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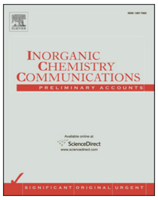

Short communication

2D Nanoflakes of metal-polyphenolic coordination assembly for high-performance supercapacitor

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ABSTRACT

A novel metal-polyphenol assembly is successfully prepared through the coordination of Ni^{2+} and a natural polyphenol ellagic acid (EA), leading to a stable micro-sized particle composed of two-dimensional (2D) nanoflakes. As electrode materials for supercapacitors, the Ni-EA coordination materials display a high capacitance of 1050 F g^{-1} at the current density of 0.5 A g^{-1}. Besides, an asymmetric supercapacitor (ASC) is assembled by using the Ni-EA nanoflakes as the positive electrode and activated carbon (AC) as the negative electrode. The ASC presents a high energy density of 31.22 Wh kg^{-1} at a power density of 800 W kg^{-1} and superior cycling stability with 91.8% specific capacitance retention over 4000 cycles at a high current density of 10 A g^{-1}. These results demonstrate the Ni-EA nanoflakes are promising electrode materials for high-performance supercapacitor.

Supercapacitors, as a kind of renewable energy equipment, have attracted great attentions due to their super high specific capacitance, excellent rate performance, better cycle properties and high energy density [1–3]. In general, supercapacitors are consisted of electrical double layer capacitors (EDLCs) and pseudocapacitors on the basis of different mechanism of energy storage. The pseudocapacitors present higher specific capacitance compared with EDLCs, therefore, the study of pseudocapacitance materials is an important topic for materials community [4,5]. Key research for supercapacitors is mainly focused on developing electrode materials with high performance. The energy storage ability of electrode materials is largely determined by their intrinsic nature and structure. A series of electrode materials have been reported and demonstrated excellent electrochemical performance, including transition metal oxides, metal hydroxides, metal sulfides and carbon materials [6–9].

Coordination polymers or metal-organic frameworks (MOFs) are recently emerged as another type of important electrodes for supercapacitors [10]. In fact, either coordination compounds or their derived materials (e.g. transition metal oxides or sulfides, carbon), have been successfully used as electrode materials for supercapacitors [11–13]. For example, cobalt-based layered MOF (Co-LMOF) [14] or nickel-based MOF ($Ni_3(btc)_2{\cdot}12H_2O$) [15] have been employed as electrode materials with high specific capacitance of 2474 and 726 F g^{-1}, respectively. Recent development of the layer structured coordination compounds opens a new pathway in electrochemical fields. For example, [Cu(hmt)(tfbdc)(H_2O)] [16], $[Ni_3(OH)_2(C_8H_4O_4)_2(H_2O)_4]{\cdot}2H_2O$ [17] and Co-based coordination polymer (CQU-Chen-OA-Co-1-1) [18] have been reported and used as electrode materials in high-performance supercapacitors. The layer structure from these 2D compounds could offer enough active sites for redox reaction and provide a quick track in the process of accelerating the Faraday reaction during the insertion and extraction of electrolyte ions.

In the past decade, metal-polyphenol assembly materials have emerged as an important type of coordination compounds. A series of natural polyphenol, such as tannic acid (TA) and ellagic acid (EA), have been employed to coordinate with a variety of transition metal ions including Ti^{+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+} and Ag^{+}. The obtained complex has been successfully used in a variety of applications, including nanofiltration membranes, initiator, drug delivery, separations, bioimaging and catalysis [19]. In addition, polyphenol as a carbon precursor has been proved to transform into carbon materials. For example, mechanochemical assembly of TA-metal has been converted into ordered mesoporous carbon [20]. Here, a novel assembled compound is

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fabricated based on the nickel-ellagic acid (Ni-EA) coordination. The obtained Ni-EA coordination materials are consisted of layered structures through stack of 2D nanoflakes. When used as an electrode material for supercapacitors, they present a high specific capacitance of 1050 F g^{-1}. Moreover, an asymmetric supercapacitor was assembled based on Ni-EA nanoflakes as the positive electrode and activated carbon (AC) as the negative electrode. The ASC delivered a high specific capacitance, energy density, power density and excellent cycling stability.

