



Fabrication of aluminum-doped α -Ni(OH)₂ with hierarchical architecture and its largely enhanced electrocatalytic performance

Xianggui Kong, Jingwen Zhao, Wenying Shi, Yufei Zhao, Mingfei Shao, Min Wei*, Liren Wang*, Xue Duan

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

Aluminum-doped α -Ni(OH)₂ microspheres with flowerlike hierarchical structure (H-Al- α -Ni(OH)₂) were successfully synthesized via a facile hydrothermal method with the assistance of ionic liquid (1-butyl-3-methyl imidazolium tetrafluoroborate, [BMIM]BF₄). The XRD pattern and elemental analysis confirm that aluminum species incorporates into the lattice of α -Ni(OH)₂; SEM and TEM images reveal that the as-prepared microspheres are composed of numerous frizzy nanoflakes shell attaching vertically to the core. The resulting H-Al- α -Ni(OH)₂ sample exhibits a specific surface area of 91.2 m²/g and a mesopore distribution (2–20 nm) based on the BET measurements. Furthermore, the hierarchical H-Al- α -Ni(OH)₂ modified electrode displays a couple of well-defined reversible redox peaks ($\Delta E_p = 67$ mV and $I_a/I_c = 0.91$) and a fast direct electron transfer rate constant ($k_s = 3.32$ s^{−1}), owing to the high dispersion of active species as well as abundant mass transfer channels which facilitate the mass/electron transfer. In addition, the modified electrode presents a significant electrocatalytic performance towards the oxidation of hydrazine with a linear response range (5.0×10^{-6} – 1.0×10^{-4} M), high sensitivity (144 μ A/ μ M cm²), low detection limit (0.8 μ M) as well as good stability. The hierarchical α -Ni(OH)₂ with largely enhanced electrochemical behavior demonstrated in this work can be used in electrochemical sensor and electroanalysis.

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1. Introduction

Nickel hydroxide is a typical lamellar material with 2D structure which has been widely used as electroactive species in secondary batteries, supercapacitors and sensors owing to its high proton diffusion coefficient, high energy, low cost and low toxicity [1–3]. Ni(OH)₂ has a hexagonal layered structure with two polymorphs, namely α - and β -form. The α -form is isostructural with hydrotalcite-like compounds, which consists of a stacking of positively-charged Ni(OH)_{2-x} layers with intercalated anions to maintain the charge neutrality. In contrast, β -form has well-ordered brucite-like structure without any intercalated species. In electrochemical fields, α -Ni(OH)₂ exhibits superior electrochemical properties due to its low oxidation potential in redox reaction process [4–6]. However, further applications of α -Ni(OH)₂ are largely restricted since this phase changes rapidly to the β -form with more stable thermodynamics [7,8]. Therefore, how to stabilize the structure of α -Ni(OH)₂ without phase transformation is a challenging goal. On the other hand, high surface area and

plentiful mesopores distribution are desirable for an excellent electroactive material, which can accommodate a large number of superficial active sites as well as facilitate mass/electron transfer. It has been reported that the proportion of mesopores (i.e., pore size: 2–50 nm) of electroactive materials is preferable for the mass transportation, resulting in a fast redox reaction [9]. Taking into account the two problems mentioned above, it is of crucial importance to develop stable and well-defined micro-/nanostructure α -Ni(OH)₂ with high surface area and abundant mesopore distribution.

Room-temperature ionic liquids (RTILs), as green and efficient recyclable solvents, have developed to a focal point of interest in both academia and industry because of their distinct properties, including nonvolatility, wide range of liquids temperatures, high ionic conductivity and wide electrochemical window [10–13]. Currently, the advantages of RTILs in the preparation of noble metal nanoparticles have been widely recognized [14–16]. Furthermore, RTILs also can be used as soft-template to synthesize some metal oxide/hydroxide with hierarchical nanostructure owing to their self-assembly ability [17,18]. In addition, it was found that a stable α -Ni(OH)₂ can be obtained through partial substitution of nickel ion by other metal ions in the nickel hydroxide lattice to form a hydrotalcite-like compound [19,20]. This therefore inspires us to fabricate a aluminum-doped α -Ni(OH)₂ material with

* Corresponding authors. Tel.: +86 10 64412131; fax: +86 10 64425385.

E-mail addresses: weimin@mail.buct.edu.cn, weimin-hewei@163.com (M. Wei), wanglr@mail.buct.edu.cn (L. Wang).

hierarchical structure with the assistance of RTILs, which would possess the following advantages: firstly, aluminum doping is beneficial to improve the stability of α -Ni(OH)₂; secondly, hierarchical structure with large surface area and plentiful mesopore distribution guarantees a high exposure of electroactive sites as well as a fast mass/electron transfer.

