN composite nanofibers has also been examined by XPS measurement, and the results are shown in Fig. 6. Figure 6a show the wide-scan XPS spectrum of the as-prepared Pd/PPy/PAN composite nanofibers, from the figure we can see that C, N, O, Pd and Cl elements were detected. The Pd 3d could be deconvoluted into two components, the peaks at 336.0 eV (Pd 3d_{5/2}) and 341.3 eV (Pd 3d_{3/2}) are assigned to Pd(0), and the other two peaks at 337.7 eV (Pd 3d_{5/2}) and 342.9 eV (Pd 3d_{3/2}) are assigned to the oxidized Pd(II) centers, identical to what was reported in the literature⁴². The oxidized palladium always formed around the small Pd NPs. The Cl 1s spectra could be deconvoluted into three components corresponding to C–C, C–H and C–N species with a binding energy of 284.7 eV , C–O with a binding energy of 286 eV , C=O with a binding energy of 287.2 eV ⁴³. As displayed in Fig.6d, the XPS spectrum for O 1s features three

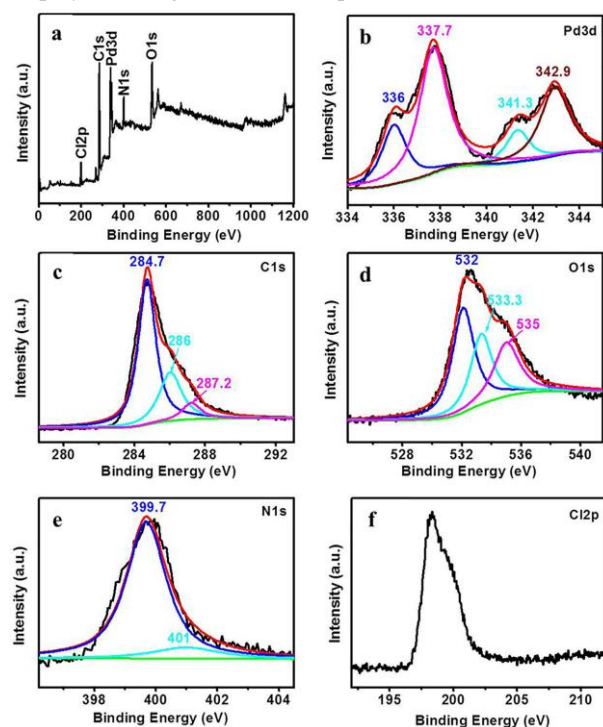


Fig. 6 XPS spectra of the as-synthesized Pd/PPy/PAN nanofibers. (a) full survey spectrum, (b) Pd3d, (c) C1s, (d) O1s, (e) N1s, (f) Cl2p.

peaks. The main peak at 532 eV is attributed to the O–H and O=C moieties, the peaks 533.3 eV and 535 eV are attributed to O–C⁴³. The high-resolution XPS spectrum of N 1s can be well fitted into two peaks. The peak at 399.7 eV is for –NH– of polypyrrole. The peak at 401 eV could be result from positively charged nitrogen N⁺. This result is in accord with the structure of PPy⁴³. The presence of Cl2p could be attributed to the existence of the dopant of Cl[–].

In our experiment, Pd/PPy/PAN composite nanofiber membrane exhibited excellent catalytic properties toward the dehydrogenation of AB to generate hydrogen. Hydrogen was produced continuously as soon as the membrane was immersed in the solution. We investigated the hydrolysis kinetics of AB catalyzed by the composite nanofiber membrane. The amount of catalyst is an important factor during the reaction, which determines the rate (the volume of H₂ produced per minute) of plots by hydrogen evolution. Fig. 7a depicts the hydrogen evolution of AB by different amount of catalyst. From the figure we can see that the rate of hydrogen evolution increased from 0.9 to 4.5 when the concentration of Pd increased from 0.83 mM to 4.96 mM during the catalytic hydrolysis of 162 mM AB solution at 300 K, the plots keep linearly almost without induction period. The rates of hydrogen release from the hydrolysis of AB by different amount of catalyst were