In principle, the inherent catechol sites existing in each EA molecular (molecular structure in Fig. S1) can coordinate with different metal ions [21]. In this work, Ni-EA complex is successfully prepared *via* a facile solution precipitation method. As shown in Scheme 1, *N*-methyl-2-pyrrolidone (NMP) solution containing nickel acetate tetrahydrate (NAT) and EA is stirring for 30 min. After standing for 7 days at ambient temperature, brown powder is obtained and collected. FT-IR spectra in Fig. 1a are monitored to track the structure evolution. A characteristic peak of EA centered at 3564 cm^{-1} is observed and ascribed to stretching vibration of phenolic hydroxyl group. After forming complex, O—H vibration peak is vanished due to the consumption between EA and Ni^{2+} coordination. The coordination is further testified *via* XRD patterns (Fig. 1b). Clearly, the strong characteristic peaks at 13.1°and 28.3°are coming from the defined crystal structures of NAT and EA, respectively [21–22]. However, both peaks disappear for Ni-EA, indicating the successful coordination between Ni^{2+} and EA as well as the amorphous phase of Ni-EA compound. The XPS spectra verify the elements composition and the chemical state of Ni-EA. As shown in Fig. 1c, XPS survey spectrum of Ni-EA reveals the co-existence of C, N, O and Ni elements. The high resolution C1s XPS spectrum (Fig. S2a) presents four characteristic peaks. The 284.6 eV binding energy obtained by XPS analysis is a standard result for specimens charging using C 1s as the reference. The 288.6 eV binding energy is attributed to the carboxylate carbon in O═C—OH and the 287.3 eV binding energy comes from the carboxylate carbon in C═O. The peak in 285.9 eV is associated with the aryl carbon from the benzene ring peck. The N1 s XPS spectrum (Fig. S2b) can be divided into two peaks, where peaks at 399.8 and 399.3 eV can be ascribed to the C—N bonds. The O1s XPS spectrum (Fig. S2c) can be divided into two peaks, where the peak at 531.5 eV is nickel—oxygen bonds, and the component at 533.3 eV may be ascribed to the O═C. The high-resolution XPS of Ni 2p is shown in Fig. 1d. Two peaks located at 873 and 855.4 eV belong to Ni 2p1/2 and Ni 2p3/2, respectively, which confirms the existence of Ni^{2+} in Ni-EA. [19,23] And the N element in Ni-EA is believed coming from the coordination of solvent NMP and Ni^{2+} [21]. Hence, a coordinated structure of Ni-EA is proposed and depicted in the structural model of Fig. S3: EA building units are linked by Ni ions to form a robust framework with solvent NMP involved in coordination with Ni^{2+}.

The morphology and microstructure of Ni-EA are recorded *via* FESEM (field emission scanning electron microscopy) and TEM (transmission electron microscopy). SEM images in Fig. 2a reveal that Ni-EA consists of numerous 2D nanoflakes. A high magnification SEM image (Fig. S4) shows that each nanoflake with 40 nm thickness is intertwined and stacked with each other to form network structure. TEM images in Fig. 2b further demonstrate the distinct stack of layered structures in Ni-EA. Energy-dispersive X-ray spectroscopy (EDS) mapping analysis of Ni-EA compound is shown in Fig. 2c. The results reveal that C, O, N and Ni are homogeneously distributed among Ni-EA and fully demonstrate the successful coordination between Ni^{2+} and EA.