In this work, aluminum-doped α -Ni(OH)₂ microspheres with 3D hierarchical architecture (H-Al- α -Ni(OH)₂) were successfully synthesized through one-step hydrothermal method with the presence of RTILs. The uniform microspheres (particle size: $2 \pm 0.3 \mu\text{m}$) consist of a solid core and a flowerlike shell in which numerous nanoflakes are aligned vertically to the core, with a specific surface area of $91.2 \text{ m}^2/\text{g}$ and a mesopore distribution (2–20 nm). The H-Al- α -Ni(OH)₂ modified electrode exhibits an excellent electrochemical behavior with a couple of well-defined reversible redox peaks and a fast direct electron transfer rate, resulting from high exposure of accessible active sites and a suitable mesopore distribution accommodating a fast transportation pathway. In addition, the modified electrode displays remarkable electrocatalytic performance towards the oxidation of hydrazine with a broad linear response range, high sensitivity and low detection limit. The stability and reproducibility of the proposed electrode were also demonstrated. Therefore, this work provides a facile and successful paradigm for the fabrication of hierarchical aluminum-doped α -Ni(OH)₂ via the RTILs approach, which can be potentially applied as electrochemical sensors.

2. Experimental

2.1. Materials

Room-temperature ionic liquid 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM]BF₄) was purchased from Sigma–Aldrich. All other chemical reagents were of analytical grade and used without further purification, and the solutions were prepared by using water purified in a Milli-Q Millipore system ($>18 \text{ M}\Omega \text{ cm}$).

2.2. Synthesis of hierarchical Al-doped α -Ni(OH)₂

In a typical experiment, Ni(NO₃)₂·6H₂O (0.004 mol), Al(NO₃)₃·9H₂O (0.002 mol), urea (0.018 mol) and ionic liquid [BMIM]BF₄ (0.8 mL) were dissolved in 100 mL of deionized water. The resulting solution was transferred into a Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h, and then cooled down to room temperature. Subsequently, the precipitate was collected and washed thoroughly with water and absolute ethanol, and finally dried at 60 °C for 8 h (denoted as H-Al- α -Ni(OH)₂). For comparison, Al-doped α -Ni(OH)₂ was also prepared in the absence of [BMIM]BF₄ under the same conditions (denoted as Al- α -Ni(OH)₂).

2.3. Preparation of the working electrode

Firstly, the suspension of H-Al- α -Ni(OH)₂ and Al- α -Ni(OH)₂ were obtained respectively by ultrasonic with the same concentration (1 mg/mL); secondly, the working electrode was modified by casting 10 μL of as-prepared suspension on the surface of glass carbon electrode (3 mm, diameter) and dried under room temperature.

2.4. Characterizations and electrochemical measurements

Powder X-ray diffraction patterns of the product were collected on a Rigaku XRD-6000 by use of a Cu-K α radiation at 40 kV, 30 mA. The morphology of the product was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55)

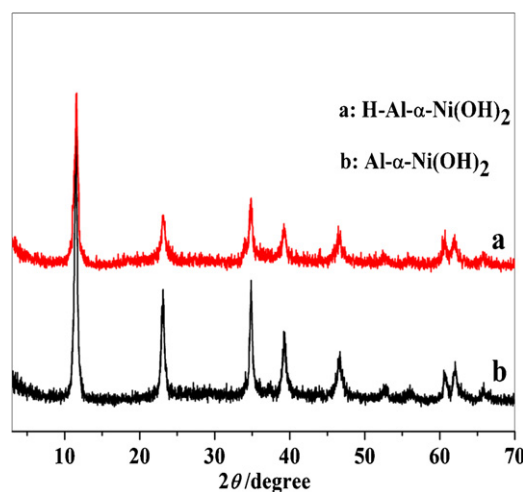


Fig. 1. XRD patterns of the (a) H-Al- α -Ni(OH)₂ and (b) Al- α -Ni(OH)₂.

with the accelerating voltage of 20 kV and the TEM image was recorded on a JEOL JEM-2100 transmission electron microscope with the accelerating voltage of 200 kV. Microanalysis was performed by inductively coupled plasma (ICP) emission spectroscopy on the Shimadzu ICPS-7500 instrument using solutions prepared by dissolving the samples in dilute HCl. The specific surface area determination and pore volume and size analysis were performed by Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods by use of a Quantachrome Autosorb-1C-VP analyzer. CHI 660B electrochemical workstation (Shanghai Chenhua Instrument Co., China) was utilized for electrochemical measurements.

3. Results and discussion

3.1. Structural and morphological characterization of H-Al- α -Ni(OH)₂

The crystallinity of as-prepared samples was examined by powder XRD measurements (Fig. 1). A series of reflections indexed to a typical hydroxide-like structure (JCPDS 48-0594) were observed for both the H-Al- α -Ni(OH)₂ and Al- α -Ni(OH)₂ sample, demonstrating that the aluminum ion was successfully doped into the lattice of α -Ni(OH)₂. Furthermore, according to the results of elemental analysis, the molar ratio of Al/Ni was calculated to be 0.46 for the H-Al- α -Ni(OH)₂ and 0.48 for the Al- α -Ni(OH)₂, in approximate accordance with the nominal molar ratio ($n_{\text{Al}}:n_{\text{Ni}} = 0.5$).

