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In Situ Construction of Ag/Ni(OH)₂ Composite Electrode by Combining Electroless Deposition Technology with Electrodeposition

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Abstract: The Ag/Ni(OH)₂ composite electrode has been designed and in situ constructed on a copper substrate by combining electroless deposition technology with electrodeposition. The products can be directly used as a high performance binder free electrode. The synergistic effect between the Ag nanocubes (AgNCs) as backbones and the deposited Ni(OH)₂ as the shell can significantly improve the electrochemical properties of the composite electrode. Moreover, this in situ growth strategy forms a strong bonding force of active materials to the substrate, which can improve the cycling performance and lower the equivalent series resistance. The Ag/Ni(OH)₂ composite electrode exhibits enhanced electrochemical properties with a high specific capacitance of 3.704 F cm⁻², coulombic efficiency of 88.3% and long-term cyclic stability.

Keywords: electroless deposition; electrodeposition; electrode material; nanocomposites

1. Introduction

In order to satisfy the increasing energy demands, much effort has been devoted to discovering efficient energy storage/conversion systems and designing various power source devices, such as the supercapacitor and lithium-ion battery [1]. Electrode materials have gained extensive attention as being the most critical part of energy storage devices and considerable efforts have been made to design various types of electrode materials [2,3]. To date, transition metal oxide/hydroxide including Ni(OH)₂/NiO, Co₃O₄ and MnO₂ have become a research hotspot due to their efficient Faradaic reaction, low cost, and environmentally friendly characteristics [4–8]. Specifically, Ni(OH)₂ and its composites have attracted extraordinary research interests because they have a high chemical stability, natural abundance and high theoretical specific capacity [9,10]. Various synthetic paths, such as the solvothermal process, electrochemical deposition, electrospinning technique and microwave-assisted methods have been explored in tailoring Ni(OH)₂ micro/nano-architectures to enhance their electrochemical activity [11–13].

Although Ni(OH)₂ has been reported in previous literature as having good electrochemical properties, the relatively poor electrical conductivity seriously limits its practical application. To solve this problem, the research mainly focuses on the design of various binary or multiple composites by adding proper components to give full play to the synergistic effect of each component, such as NiO/Ni(OH)₂ [14], Ag@Ni(OH)₂/graphene [15], Ni(OH)₂/C/Cu [16]. The addition of conductive materials or elements significantly improves the overall performance. Typically, graphene, Ag, Au and Cu can be combined with metal oxides/hydroxides in order to achieve a high performance owing to their high electrical conductivity [17–20]. In particular, the Ag nanostructures have been extensively studied owing to its excellent electronic conductivity and electrochemical properties.

For example, when Unalan et al. presented the coaxial growth of silver nanowires as the core and $\text{Ni}(\text{OH})_2$ nanoflakes as the shell, the electrodes achieved specific capacitance of 1162.5 F g^{-1} with a current density of 3 A g^{-1} [21]. Yu et al. synthesized Ni-Co double hydroxide nanosheets coated on Ag nanowires through the electrochemical deposition method, which exhibited the areal capacitance of $1133.3 \text{ mF cm}^{-2}$ at 1 mA cm^{-2} [22]. In addition, Narciso et al. prepared 3D aluminum foam through a replication process. The Pt/aluminum foam electrodes then obtained by electrodeposition had obvious electrocatalytic behavior [23]. Metal foams are used as substrates based on their high surface area and conductivity. Therefore, it is reasonable to believe that the participation of Ag nanostructures enhances the conductivity and increases the specific capacity to some extent.

Herein, the $\text{Ag}/\text{Ni}(\text{OH})_2$ composite electrode has been designed and in situ constructed on a copper foam substrate through a simple two-step process. Ag nanocubes (AgNCs) were formed initially on copper foam by a displacement reaction between AgNO_3 and the copper foam (electroless deposition), and then $\text{Ni}(\text{OH})_2$ layers were constantly loaded onto the AgNCs surface by electrodeposition. The fabricated $\text{Ag}/\text{Ni}(\text{OH})_2$ samples were directly used as electrodes, avoiding the process of making electrodes by mixing them with a binder and then pressing them onto the substrates. This possessed a high specific capacitance, low R_{ESR} , higher coulombic efficiency and long-term cyclic stability. The improved electrochemical performance was attributed to the in situ growth mode, which was bound to produce strong adhesion between the electrode materials and substrates, ensuring the full utilization of the active electrode materials. At the same time, the effective participation of AgNCs by the direct growth mode can improve the conductivity, providing a large surface area for the $\text{Ni}(\text{OH})_2$ layer deposition, and directly participating in the Faradaic reaction as an active component.