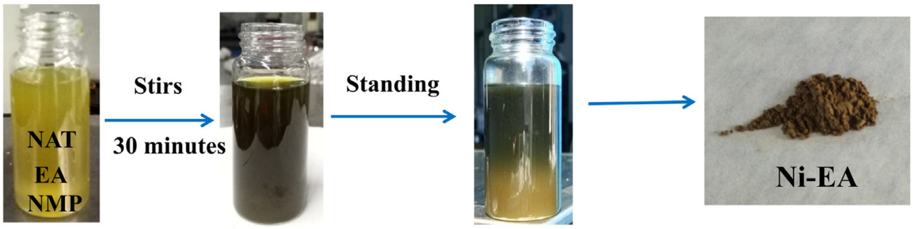
The electrochemical performance of Ni-EA for supercapacitors is evaluated *via* cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) in a three-electrode system. Fig. 3a shows the CV curves of Ni-EA electrode within a potential window of 0–0.6 V at different scan rates from 5 to 40 mV s^{-1}. Clearly, each CV curve contains a pair of strong redox peaks, which manifests the Faradaic pseudocapacitance behavior originated from the surface Ni^{2+} redox reactions. The redox reaction process is believed to be represented *via* the following Eqs. (5) and (6):

$$Ni^{2+} + OH^{-} \leftrightarrow Ni(OH)^{+} \tag{5}$$

$$Ni(OH)^{+} \leftrightarrow Ni(OH)^{2+} + e^{-} \tag{6}$$

During electrochemical performance measurements, the OH^{-} first combines with Ni ions on the surface of the electrode material. The anodic peak then appears due to the oxidation of Ni(II) to Ni(III) and the cathodic peak from the reverse process, which are similar to the previous reports of nickel compound electrode materials, such as $Ni_3(btc)_2{\cdot}12H_2O$ [15] and $Ni(4,4\text{-bpy})(tfbdc)(H_2O)_2$ [24]. Meanwhile, the position of redox peaks is shifted with the increase of scan rate, which might be related to the electrode internal resistance [14]. Fig. 3b depicts the charge–discharge curves of Ni-EA electrode within the potential window of 0 to 0.45 V at different current densities. A smooth slope is clearly seen in each discharge curve, revealing the pseudocapacitive behavior of Ni-EA electrode, which is consistent with the CV results. As shown in Fig. 3c, the calculated specific capacitances of Ni-EA electrode for the first discharge are 1050, 962.5, 835.6, 782.5 and 713.9 and 550 F g^{-1} at different discharge current densities of 0.5, 1, 2, 3, 5 and 10 A g^{-1}, respectively. When the current density increases 20 times (from 0.5 A g^{-1} to 10 A g^{-1}), the capacitance retention of Ni-EA is 52.4%. The diminished specific capacitance might be ascribed to the decreasing interaction between electrode and electrolyte ions with the increase of current density [14]. In order to explore the effect of pure foam nickel, the electrochemical performance of the bare nickel foam is tested using same method. As shown in Fig. S5a, Ni-EA exhibits a larger integral area than that of the bare nickel foam electrodes, indicating a lower specific capacitance of the bare nickel foam. Fig. S5b compares the GCD curves of Ni-EA and bare nickel foam electrodes at the current density of 0.5 A g^{-1}. Obviously, the time of charge-discharge of the bare nickel foam is much less than that of Ni-EA, illustrating a lower specific capacitance of bare nickel foam. Fig. S5c shows the calculated specific capacitances of pure nickel foam are near-zero, which fully illustrates the bare nickel foam has no effect on electrochemical properties. The cycle reliability of Ni-EA is executed *via* charge-discharge cycles measurement at a current density of 10 A g^{-1}. The value of capacitance retention still retains 89% after 1000 cycles (Fig. 3d). Compared with the reported Ni-based/MOF-based electrode materials (data in Table S1) [25–29], the reported Ni-EA electrode performs remarkable electrochemical property and represents a promising electrode material.

Electrochemical impedance spectroscopy (EIS) is tested in the frequency from 100 kHz to 0.01 Hz to further examine the electrochemical property of Ni-EA compound. The Nyquist plots of Ni-EA before and



Scheme 1. Synthesis process of Ni-EA compounds.