Fig. 2A displays typical SEM image of the H-Al- α -Ni(OH)₂ microspheres obtained in the presence of [BMIM]BF₄, illustrating a well dispersed and near-spherical morphology with a size of $2 \pm 0.3 \mu\text{m}$. Fig. 2B and C reveals the morphology of an individual flowerlike architecture which consists of dozens of nanoflakes ($\sim 20 \text{ nm}$ in thickness) intercrossed with each other. For comparison, the morphology of the Al- α -Ni(OH)₂ fabricated in the absence of [BMIM]BF₄ was illustrated in Fig. 2D, exhibiting uniform nanoplatelets with diameter size of $\sim 500 \text{ nm}$ and thickness of $\sim 40 \text{ nm}$. On the basis of the results above, it is concluded that [BMIM]BF₄ plays a crucial role in determining the hierarchical structure of aluminum-doped α -Ni(OH)₂ material. The microstructure of the H-Al- α -Ni(OH)₂ was further examined with HRTEM. As shown in Fig. 3A, the hierarchical flowerlike microspheres are uniform in both size and shape with particle diameter of $2 \pm 0.3 \mu\text{m}$. Furthermore, the resulting H-Al- α -Ni(OH)₂ was composed of a solid core ($\sim 1 \mu\text{m}$ in diameter) and a loose density shell ($\sim 500 \text{ nm}$ in thickness) (Fig. 3B), which can be further confirmed by the sectional image of a H-Al- α -Ni(OH)₂ microsphere (Fig. S1). The HRTEM

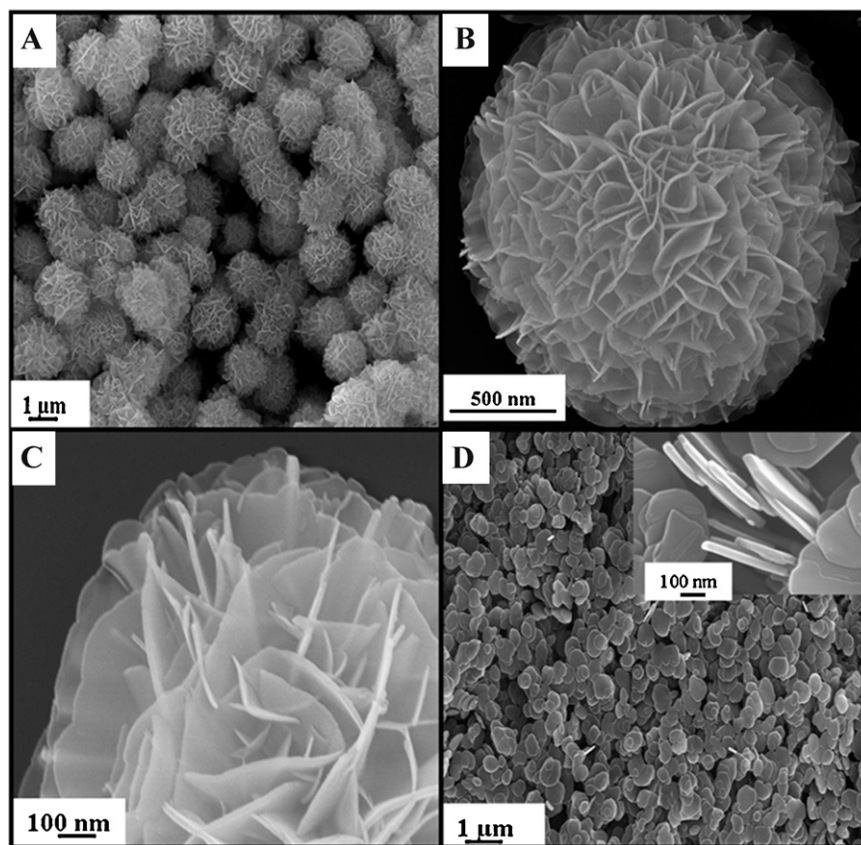


Fig. 2. SEM images of the (A) overall of the H-Al- α -Ni(OH) $_2$, (B and C) low- and high-magnification images of an individual H-Al- α -Ni(OH) $_2$ hierarchical microsphere and (D) Al- α -Ni(OH) $_2$ nanoparticles with high-magnification shown in the inset.

image (Fig. 3C) shows lattice fringes corresponding to an interplanar distance of ~ 0.26 nm that can be attributed to the (1 0 1) plane of the α -Ni(OH) $_2$ phase [21].

