

Natural Rosin-based Phosphate Diester Surfactant Assisted One-step Synthesis of 3D Flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ Composite Nano-microspheres

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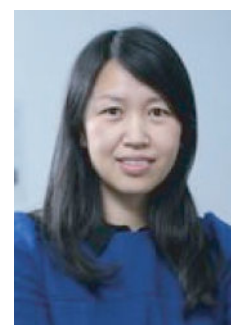
Abstract: Self-assembled uniform 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres with hollow interiors were successfully synthesized via a facile aqueous-ethanol mixed solvothermal method, using nickel sulfate as a precursor, urea as a precipitant, and dehydroabietic based phosphate diester sodium (DDPDS) as a surfactant. The prepared 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres were tested as supercapacitors in a two-electrode cell with 6 mol/L KOH electrolyte. In addition, the influence of DDPDS concentration on the morphology and size of 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres was studied at 180 °C. X-ray diffraction (XRD), scanning electron microscopy (SEM), BET (Brunauer, Emmett and Teller) techniques, and energy dispersive X-ray (EDS) were used to characterize the structure, morphology, and size of the as-prepared samples. Moreover, a possible formation mechanism of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres was proposed based on the effects of DDPDS concentration and reaction time. The surfactant micelles were used as soft templates to induce the self-assembly of nanosheets. The crystallinity of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres improved with the increase of DDPDS concentration, and the morphology and size of synthetic nano-microspheres could be controlled.

Keywords: hydrothermal synthesis; rosin; phosphate diester surfactant; nickel hydroxide composites; nanomaterial



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1 Introduction

Nickel hydroxide ($\text{Ni}(\text{OH})_2$) is an important transition metal hydroxide with unique phase architectures. It has many advantages when used as an electrode material in nickel-based rechargeable batteries and supercapacitors, including environmental friendliness, low cost, low toxicity, high chemical/thermal stability, and excellent electrochemical redox activity^[1-5]. It is well-known that the performance of oxide/hydroxide electrodes is determined by their specific surface area, which greatly depends on the size and morphology of the electrode material^[6-7]. Previous reports have demonstrated that the introduction of nano-structure into micro-sized spherical nickel hydroxide/oxide significantly improved its chemical and physical properties^[8]. Therefore, the morphology-controlled synthesis of $\text{Ni}(\text{OH})_2$ hierarchical nano-microspheres is of great importance for energy storage. To date, a large number of synthetic strategies have been developed to construct hierarchical $\text{Ni}(\text{OH})_2$ nano-microspheres with tunable morphology^[9-12].

Nickel hydroxide has a hexagonal layered structure, and $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ exhibits super-stability, which has led to its widespread use as a material in rechargeable batteries due to its outstanding chemical and thermal stability^[13]. Besides its crystal structure, the morphology of $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ also significantly influences its electrochemical properties, suggesting that the development of a controlled synthesis to tune the morphological features is important^[14-15]. Among the known $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ structures, hollow structured materials with low densities and high surface area have attracted significant attention due to their numerous potential applications^[16-17]. Moreover, $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres with high power density, high energy, low toxicity, and excellent electrochemical redox activity, have been investigated as a potential electrode material for application in electrochemical supercapacitors^[18-21]. To date, many attempts have been made to achieve the surfactant assisted synthesis of nano- and micro-structured hollow $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$. Cetyltrimethyl

ammonium bromide (CTAB) and sodium dodecyl benzene sulfonate (SDBS) have been used as surfactants to modify the crystallization behavior of $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$, and its performance was significantly improved with surfactant addition^[22-23].

Rosin and its derivatives are widely applied as eco-friendly and renewable materials in many fields^[24-25]. Natural and renewable rosin-based surfactants can be synthesized from raw rosin, which is eco-friendly, biodegradable, and biocompatible because of its three ring structure^[26-29]. Natural rosin-based surfactants have a higher affinity for synthetic inorganic compounds because of the rigid ring structure of rosin. In our previous studies, we prepared $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres assisted by rosin-based surfactants, and found that the morphology and size of the $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres could be easily controlled^[30-32].