2. Materials and Methods

2.1. Materials

The copper foam substrate was carefully cleaned with acetone, ethanol and deionized water before use. Silver nitrate (AgNO_3 , 99.8%), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%) and NaOH were used in this report.

2.2. Synthesis of $\text{Ag}/\text{Ni}(\text{OH})_2$ Composite Electrode

Firstly, the pre-cleaned copper foam was suspended and immersed in a AgNO_3 aqueous solution (0.1 M) and the growth of Ag nanostructures on copper foam was allowed for 10 min. Next, the copper foam with the gray silver precipitates was rinsed with ethanol and deionized water. After that, a freshly prepared $\text{Ni}(\text{NO}_3)_2$ solution (0.05 M) was deposited $\text{Ni}(\text{OH})_2$ on the Ag core, where the Ag/copper foam worked as an electrode, a platinum foil acted as a counter electrode, and saturated calomel electrode (SCE) worked as a reference electrode. The potentiostatic deposition was performed at about 300 s at -1.0 V vs. SCE . Finally, the prepared composite electrode was rinsed with ethanol and deionized water.

2.3. Materials Characterization

The results were collected by XRD measurements (Shimadzu Co., Ltd, Kyoto, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and FE-SEM (FE-SEM JEOL JSM-7610F, Tokyo, Japan). XPS measurements were performed by an ESCALAB 250Xi (Thermo Fisher Scientific Co., Ltd, Waltham, MA, USA) with $\text{Al K}\alpha$ as the X-ray source.

2.4. Electrochemical Measurements

Cyclic voltammetry (CV) and the galvanostatic charge-discharge test (GCD) were carried out with a CHI 660E electrochemical workstation. The obtained $\text{Ag}/\text{Ni}(\text{OH})_2$ composite sample was used as an working electrode, platinum foil and Hg/HgO as a counter electrode and reference electrode,

respectively, and electrolyte was the 5 M NaOH solution. The cycling performance was Neware testing system.

3. Results

The Ag/Ni(OH)₂ composite is in situ constructed through the combination of the displacement reaction followed by an electrodeposition process as illustrated in Scheme 1. Firstly, AgNCs affixed to a copper foam substrate are fabricated by immersing copper foam into the AgNO₃ solution based on the displacement equation: $\text{Cu}_{(s)} + 2 \text{Ag}^+_{(aq)} \rightarrow 2 \text{Ag}_{(s)} + \text{Cu}^{2+}_{(aq)}$ [24], which is an electroless deposition technology. Copper foam acts as both a reducing agent and substrate. After that, the AgNCs/copper foam is used as the working electrode for electrochemical deposition through the three-electrode system in Ni(NO₃)₂ aqueous solution. The OH[−] generated by the dissolution of NH₃, produced by reduction of NO₃[−] near the electrode surface, which were captured by Ni²⁺ on the surface of the Ag electrode and Ni(OH)₂ layer, formed. Therefore, the AgNCs as cores dominated the final morphology of the composite, and the Ag/Ni(OH)₂ composite was finally obtained.

Scheme 1. The illustration of the construction procedure of Ag/Ni(OH)₂ electrode on copper foam.

Figure 1 displays FE-SEM images of samples obtained through combining the electroless deposition technology with electrodeposition. Densely distributed deposits are covered on the copper foam substrate after immersing the copper substrate into AgNO₃ solution (0.1 M) at room temperature without stirring, as shown in Figure 1a. An automatic displacement reaction occurs (electroless deposition) between the AgNO₃ solution and copper foam substrate. The high magnification image (Figure 1b) shows that the AgNCs with an average length of 180–250 nm are uniformly grown on the copper substrate, and the AgNCs surface is smooth (inset in Figure 1b). Subsequent electrochemical deposition allows the uniform Ni(OH)₂ nanostructures to coat the AgNCs/copper foam substrate with a high density (Figure 1c). AgNCs are surrounded tightly by large numbers of Ni(OH)₂ nanoparticles when the deposition takes only 30 s, while the original shape of the AgNCs is clearly visible. The FE-SEM image of the Ag/Ni(OH)₂ electrode and the corresponding EDS element mapping images recorded in Figure S1 reveal that the co-existence of different elements including Cu, Ag, Ni and O. The amount of Ni(OH)₂ nanoparticles deposited onto the AgNC surface continuously increases with time. When the deposition time reaches 300 s, Ag/Ni(OH)₂ nanospheres are obtained with a diameter of about 350–560 nm and they are packed closely with each other. From the enlarged image in the inset of Figure 1d, the nanospheres are actually made up of a large number of nanoparticles about 10 nm in diameter, and the smaller nanoparticles interconnect with each other to form a worm-like structure.