The surface area and pore-size distribution are two key factors for active materials in electrochemical reaction; therefore, the surface area and porosity of the as-prepared samples were investigated by nitrogen sorption measurement (Fig. 4). In all cases, typical IV isotherms with a H3-type hysteresis loop ($P/P_0 > 0.4$) are observed, indicating the presence of mesopores. For the Al- α -Ni(OH) $_2$, a mesoporous distribution of 6–10 nm was observed from the desorption branch of the nitrogen sorption isotherm by using the BJH model (Fig. 4A, inset). In the case of H-Al- α -Ni(OH) $_2$ however, abundant mesopores were obtained with pore size distribution in 2–20 nm (Fig. 4B, inset), which is commonly attributed to particle aggregation with slit-shaped pores [22]. Moreover, the BET surface area of the H-Al- α -Ni(OH) $_2$ was calculated to be 91.2 m 2 /g,

much larger than that of the Al- α -Ni(OH) $_2$ (44.5 m 2 /g). The large surface area and abundant mesopores of the hierarchical H-Al- α -Ni(OH) $_2$ would facilitate the effective exposure of active sites and the mass transportation, which will be discussed in the next section.

3.2. Formation process of the H-Al- α -Ni(OH) $_2$ in the presence of [BMIM]BF $_4$

In order to study the growth process of the H-Al- α -Ni(OH) $_2$ in the presence of [BMIM]BF $_4$, the intermediates of H-Al- α -Ni(OH) $_2$ at different reaction stages were examined by XRD (Fig. 5A). After the reaction of 1.5 h, all the reflections of the sample can be indexed to a β -Ni(OH) $_2$ phase (Fig. 5A, curve a). As the reaction time is prolonged up to 2 and 4 h, the reflection intensity attributed to β -Ni(OH) $_2$ phase decreases continuously while a new phase, α -Ni(OH) $_2$ is observed with increasing intensity (Fig. 5A, curve b and c). After

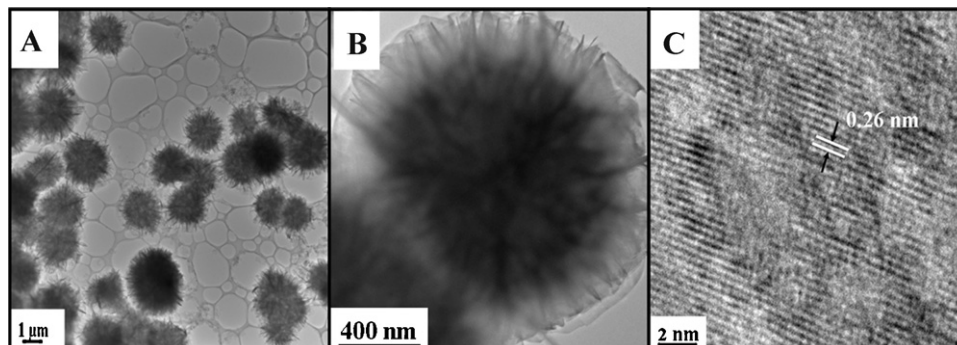


Fig. 3. (A) Low- and (B) high-magnification TEM images and (C) HRTEM image of the H-Al- α -Ni(OH) $_2$ material.

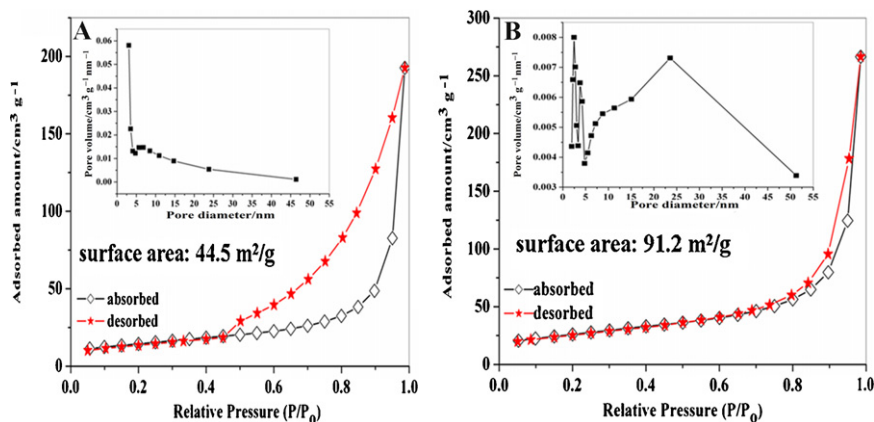


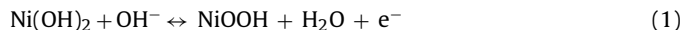
Fig. 4. Nitrogen adsorption and desorption isotherms and pore-size distribution curves (inset) of the (A) Al- α -Ni(OH) $_2$ and (B) H-Al- α -Ni(OH) $_2$.