Herein, we designed a facile mixed solvothermal route for the successful preparation of 3D flowerlike $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres with dehydroabietic-based phosphate diester sodium (DDPDS). The resulting material was characterized by Nuclear Magnetic Resonance (^{13}C NMR), Automatic tensiometer, Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The effects of DDPDS concentration on the morphology and size of the $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres were discussed in detail. In addition, a possible formation mechanism of the 3D flowerlike $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres assisted by the rosin-based surfactant was proposed, which differs from the previously proposed bubble-template mechanism.

2 Experimental

2.1 Reagents and materials

Unless stated otherwise, all chemicals (except for the rosin-based phosphate diester sodium) are of analytical grade and used as received. These $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and

$\text{CO}(\text{NH}_2)_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. DDPDS was prepared via self-synthesis and the synthetic route is shown in Fig.1^[33]. DDPDS is a rosin-based phosphate diester surfactant with a bilaterally symmetric structure, resulting in similar NMR peaks for the symmetric carbon atoms. The chemical structure of DDPD was investigated by ^{13}C NMR and the analysis confirmed that the DDPDS was successfully synthesized (Fig.2, Table1).

2.2 Preparation of $\beta\text{-Ni}(\text{OH})_2/\gamma\text{-Ni}(\text{OH})_2$ composite nano-microspheres

In the typical synthesis, 0.5 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.5 mol/L $\text{CO}(\text{NH}_2)_2$ were dissolved in aqueous-ethanol (1 : 1, *V/V*) solution under magnetic stirring to obtain a homogeneous solution. Then DDPDS with 1, 2, 5, and 15 critical micelle concentration (CMC, 1 CMC of DDPDS is 1.35 g/L at 25°C), respectively, was sequentially added to the solution under vigorous stirring for 10 min to ensure complete mixing. Then,

