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In-situ synthesis of Ni nanofibers via vacuum thermal reduction and their

efficient catalytic properties for hydrogen generation

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Abstract: Simple, safety and economic methods to prepare Ni nanofibers are required for practical application. Herein, an in-situ vacuum thermal reduction strategy is proposed to synthesize Ni nanofibers with which involves electrospinning of nickel large scale, acetate/polyvinylpolypyrrolidone/ethyl cellulose (NiAc/PVP/EC) precursor solution and following vacuum thermal treatment. The characterization of morphology and microstructure reveals that as-prepared Ni nanofibers were composed of nano-size Ni grains and possess large surface areas. Moreover, it has been demonstrated that contents of EC are closely relate to the sizes of Ni grains and then surface areas of Ni nanofibers. Depending on the high specific surface areas, the as-prepared Ni nanofibers exhibit efficient catalytic properties for the H_2 generation from hydrous hydrazine in an alkaline solution.

Key words: vacuum, electrospinning, nickel nanofiber, catalyst

Introduction

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Ni nanofiber, which is considered a novel nanoscale material, has attracted much attention owing to its extensive applications in fields such as supercapacitor,¹ catalyst support,² biomagnetic device,³ microwave absorber,⁴ and hydrogen fuel cell.⁵ Therefore, a variety of methods have been used to synthesize Ni nanofibers, such as solution-liquid-solid methods,⁶ electrodeposition method,⁷ template method,⁸ chemical reduction method⁹ and electrospinning.¹⁰ Among all the methods, electrospinning is a simple, economic and efficient approach to prepare nanofibers. Generally, preparation of electrospun nickel nanofibers, involves three main steps: (1) electrospinning of polymer/nickel salt precursor solution (to obtain polymer/nickel salt composite nanofibers) and (2) calcination in air of the as-electrospun nanofibers (to remove the polymer and convert nickel salt to nickel oxide) and (3) reduction of NiO in a reductive atmosphere (to obtain Ni nanofibers).¹⁰⁻¹² Nevertheless, using of reductive gases, such as compressed hydrogen, at high temperature will result in energy consumption and potential safety risks.

Herein, an in-situ reduction strategy is proposed to prepare electrospun Ni nanofibers, which involves electrospinning the nickel acetate /polyvinylpolypyrrolidone (NiAc/PVP) precursor solution and followed by a vacuum heat treatment. Furthermore, ethyl cellulose (EC) was introduced in precursor solution to modify the morphology and structure of Ni nanofibers. The effects of EC concentration on morphology and structure of Ni nanofibers were also investigated in detail. Depending on the low cost and good catalytic activity of Ni,¹³⁻¹⁶ the electrospun Ni nanofibers were directly used as the catalyst to generate H₂ from decomposition of hydrous hydrazine. Conventional methods to generate H₂ from hydrous hydrazine have to involve various reductants, such as sodium borohydride,¹⁷ ammonia borane,¹⁸ hydrazine borane¹⁹ and hydrogen,²⁰ while the method proposed in this paper does not require any reductants. Results show that electrospun Ni nanofibers exhibit excellent catalytic activity and H₂ selectivity in the hydrous hydrazine decomposition reaction.

Experimental Section

Chemicals and Materials

Hydrous hydrazine (N₂H₄·H₂O, 85%), nickel acetate tetrahydrate (NiAc·4H₂O, 99%), ethyl cellulose (EC, 99%), polyvinylpolypyrrolidone (PVP, Mw = 1, 300, 000), acetic acid (HAc, 99%), hydrochloric acid (HCl, 36.5%) and sodium hydroxide (NaOH, 98%) were obtained from Aladdin Ltd. (Shanghai, China). All chemicals used as received without any purification.

Preparation of Ni nanofibers

The simple method to prepare Ni Nanofibers was illustrated in Scheme 1. A typical precursor solution was prepared by mixing NiAc·4H₂O (5.70 g), polymers (PVP and EC, 1.12 g) and HAc (6 mL) in ethanol (25 mL) with vigorous stirring until a homogeneous and viscous solution was formed. The obtained solution was transferred into a plastic vessel (20 mL). The voltage and the

distance between spinning wheel and collector were set up at 60 kV and 15 cm. The prepared NiAc/polymers composite nanofibers were collected on a piece of aluminum foil. Then NiAc/polymers composite nanofibers were heat treated in a furnace at 773 K for 3 h with 1 K min⁻¹ heating rate under vacuum condition to obtain Ni nanofibers. Four Ni nanofibers were prepared with varying PVP:EC mass ratios: 10:0, 9:1, 7:3, and 5:5. For simplicity, these are denoted as NF10, NF91, NF73 and NF55, respectively.