12 h, the β -Ni(OH) $_2$ phase disappears completely and all the reflections of the product can be indexed to a typical hydroxalite-like structure (JCPDS 48-0594) (Fig. 5A, curve d). This phase transformation process was further confirmed by the elemental analysis of these samples (Table S1), from which the molar ratio of Al/Ni increased from 0 to 0.46 with the increase of reaction time, further demonstrating that the aluminum cations enter into the lattice of α -Ni(OH) $_2$. However, this phenomena of phase transformation was not observed in the growth process of Al- α -Ni(OH) $_2$ (Fig. 5B), indicating that [BMIM]BF $_4$ imposes a great influence on the formation of H-Al- α -Ni(OH) $_2$: [BMIM]BF $_4$ retards the incorporation of aluminum in the initial stage, and then Al $^{3+}$ gradually enters into the lattice of β -Ni(OH) $_2$ accompanied with a phase transformation process, resulting in the aluminum-doped α -Ni(OH) $_2$ material. In addition, the morphology evolution process of the H-Al- α -Ni(OH) $_2$ was also investigated. As shown in Fig. S2, particles with serious aggregation with diameter ranging in 30–100 nm were obtained after 1.5 h. As the reaction time increases to 2 h and 4 h, nanoflakes appear on the exterior of the spheres accompanied with size enhancement. After 12 h, hierarchical microspheres ($2 \pm 0.3 \mu\text{m}$) composed of numerous frizzy nanoflakes intercrossing with each other were obtained. Based on the results above, the presence of [BMIM]BF $_4$ plays a critical role in the structure and morphology of H-Al- α -Ni(OH) $_2$. It has been reported that the hydrogen bond-co- π - π stack come into formation between [BMIM]BF $_4$ and OH $^-$ or O $_2^{2-}$, resulting in the growth of hierarchical nanostructure [23,24]. This can be used to explain the formation mechanism of

flowerlike microspheres H-Al- α -Ni(OH) $_2$, i.e., the hydrogen bond probably formed between the hydroxyls in the surface of H-Al- α -Ni(OH) $_2$ and [BF $_4$] $^-$ anions (Fig. S3), resulting in the self-organization and epitaxial growth of the hierarchical structure.

3.3. Electrochemical properties of the H-Al- α -Ni(OH) $_2$

The electrochemical properties of the as-obtained products were investigated by cyclic voltammetry measurement in 1.0 M NaOH solution at a scan rate of 0.1 V s $^{-1}$. No redox peaks were observed for the bare electrode (Fig. 6A, curve a). The Al- α -Ni(OH) $_2$ modified electrode shows one pair of redox peaks which are not well-resolved (Fig. 6A, curve b). The redox transition involved is attributed to the presence of Ni $^{2+}$ /Ni $^{3+}$ species:



However, for the electrode modified by H-Al- α -Ni(OH) $_2$ (Fig. 6A, curve c), a pair of well-defined redox peaks were observed at 0.363 and 0.296 V. Compared with the Al- α -Ni(OH) $_2$ modified electrode, the oxidation peak potential of the H-Al- α -Ni(OH) $_2$ modified electrode moved to lower potential with a shift of 75 mV, demonstrating a higher electrochemical activity for the H-Al- α -Ni(OH) $_2$. Furthermore, the peak-to-peak separation (ΔE_p) of the H-Al- α -Ni(OH) $_2$ is 67 mV, much smaller than the reported values for α -Ni(OH) $_2$ [25,26], and the ratio between the anodic and cathodic peak current is ~ 0.91 , indicating a high reversibility for the H-Al- α -Ni(OH) $_2$ modified electrode. In addition, the effect of

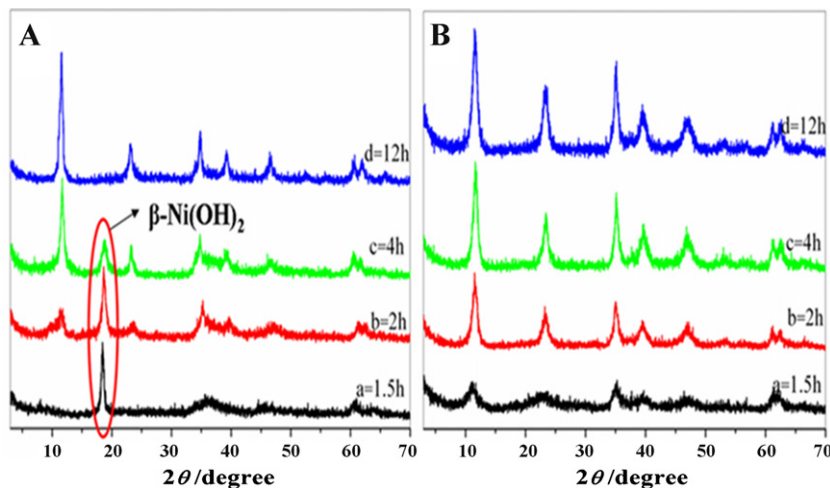


Fig. 5. XRD patterns of the (A) H-Al- α -Ni(OH) $_2$ and (B) Al- α -Ni(OH) $_2$ with different reaction time.