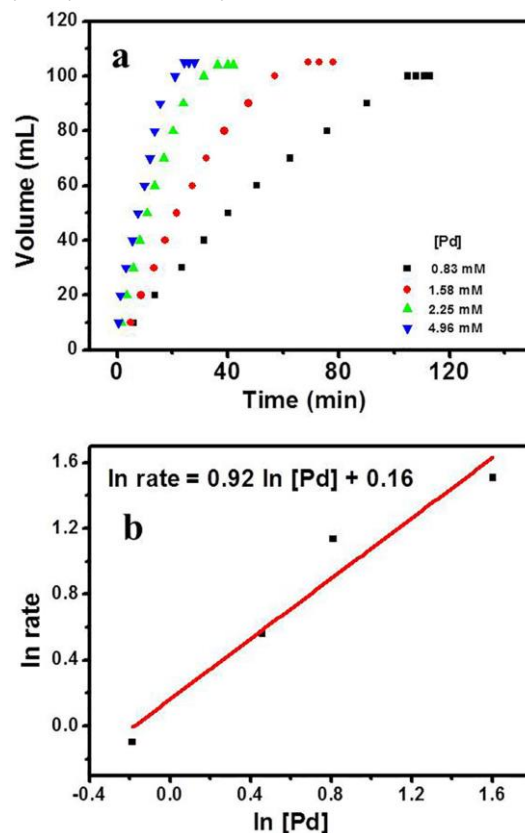


Fig. 7 Hydrogen evolution generated from hydrolysis of 162 mM AB catalyzed by Pd/PPy/PAN nanofibers at different catalyst concentrations at 300 K.

calculated from the linear parts of the plots in Fig. 7a. The

dehydrogenation of AB could be assumed to be a pseudo-first-order reaction from Fig. 7b of the hydrogen generation rate with respect to the Pd concentration (both in logarithmic scale) with a slope of 0.92 (≈ 1.0).

Fig. 8a shows the volume of hydrogen generated from the hydrolysis of AB (162 mM) catalyzed by Pd/PPy/PAN composite nanofiber membrane versus different temperature from 300 K to 330 K. The rates (k) of hydrogen generation from the hydrolysis of AB by different temperatures were calculated from the linear parts of the plots in Fig. 8a. The results indicate that there is a consistently increase of rate as the reaction temperature is elevated. Activation energy (E_a) could be calculated from the slope in Arrhenius plot of $\ln k$ versus $1/T$ (Fig. 8b). In our experiment, E_a was calculated to be 33.5 kJ mol⁻¹, which is lower than most of the E_a values reported previously. A comparison of E_a values between our Pd/PPy/PAN composite nanofibers and other metal-based catalyst reported in literature has been presented in Table S1 (supporting information). The value of activation energy of our Pd/PPy/PAN composite nanofiber membrane is the lowest

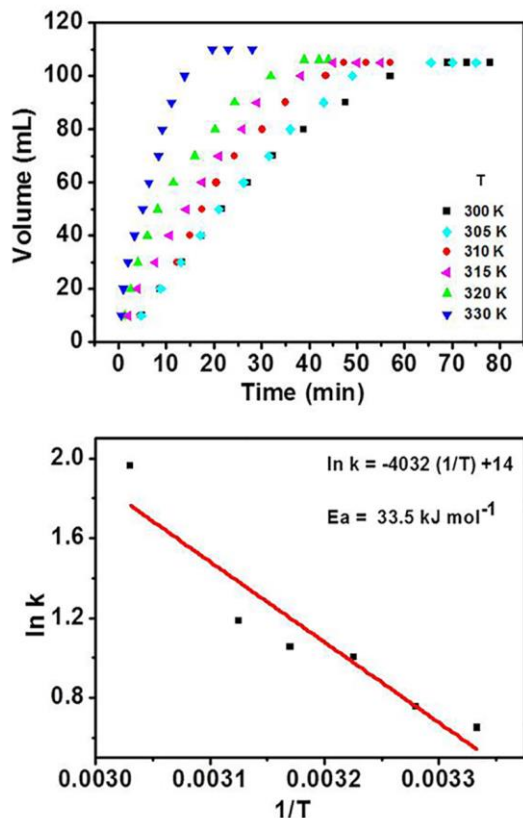


Fig. 8 Hydrogen evolution generated from hydrolysis of 162 mM AB catalyzed by 21 mg Pd /PPy/PAN nanofibers at different temperature