The low-magnification FE-SEM image of Ag/Ni(OH)₂ composite and EDS mapping images reveal the presence of uniformly distributed Cu, Ag, Ni and O elements (Figure 2a). The EDS spectrum in Figure 2b also confirms the presence of Ni, Ag and O in fabricated copper foam substrates.

Figure 1. FE-SEM images: (a,b) AgNCs and (c,d) Ag/Ni(OH)₂ composite with 30 s and 300 s the deposition time of Ni(OH)₂, respectively.

Figure 2. Ag/Ni(OH)₂ composite: (a) FE-SEM images and the corresponding EDS element mapping images of Cu, Ag, O and Ni elements; (b) EDS spectrum.

Figure 3a presents the XRD patterns of AgNCs and Ag/Ni(OH)₂ composite. Three characteristic peaks labeled with asterisks belong to the copper substrate (JCPDS card No. 01–1241). The AgNCs demonstrate crystalline peaks at about 38.12°, 44.28° and 77.48°, corresponding to (111), (200) and (311) crystalline plane of face-centered cubic (fcc) Ag (JCPDS card No. 04–0783), respectively. The Ag/Ni(OH)₂ composite exhibits (001), (100), (101), (110) and (111) crystalline peak at 19.00°, 33.52°, 38.64°, 59.02°, 62.66°, respectively, indicating the β phase of the Ni(OH)₂ (JCPDS card No. 14–0117). The composition and electron structure of the composite was further performed by XPS. The survey spectrum (Figure 3b) confirms the presence of C, O, Ni and Ag signals, consistent with the EDS data.

The peaks of Ag 3d_{5/2} and Ag 3d_{3/2} located at 368.65 eV and 374.70 eV are observed in Figure 3c. The main peaks at 856.1 and 873.8 eV in Figure 3d are ascribed to the binding energies of Ni 2p_{3/2} and Ni 2p_{1/2}, respectively. So the spin energy separation is 17.7 eV [21]. The Ni 2p_{3/2} peak at 861.6 eV and Ni 2p_{1/2} peak at 880 eV are two satellite peaks. The O 1s spectrum (Figure 3e) can be deconvoluted into two peaks, one located at 531.2 eV corresponding to OH- group and the other is ascribed to adsorbed water at 532.8 eV [22].

Figure 3. XRD patterns (a) Ag and Ag/Ni(OH)₂. XPS of the Ag/Ni(OH)₂: survey scan (b), Ag 3d (c), Ni 2p (d) and O 1s (e) spectra.

To estimate the electrochemical properties of the Ag/Ni(OH)₂ electrode, CV and GCD tests were performed. Figure 4a records the CV curves of Ag/Ni(OH)₂, Ni(OH)₂, Ag electrode and copper substrate at the scan rate of 10 mV s⁻¹ in 5 M NaOH aqueous solution. Among all the samples, the Ag/Ni(OH)₂ electrode has the largest enclosure area, revealing its highest specific capacity according to the equation [25]. Figure 4b shows the GCD curves of Ag/Ni(OH)₂, Ni(OH)₂ and Ag electrode at 2 mA cm⁻². Ag/Ni(OH)₂ electrode shows the longest discharge time, which indicates that it has the highest pseudocapacitance.

Figure 4. (a) CV curves of Ag/Ni(OH)₂, Ni(OH)₂, Ag electrode and copper foam substrate at a scan rate of 10 mV s⁻¹; (b) a comparison of GCD curves of the three electrode.

Figure 5a records the representative CV curves of Ag/Ni(OH)₂ electrode at potential window (0–0.6 V) at different scan rates ranged from 2 to 20 mV s⁻¹. A pair of strong redox peaks is visible

in each CV curve, which indicates a strong pseudocapacitive behavior of the hybrid material by the following reversible Faradaic reactions:

Figure 5. Electrochemical performance of the Ag/Ni(OH)₂ composite electrode: (a) The CV curves, (b) GCD curves, (c) plots of specific capacitance versus current density, (d) cycling performance, inset is voltage drops during the GCD tests of the Ag/Ni(OH)₂ composite electrode.