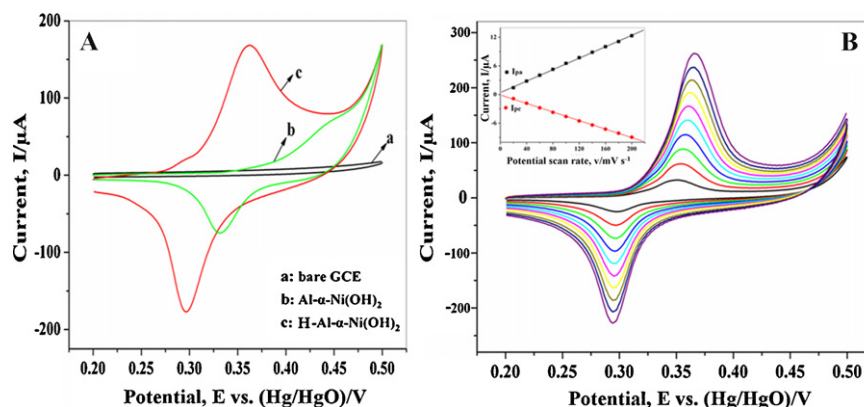


Fig. 6. (A) CVs of the bare GCE, the Al- α -Ni(OH) $_2$ modified and the H-Al- α -Ni(OH) $_2$ modified electrode in 1.0 M NaOH at a scan rate of 0.1 V s $^{-1}$; (B) CVs of the H-Al- α -Ni(OH) $_2$ modified electrode with scan rate ranging from 0.02 to 0.20 V s $^{-1}$; inset: plots of peak current vs. scan rate in 1.0 M NaOH.

scan rate on the electrochemical response of the modified electrode is displayed in Fig. 6B. Both the anodic and cathodic peak current increase linearly with the increase of the scan rate from 0.02 to 0.20 V s $^{-1}$ (Fig. 6B, inset), indicating that the redox reaction is a surface-controlled electrochemical process. Based on the Laviron theory and the plots of E_p vs. $\log v$ (Fig. S4) [27], the electron transfer rate constant (k_s) was calculated to be 3.32 s $^{-1}$, larger than that the reported value for nickel hydroxide modified electrode [28], revealing a fast electron transfer for the H-Al- α -Ni(OH) $_2$ material.

The enhanced electrochemical performance of the H-Al- α -Ni(OH) $_2$ was further confirmed by the electrochemical impedance spectroscopy measurements (EIS), which is an effective method for probing the interfacial properties of surface-modified electrode. Fig. 7 displays the typical EIS for the H-Al- α -Ni(OH) $_2$ and Al- α -Ni(OH) $_2$ modified electrode in 0.1 M KCl solution containing the redox probe Fe(CN) $_6^{4-/3-}$. The Nyquist plots consist of two sections: one is the linear part at lower frequencies representing the diffusion-limited process; the other one is a semicircle portion observed at higher frequencies corresponding to the electron-transfer-limited process. The semicircle diameter equals the electron transfer resistance (R_{et}), which controls the electron transfer kinetics of the redox probe at the electrode interface [29]. In this work, R_{et} reflects the restricted diffusion of the redox probe through the electrode interface, which relates directly to the accessibility of the underlying electrode. The R_{et} of the H-Al- α -Ni(OH) $_2$ modified electrode is much smaller than that of the Al- α -Ni(OH) $_2$ modified electrode, demonstrating a lower resistance in the H-Al- α -Ni(OH) $_2$ modified electrode and a faster electron transfer between redox probe and electrode surface. This can be attributed

to the unique structure of the H-Al- α -Ni(OH) $_2$: the mesopore distribution provides mass transportation channels and shortens the diffusion path, which facilitates the electron transfer between the probe molecule and electrode.