Scheme 1 Schematic illustration of the preparation of Ni nanofibers

Characterizations

The morphologies of Ni nanofibers were performed using a high resolution scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, Hitachi HT7700). The crystal structures and compositions of the Ni nanofibers were measured by X-ray diffraction (XRD, Bruker D2) with Cu K α radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA, and the crystal sizes were obtained by Scherrer's equation. Surface elemental valance analysis was performed using X-ray photoelectron spectroscopy (XPS, Escalab 250xi) with Al K α radiation (hv = 1486.6 eV). N₂ adsorption-desorption isotherms were collected on the Quantachrome surface area analyzer at 77 K. Before adsorption, all samples were degassed under vacuum at 573 K for 5 h. Pore size distributions were collected by Barrett-Joyner-Halenda (BJH) model using the desorption branch of the isotherm.

Catalytic tests

In a typical experiment, a specific amount of Ni nanofibers catalyst was dispersed in NaOH solution (0.5 M, 3 mL) with stirring for 10 min at constant temperature, and then a calculated amount of hydrous hydrazine was added into the suspension. Generally, decomposition of hydrous hydrazine via two competitive reactions:

$$N_2H_4(l) \rightarrow N_2(g) + 2H_2(g)$$
 (1)

$$3N_2H_4(l) \rightarrow N_2(g) + 4NH_3(g)$$
 (2)

From the perspective of hydrogen generation, the undesirable decomposition to ammonia must be avoided.^{21,22} Herein, by-product ammonia was absorbed by HCl (1.0 M) before measured volumetrically. The durability of the obtained Ni nanofibers catalyst was tested: we took five cycles of reactions over the same catalyst at 333 K with NaOH solution (0.5 M), after the first cycle of hydrous hydrazine decomposition reaction was completed, another equivalent of hydrous hydrazine was introduced into the three-neck.

The selectivity of H_2 generation from hydrous hydrazine (defined as *X*) was evaluated on equation (3), which could be derived based on equations (1) and (2).

$$X = \frac{3Y-1}{8}, \left[Y = \frac{n(N_2 + H_2)}{n(N_2 H_4)}, \frac{1}{3} \le Y \le 3\right]$$
(3)

In the determination of TOF, all the Ni atoms of Ni nanofibers were assumed to catalyze the reaction of hydrous hydrazine decomposition, and the time required for 50% conversion of hydrous hydrazine was used in the calculation.

Results and discussion



Fig. 1 XRD patterns of a) NF10 before annealing, b) NF10, c) NF91, d) NF73 and e) NF55.

The XRD patterns of NF10 precursor nanofibers and Ni nanofibres with different EC contents were shown in Fig. 1. The prepared NF10 precursor nanofibers do not exhibit any crystalline peaks, indicating that PVP have an amorphous nature and masked the diffraction peaks of NiAc,²³ as shown in Fig. 1a. Notably, after calcination, the amorphous peak for PVP disappeared due to the degradation of PVP at high temperature.^{24,25} As shown in Fig. 1b-1e, the three well-resolved XRD peaks at $2\theta = 44.5^{\circ}$, 51.9° and 76.4° for all obtained Ni nanofibers are attributed to (111), (200) and (220) planes of face center cubic nickel, respectively (JCPDS: no. 04-0850). These results indicate that NiAc was totally transformed to Ni during the vacuum heat–treatment process. Reducing gases (CO, H₂) and reducing carbon could be generated by thermal decomposition of nickel acetate, and then convert nickel (II) to nickel (0).²⁶⁻²⁹ Besides, there is no obvious C diffraction peak ($2\theta = 25^{\circ}$) is observed in the XRD patterns, which can be ascribed to the consumption of the carbon during the carbon thermal reduction process (NiO + C = Ni + CO).²⁹⁻³¹ The grain sizes of all the Ni nanofibers are estimated using the full widths at half maximum (FWHM) of Ni (111) peaks, through the

Scherrer's equation. The mean crystallite sizes of NF10, NF91, NF73 and NF55 are calculated to be 42 nm, 30 nm, 15 nm and 17 nm, respectively. This result suggests that Ni grain sizes decreased with EC content and have a minimum value as the mass ratio of PVP:EC = 7:3.



Fig. 2 SEM images of a) NF10, b) NF91, c) NF73 and d) NF55.