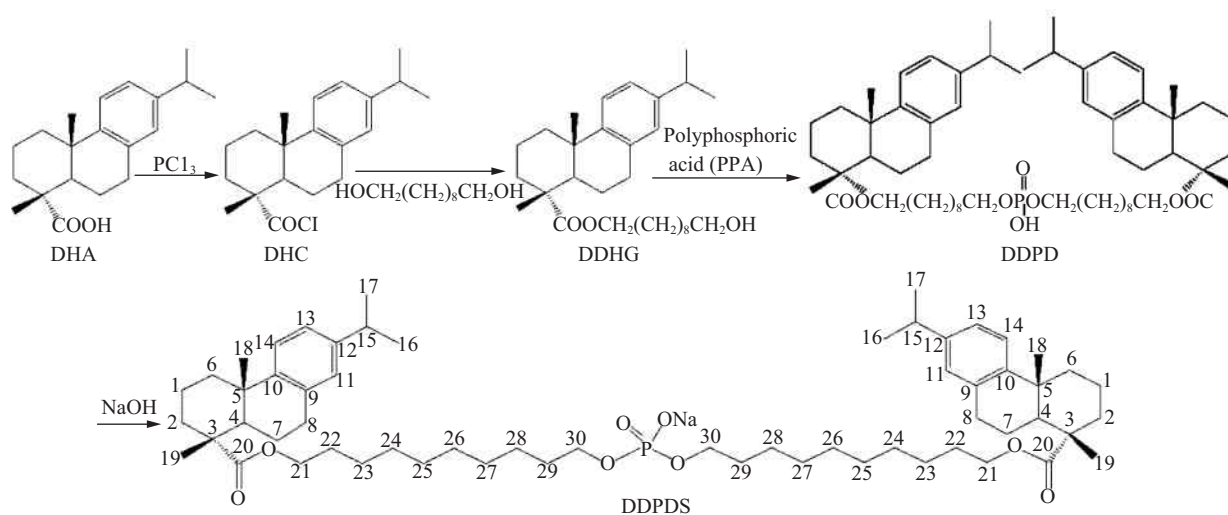


Fig.1 Synthetic route of DDPDS

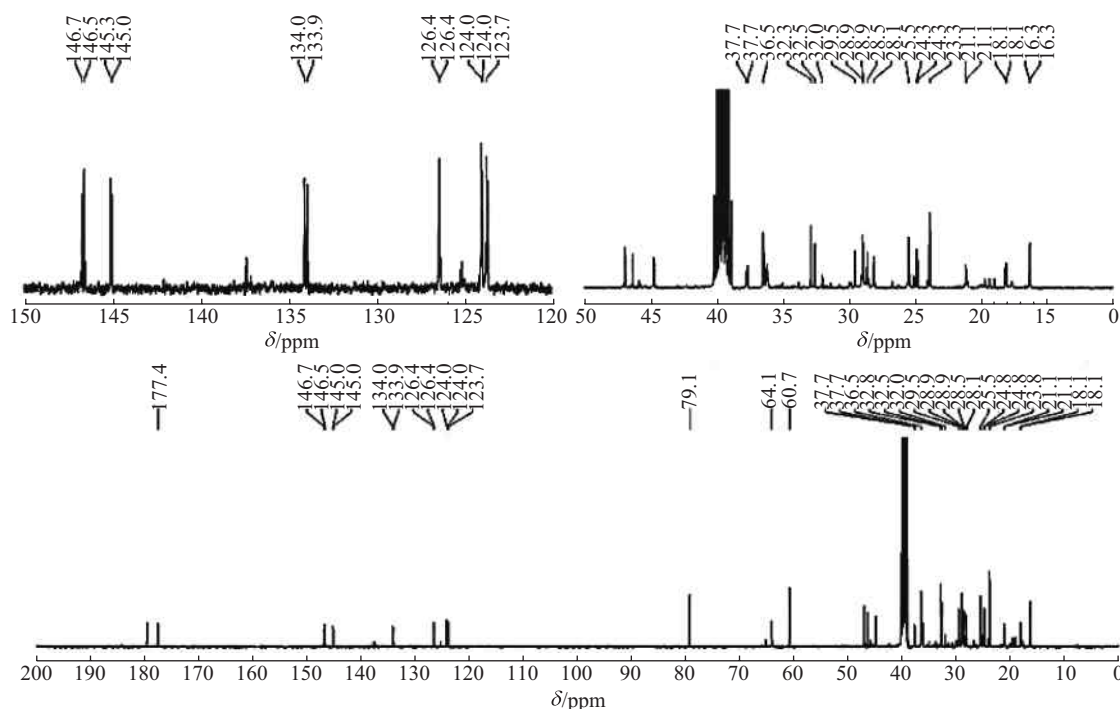


Fig.2 ^{13}C NMR spectrum of the prepared DDPDS

Table 1 The ascription of each carbon atom peak of DDPDS

Carbon atom	δ/ppm
C1	16.3
C2	32.5
C3	37.7
C4	60.7
C5	25.5
C6	36.5
C7	28.1
C8	29.5
C9	133.9
C10	145.0
C11	123.6
C12	146.5
C13	123.7
C14	126.4
C15	32.8
C16	21.1
C17	21.1
C18	23.8
C19	18.1
C20	177.4
C21	63.9
C22	28.5
C23	24.8
C24	28.6
C25	28.9
C26	28.9
C27	29.5
C28	24.8
C29	32.0
C30	79.1

the solution was transferred to an autoclave and the reaction containers were placed in ovens at 180°C for 8 h. Finally, the products were obtained, washed with the aqueous-ethanol (1 : 1, *V/V*) solution, and dried at 105°C for 3 h. To analyze the electrochemical performance, a BET specific surface area analyzer (ASAP 2020 Micromeritics company) was used to determine the specific surface area of the synthesized materials.