3.4. Electrocatalytic behavior of the H-Al- α -Ni(OH) $_2$ towards hydrazine

The electrocatalytic behavior of the H-Al- α -Ni(OH) $_2$ modified electrode towards the oxidation of hydrazine was investigated by CVs in a 1.0 M NaOH solution (Fig. 8A). For the bare GCE, no obvious current response was found in the presence of 20 μ M hydrazine (Fig. 8A, inset). For the H-Al- α -Ni(OH) $_2$ modified electrode, however, a remarkable increase in anodic peak current was observed after the addition of 20 μ M hydrazine, demonstrating that the H-Al- α -Ni(OH) $_2$ material has a strong electrocatalytic activity towards hydrazine. Furthermore, the anodic peak current enhances along with the increase of hydrazine concentration. The amperometric response of the H-Al- α -Ni(OH) $_2$ modified electrode towards hydrazine was further examined by chronoamperometry. Curve a in Fig. 8B exhibits the typical current-time curve for the H-Al- α -Ni(OH) $_2$ modified electrode with a successive addition of hydrazine. A linear relationship between anodic current and the concentration of hydrazine was obtained in the range 5.0×10^{-6} – 1.0×10^{-4} M. The calibration equation can be expressed as i (μ A) = 12.4 + 10.2*c* (μ M), with a correlation coefficient of 0.9993. The detection limit was estimated to be as low as 0.8 μ M based on $S/N=3$. The sensitivity was calculated to be 144 μ A/ μ M cm 2 , which is superior to the previously reported modified electrodes (such as C/ZnO, Au/ppy/GCE and Nano-Au/Ti [30–32]). Furthermore, the required time for steady-state response was 2.0 s, faster than those reported values [33–35]. In addition, the electrocatalytic activity of the Al- α -Ni(OH) $_2$ modified electrode was also investigated (Fig. 8B, curve b), which shows much weaker response with lower sensitivity with the same hydrazine concentration. The results above demonstrate that the H-Al- α -Ni(OH) $_2$ possesses better electrocatalytic activity than that of Al- α -Ni(OH) $_2$, owing to its specific hierarchical structure. Moreover, the electrocatalytic response of α -Ni(OH) $_2$ modified electrode towards hydrazine was also investigated as a comparison sample (Fig. S5), further confirming that the electrocatalytic activity of α -Ni(OH) $_2$ can be largely enhanced by forming Al-doped α -Ni(OH) $_2$ with hierarchical architecture.

In order to give an insight into the electrocatalytic process, the relationship between currents and the scan rate was investigated. As can be seen in Fig. 9A, the catalytic oxidation current increases with increasing scan rate and the peak current is proportional to

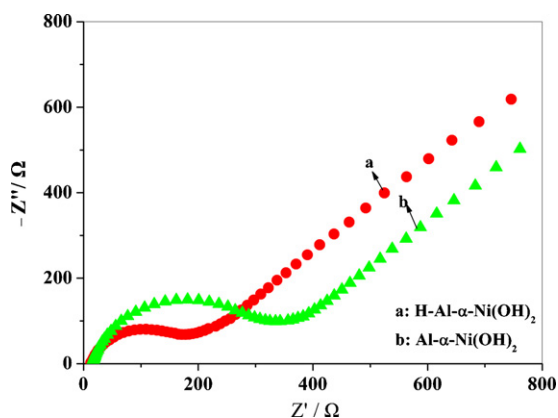


Fig. 7. Nyquist plots of the EIS for the (a) H-Al- α -Ni(OH) $_2$ and (b) Al- α -Ni(OH) $_2$ modified electrode in the presence of 5 mM Fe(CN) $_6^{4-/3-}$ in 0.1 M KCl solution.

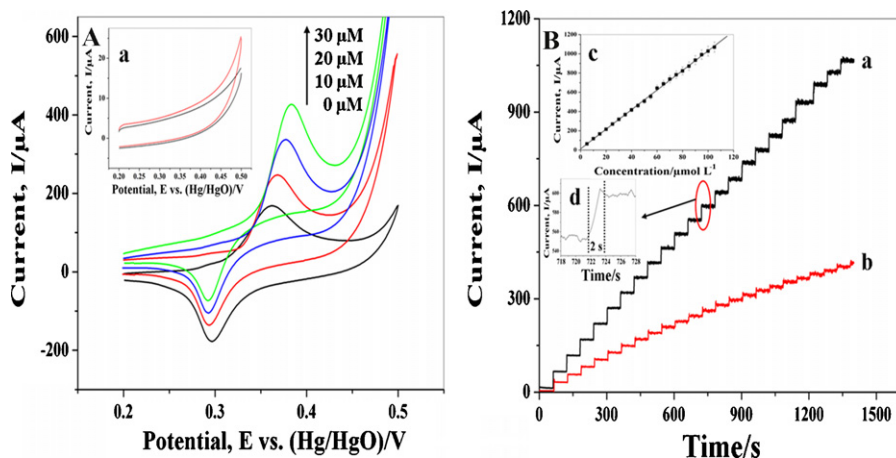


Fig. 8. (A) CVs for the H-Al- α -Ni(OH) $_2$ modified electrode with different concentration of hydrazine at a scan rate of 0.1 V s $^{-1}$ in 1.0 M NaOH solution; inset was the CVs of the bare GCE in the absence and presence of hydrazine (20 μ M); (B) typical amperometric response of the (a) H-Al- α -Ni(OH) $_2$ and (b) Al- α -Ni(OH) $_2$ modified electrode to successive addition of 5 μ M hydrazine into 1.0 M NaOH solution. Applied potential was 0.35 V. Inset: (c) the calibration curve of I - C obtained by chronoamperometry and (d) the magnification of one step.