Fig. 2 shows the SEM images of NF10, NF91, NF73 and NF55 after annealing. It can be seen that all the Ni nanofibers have a continuous structure with diameters about 400 nm. The morphologies of Ni nanofibers gradually become rough with adjusting the mass ratio of PVP:EC from 10:0 to 5:5. In particular, NF55 (PVP:EC = 5:5) shows a gully structure. This morphological difference among these four Ni nanofibers is owing to the different pyrolysis process of EC (573 K \sim 673 K) and PVP (653 K \sim 773 K) during heating.^{25,32} When the heating temperature was increased to 673 K, the EC was completely degraded and a porous nanofiber was formed. Subsequently, the PVP was gradually removed during heat treatment. Finally, a rough Ni nanofiber was obtained through continuous shrinkage of nanofiber during the heat preservation process at 773

K.

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Fig. 3 TEM images of microstructures of a) NF10, b) NF91, c) NF73 and d) NF55.

Taking a deep insight into the microstructure of electrospun Ni nanofibers, TEM characterization was carried out. Remarkably, to obtain clear images of Ni grains, thin Ni nanofibers (about 100 nm) were chosen as subjects. Fig. 3a-3d shows the TEM images of NF10, NF91, NF73 and NF55. From TEM images, it can be seen that the Ni nanofibers were composed of large amounts of Ni nanocrystals with average diameters about 18 nm, 16 nm, 11 nm and 12 nm for NF10, NF91, NF73 and NF55, respectively (Fig. S1). This result further confirms that the grain sizes of Ni nanofibers could be changed by adjusting EC content, which coincides with XRD result in Fig. 1. However, the grain sizes reported from TEM are smaller than the ones calculated from Scherrer's equation, but follow the same transformation trend. This may be due to the fact that thin Ni nanofibers were composed of small Ni nanocrystals. As shown in Fig. S2, the selected area electron diffraction (SAED) patterns of four Ni nanofibers consist of recognizable diffraction rings, suggesting that Ni nanofibers have a polycrystalline nature. The squares of radius of the (111), (200), (220), (311), and (222) diffraction rings are in good agreement with 3: 4: 8: 11: 12, which indicate that Ni nanocrystals have face center cubic structure.^{33,34}



Fig. 4 N₂ adsorption-desorption isotherms of a) NF10, b) NF91, c) NF73 and d) NF55.

To get more surface properties of electrospun Ni nanofibers, N₂ adsorption -desorption isotherms at 77 K were measured. As shown in Fig. 4, all Ni nanofibers followed the obvious hysteresis loops of type IV isotherms, indicating the presence of mesopores (Fig. S3). The detailed surface and pore textural parameters are listed in Table 1. The Brunauer-Emmett-Teller (BET) surface areas and average pore sizes of Ni nanofibers increase with increasing EC concentration. However, NF73 possesses the highest specific surface area and pore sizes, instead of NF55. The reason might be that some pores in NF55 connected to be a gully, which reduces the surface area of Ni nanofibers, as shown in SEM images (Fig. 2d). The above results reveal that EC plays a key role in controlling surface properties of Ni nanofibers.

Table 1 Surface and pore parameters of NF10, NF91, NF73 and NF55.

Sample	$S_{BET} (m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹) Average pore sizes (nm)	
NF10	48.586	0.065	17.084
NF91	71.777	0.059	17.090
NF73	132.775	0.136	19.148
NF55	103.522	0.132	17.083



Fig. 5 Time course plots for the decomposition of N_2H_4 · H_2O catalyzed by a) NF10, b) NF91, c) NF73 and d)

NF55 at 333 K (catalyst $/N_2H_4 \cdot H_2O = 0.5, 0.5$ M NaOH).

It is generally known that nano-size and high specific surface area play quite vital role in catalytic reaction. As shown in Fig. 5, catalytic activities of different Ni nanofibers catalysts were tested in the reaction of hydrous hydrazine decomposition at 333 K with NaOH solution (0.5 M). The catalytic performance of NF73 is highest, which could be attributed to the high specific surface area and small Ni grain size. This catalytic performance is consistent with the results of Ni grain sizes and BET surface areas (shown in Table 2). Moreover, all Ni nanofibers catalysts exhibited nearly 100% selectivity to H_2 generation.

Sample	$S_{BET} (m^2 g^{-1})$	$D_{TEM} \left(nm \right)^{(a)}$	$D_{Scherrer} \left(nm \right)^{(b)}$	$TOF(h^{-1})$
NF10	48.586	18	42	4.1
NF91	71.777	16	30	4.9
NF73	132.775	11	15	6.9
NF55	103.522	12	17	5.1

Table 2 Textural parameters of NF10, NF91, NF73 and NF55.

(a) Evaluated by TEM images.