In addition, a pair of weak redox peak of oxidation (0.3 V) and reduction peaks (0.1 V) can be attributed to the redox couple of Ag/Ag⁺ [21,26–28]. It is noteworthy that the current response increases with increasing scan rates, and the potential of oxidation peak and reduction peak moves to more positive and negative directions, respectively, and the specific capacity decreases accordingly. This ascribes to the fact that many internal electroactive sites of the electrode are not sufficiently involved in Faradaic reactions at relatively high scan rates due to the limitation of ionic/electronic diffusion. Typical GCD tests were further performed at potential from 0 to 0.5 V at different current densities of 2–20 mA cm⁻² (Figure 5b). Corresponding to current density of 2, 4, 8, 12, 16, 20 mA cm⁻², the specific capacitances are about 3.692, 3.258, 2.632, 2.376, 2.186 and 2.024 F cm⁻², respectively (Figure 5c). The areal capacitance of Ag/Ni(OH)₂ electrode are derived from the equation in Supplementary Materials [29,30]. When the current density is 2 mA cm⁻², the coulombic efficiency reaches 88.3%, which illustrates the great redox reversibility of the pseudocapacitive material. Furthermore, the tiny plateaus at about 0.17 V in GCD curve should attribute to the redox pair Ag/Ag⁺, consistent with the CV measurements and previous reports [26,28]. Moreover, the electrochemical properties of the Ni(OH)₂ and Ag electrode were also performed for comparison. The specific capacitances of Ni(OH)₂ and Ag electrodes achieved at various current density are also recorded in Figure S2 and Table S1 in the Supplementary Materials. The capacitance retention curve of the Ag/Ni(OH)₂ electrode are displayed in Figure 5d. It maintains 88.4% and 83.7% of its original specific capacity after 1000 and 3000 cycles, respectively. No obvious structure deformation is observed (Figure S3). The good cyclic

properties are beneficial from the effective bonding between the active material and copper foam. Furthermore, as seen from the inset of Figure 5d, the average equivalent series resistance (R_{ESR}) is $0.952 \Omega \text{ cm}^{-2}$ based on the equation in the Supplementary Materials [30]. The low R_{ESR} is attributed to the direct growth of AgNCs on copper foam substrate, which ensures a close bonding between them. Meanwhile, Ag nanostructures with good conductivity act as both collector and effective constituent of the active material.

The enhanced electrochemical properties of the Ag/Ni(OH)₂ electrodes are mainly attributed to the following reasons: (1) AgNCs are grown directly on the copper substrate, and such a strong adhesion avoids the utilization of conductive agent and binder to make electrode, which reduces the contact resistance. At the same time, the AgNCs act as the bridge between the Ni(OH)₂ layer and copper substrate, favorable for electron transmission. Furthermore, AgNCs as an active component improve the conductivity of the active materials [25]; (2) the Ag-decorated copper foam substrate provides a much higher surface area for subsequent electrodeposition of Ni(OH)₂, which keeps the active materials from conventional aggregation [31]; (3) the electrodeposition of smaller Ni(OH)₂ nanoparticles interconnected with each other on the surface of the AgNCs generates abundant space, making the electrolyte fully accessible to the internal area of the electrode. This facilitates the transmission of the electrolyte, and a full contact between the electrodes and electrolytes is ensured [25,31].

4. Conclusions

In summary, we have developed a cost-effective approach to fabricate Ag/Ni(OH)₂ composite electrode on copper foam substrate through the combination of electroless deposition technology with electrodeposition. Copper foam acts as both reducing agent and substrate. The Ag/Ni(OH)₂ electrode shows a high specific capacitance value, low R_{ESR} , good coulombic efficiency and cycling performances. The good electrochemical performance should be related to the effective utilization of Ag by electroless deposition technology, which increases the electrical conductivity and increase the specific surface area of the active material. Moreover, this convenient method can be extended to design other binary or multiple composites with Ag as core.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/9/8/826/s1>, Figure S1: FE-SEM image of the Ag/Ni(OH)₂ electrode (the deposition time of Ni(OH)₂ is 30 s) and the corresponding EDS element mapping images of Cu, Ag, Ni and O elements. Figure S2: The plots of specific capacitance versus current density of the Ni(OH)₂ (a) and Ag electrode (b), respectively. Insets are the corresponding GCD test curve. Figure S3: FE-SEM images of the Ag/Ni(OH)₂ composite at different magnifications after 3000 cycles. Table S1: The specific capacitance versus current density of the three electrodes. Formulas for calculating specific capacitance and average equivalent series resistance.

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