activation energy for the hydrolysis of AB except for Pt/ γ -Al₂O₃ and Ag@Co/graphene NPs. The lower E_a value indicated a good catalytic performance of the as-prepared Pd/PPy/PAN composite nanofiber membrane. Further, the TOF of Pd/PPy/PAN was calculated to be about 3.9 mol H₂/mol

catalyst⁻¹.min⁻¹ at room temperature, which is higher than 2 wt % Pd/ γ -Al₂O₃, Pd black, 10 wt % Co/ γ -Al₂O₃, 10 wt % Co/SiO₂, 10 wt % Co/C in the literature reported before^{44, 45}. The mechanism for the good performance of Pd/PPy/PAN could be interpreted as follows: during the hydrolysis reaction, AB could interact with the surface of metal and form an activated complex⁴⁶. This complex will be attacked by a molecule of water and release H₂. As Pd is an efficient catalyst toward many catalytic reactions, the small size of Pd NPs in Pd/PPy/PAN composite nanofibers could make full use of the surface of Pd NPs. Furthermore, the hydrolysis reaction involves electron transfer. It is well known that PPy possesses good electron conductivity and has some synergistic effect with active metal particles to fulfill their functions. The work function of PPy (about 5.0 eV) is a little lower than Pd (5.12 eV)^{33, 47}, there will be an electron-enriched region near Pd/PPy interface, which will accelerate the electrons transfer.

The reusability is also an important aspect for the catalysts. After the reaction, the Pd/PPy/PAN composite nanofibers could be separated from the solution easily just by a tweezer (see the inset in Fig. S2). After washed with water and ethanol for several times, the membrane was dried for next cycles. It is noteworthy to mention that after five cycles, the Pd/PPy/PAN composite nanofibers did not exhibit obvious loss of catalytic activity, demonstrating the stable recycling catalytic ability (Fig.

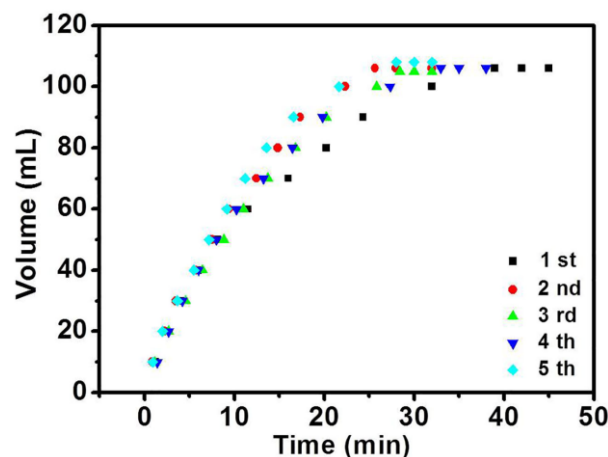


Fig. 9 Hydrogen evolution generated from hydrolysis of 162 mM AB catalyzed by 21 mg Pd /PPy/PAN nanofibers recycled for five times at 320 K.

9). The morphology of Pd/PPy/PAN composite nanofibers was shown in Fig. S2 (supporting information). The composite nanofiber remained continuous and the size of most of the Pd NPs immobilized on the surface of PAN nanofibers did not change significantly only some Pd NPs on the surface of composite nanofibers were found to be partially aggregated.

Conclusions

Pd/PPy/PAN composite nanofibers were successfully prepared by a simple and effective one-pot approach in the presence of Na₂PdCl₄, pyrrole and PAN nanofibers. The

Pd/PPy/PAN composite nanofibers were employed as catalyst in the hydrolysis of AB to produce hydrogen and showed superior catalytic properties. The hydrolytic dehydrogenation of AB is first order with respect to the Pd concentration. The E_a was calculated to be 33.5 kJ mol⁻¹ by the Arrhenius equation, indicating a good catalytic performance of the Pd/PPy/PAN composite nanofiber membrane. Moreover, the Pd/PPy/PAN composite nanofiber membrane could be separated from AB solution easily and it showed no decrease of catalytic reactivity in successive five runs. It is anticipated that this simple method could be extended to prepare many other kinds of functional composite membranes, which produce new features and applications.

Acknowledgements

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