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(b) Calculated by the XRD patterns $(2\theta = 44.5^{\circ})$ using the Scherrer's equation.



Fig. 6 XPS wide scan spectra and detail spectra of Ni 2p, C 1s, O 1s in NF73.

In order to explore the surface element valance information of NF73 with highest catalytic performance, X-ray photoelectron spectroscopy (XPS) measurement was carried out (Fig. 6). In the Ni 2p XPS spectrum, the two peaks with binding energy of 852.9 eV and 870.2 eV can be assigned to Ni (0) $2p_{3/2}$ and Ni (0) $2p_{1/2}$, respectively. Two lower intensity peaks at 855.6 eV and 874.2 eV can be assigned to Ni (II) $2p_{3/2}$ and Ni (II) $2p_{3/2}$ and Ni (II) $2p_{1/2}$, respectively. The relative intensities of the $2p_{3/2}$ and $2p_{1/2}$ are about 1:2. Besides, the two satellite peaks at 861.0 eV and 879.4 eV located at the side of the Ni (II) $2p_{3/2}$ and Ni (II) $2p_{1/2}$ edge. In the O 1s XPS spectrum, besides the lattice oxygen (O_{latt}) of NiO (530.1 eV), two peaks located at 531.5 eV and 532.3 eV corresponding to hydroxyl oxygen (O_{hyd}) and physically adsorbed oxygen (O_{ads}), respectively.^{35,36} Additionally, the C1s spectrum can be deconvoluted into three peaks, which are located at 284.6 eV (sp² C), 285.5 eV (C-O) and 288.6 eV (O-C=O), respectively. This result indicates that small amounts of NiO were formed by the surface oxidation of sample in air atmosphere, and the NiO thin film could further results in the formation of surface carbonates before XPS test.³⁷

NaOH acts as inhibitor for NH₃ evolution from the undesirable reaction of hydrous hydrazine

decomposition $(3N_2H_4 \rightarrow 4NH_3 + N_2)$. As shown in Fig. S4, the H₂ selectivity and catalytic activity of NF73 catalyst for the hydrous hydrazine decomposition increased with the concentration of NaOH solution until the high concentration NaOH solution (0.5 M) was used. After that, further increasing the concentration of NaOH, there was no obvious effect on the H₂ selectivity and catalytic activity.

Moreover, the activation energy value E_a is calculated to be 52.07 kJ mol⁻¹ (see details in Fig. S5), which is smaller than the reported values using NiFe/Cu (79.2 kJ mol⁻¹),³⁸ Rh_{0.8}Ni_{0.2}@CeO_x/rGO (58.0 kJ mol⁻¹)³⁹ and NiMoB-La(OH)₃ (55.1 kJ mol⁻¹)⁴⁰ as catalysts. In addition, the effect of hydrazine concentration ([N₂H₄]) on the hydrogen generation rate (RH₂) was investigated (see details in Fig. S6a). As shown in Fig. S6b, the kinetic of hydrous hydrazine decomposition catalyzed by Ni nanofibers is zero order with respect to hydrous hydrazine concentration.

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Fig. 7 Durability tests of NF73 for the H₂ generation at 333 K (NF73 $/N_2H_4 \cdot H_2O = 0.5$).

The durability of catalyst is very important for practical application. Fig. 7 illustrates the durability of NF73 for the hydrous hydrazine decomposition. Even after five cycles, NF73 showed a nearly 100% H₂ selectivity and slight decrease of catalytic activity. In addition, the morphology of

the reused NF73 is still partially maintained (Fig. S7). The recycle test result indicates that NF73 has good stability in hydrous hydrazine decomposition reaction.

Conclusion

Ni nanofibers with different morphologies and microstructures were prepared through electrospinning and in-situ vacuum thermal reduction. The introduction of EC not only affects the morphologies of Ni nanofibers, but also the sizes of Ni nanocrystals. The catalytic performance of the prepared Ni nanofibers for hydrous hydrazine decomposition reaction shows that morphologies and Ni grain sizes strongly affect the catalytic activity. The NF73 catalyst, which has a high specific surface area and small crystal size, enables rapid conversion of N_2H_4 ·H₂O into N₂ and H₂ in NaOH solution (0.5 M) at 333 K with nearly 100% H₂ selectivity and a TOF of 6.9 h⁻¹. Considering the simplicity, safety and economy of preparation method to produce Ni nanofibers, we suggest that this facile preparation method could be widely applied to other nanofibers for more applications.

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Ni nanofibers have been prepared by a vacuum thermal reduction method, and further used as

efficient catalysts for the hydrogen generation from hydrous hydrazine decomposition reaction.