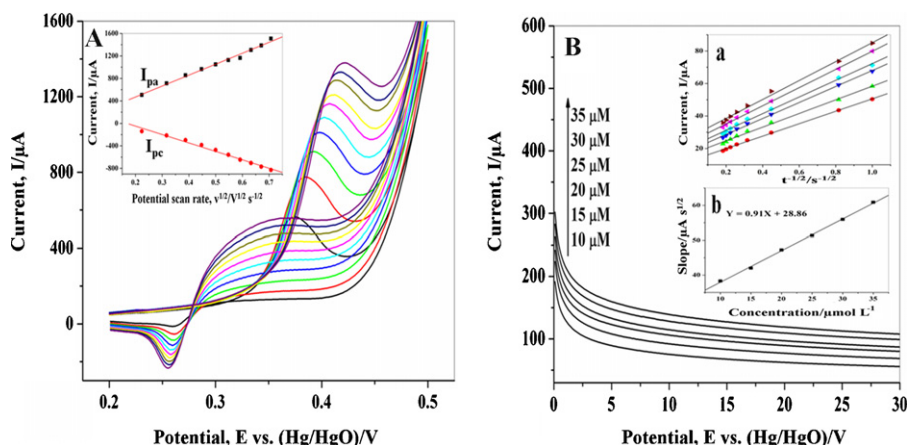


Fig. 9. (A) CVs of the H-Al- α -Ni(OH) $_2$ modified electrode in 1.0 M NaOH solution containing 60 μ M hydrazine at different scan rate; inset: plots of peak current vs. scan rate. (B) Chronoamperometric response of the modified electrode at potential step of 0.35 V for various hydrazine concentrations; inset: (a) plots of I vs. $t^{-1/2}$ and (b) plot of the slopes of the straight lines shown in (a) against the hydrazine concentration.

$v^{1/2}$, indicating a diffusion controlled electron transfer mechanism for the oxidation of hydrazine on the H-Al- α -Ni(OH) $_2$ modified electrode. Furthermore, the diffusion coefficient of hydrazine on the modified electrode was studied by chronoamperometry method (Fig. 9B). The diffusion coefficient can be obtained according to the Cottrell equation [36]:

$$I = nFAD^{1/2}C/\pi^{1/2}t^{1/2} \quad (2)$$

where D is the diffusion coefficient; C is the concentration of hydrazine; n is the number of transferred electron; F is the Faraday constant; A is the electrode area. According to Eq. (2), the plot of current (I) versus the reciprocal of the square root of time ($t^{-1/2}$) should be linear (Fig. 9B, inset a); inset b shows the slope as a function of hydrazine concentration. Based on Eq. (2), the diffusion coefficient (D) is calculated to be 2.4×10^{-4} cm 2 s $^{-1}$, much higher than those reported values for the PHQ/Pt and CoPP/GCE modified electrodes (1.4×10^{-5} cm 2 s $^{-1}$ and 4.0×10^{-5} cm 2 s $^{-1}$, respectively) [37,38], revealing a fast diffusion rate for the hydrazine on the H-Al- α -Ni(OH) $_2$ modified electrode. The results above demonstrate that the H-Al- α -Ni(OH) $_2$ displays a high electrocatalytic activity towards hydrazine, which is related to the following reasons: the large surface area of the H-Al- α -Ni(OH) $_2$ provides a large number of superficial electroactive sites; furthermore, the abundant

mesopores in the structure offer effective diffusion channels for mass transportation between active sites and underlying electrode.

Furthermore, the stability and reproducibility of the modified electrode were also investigated. Ten successive amperometric measurements of 10 μ M hydrazine on the same modified electrode yielded a reproducible current with the relative standard deviation (RSD) of 2.9%, demonstrating that the electrode can be used repeatedly for the detection of hydrazine. The stability of the modified electrode was also checked in 10 μ M hydrazine by using the same electrode over a period of one week, and the electrochemical response maintained 93.2% of its initial response. In addition, to evaluate the applicability of the modified electrode, the recovery of hydrazine was determined by standard addition method for three samples. The dates given in Table S2 display satisfactory results with the recovery in the range 97.2–103.5%. The results indicate that the H-Al- α -Ni(OH) $_2$ modified electrode can be effectively used as electrochemical sensor for the determination of hydrazine.

4. Conclusions

In summary, three-dimensional hierarchical Al-doped α -Ni(OH) $_2$ microspheres were successfully synthesized via a facile hydrothermal method with the assistance of ionic liquid

([BMIM]BF₄). The flowerlike H-Al- α -Ni(OH)₂ microspheres consist of a solid core and a loose shell composed of intercrossed nanocrystals. Furthermore, the H-Al- α -Ni(OH)₂ modified electrode displays improved electron transfer kinetics and excellent electrocatalytic activity towards hydrazine. This can be ascribed to the specific 3D architecture with enhanced surface area and suitable mesopore distribution, providing sufficient active sites and diffusion channels for the reactant and thus facilitating the mass/electron transfer. It is expected that the approach in this work can be used to synthesize other hierarchical materials with enhanced electrochemical behavior for the fabrication of electrochemical sensors and electronic devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2012.07.010>.

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