2.3 Fabrication of the supercapacitors and electrochemical testing

Electrodes used for fabrication of the supercapacitors were prepared by mixing the 3D flowerlike β -Ni(OH)₂/

γ -Ni(OH)₂ composite nano-microspheres, acetylene black, and polytetrafluoroethylene (PTFE) in a mass ratio of 75 : 20 : 5. The resulting mixture was then coated onto a nickel foam substrate (approximately 1 cm²) and dried in an oven at 100°C for over 12 h. To investigate the electrochemical behavior of the as-prepared samples, cyclic voltammetry (CV) was performed using a BT2000 battery testing system (Arbin Instruments, USA) and a 1260 electrochemical workstation (Solartron Metrology, UK). The capacitive performance of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres was investigated in 6 mol/L KOH using two-electrode cells at a scan speed of 10 mV/s.

2.4 Analytical methods

¹³C NMR spectra were recorded on a Bruker AVIII 150 MHz spectrometer at 25°C in dimethyl sulfoxide (DMSO). The surface tension of the DDPDS at various concentrations was determined by the Du Nouy ring method on the automatic tensiometer (model JK99B, China) at 20°C in an aqueous medium. The shapes of the DDPDS micelles were investigated by high contrast transmission electron microscopy (TEM, JEM-1010, Japan) in a dark environment at 25°C.

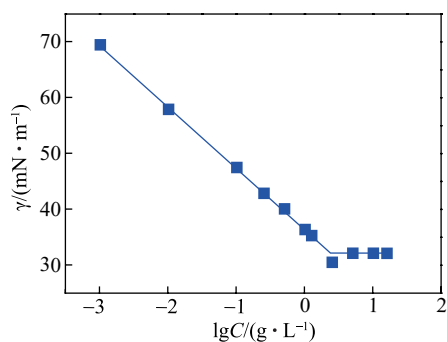
SEM microanalyses of the samples were performed using a Hitachi S-3400N II apparatus with an applied voltage of 20 kV. The XRD patterns of the as-prepared samples were recorded on a Rigaku D/Max 2200-PC diffractometer with Cu K α radiation ($\lambda=0.15418$ nm), at a scanning rate of 2°/min from 5° to 75°.

3 Results and discussion

3.1 DDPDS characterization

Fig.3 shows the γ -lgC curve of DDPDS. The surface tension of DDPDS decreased with increasing the concentration of DDPDS, and became relatively stable at 32.13 mN/m at a concentration of 3.7 CMC. And the surface tension (γ_{CMC}) was 31.75 mN/m. The results indicate excellent surface activity of the DDPDS solution.

The self-assembled morphologies of the DDPDS

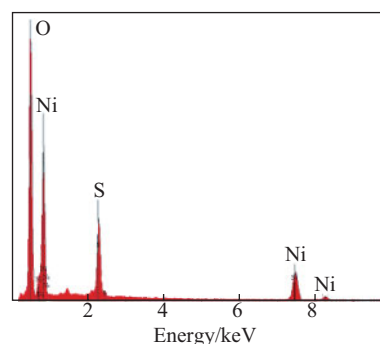
Fig.3 γ -lgC curve of DDPDS

surfactant in the water-ethanol (1 : 1, V/V) solution were characterized by TEM, and it could be seen that the DDPDS self-assembled to form spherical micelles (Fig.4). As can be seen from the TEM image in Fig.4(a), the DDPDS micelles at low concentration of approximately 1 CMC have an almost regular spherical shape with a diameter of 40~50 nm. When the concentration of DDPDS was increased to 5 CMC, vesicle structures with different shapes and sizes of approximately 2 μm formed, as shown in Fig.4(c). When the concentration of DDPDS was further increased to 15 CMC (Fig.4(d)), micellar polymerization occurred in the vesicle intestine. In addition, aggregation of particle-stabilized drops can occur due to the adsorbed surfactants of DDPDS acting as bridges between particle-stabilized drops.

3.2 Characterization of β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres

3.2.1 EDX, XRD, and BET analysis

The elemental composition of the materials was determined by EDX analysis. Fig.5 shows the EDX profile of β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-

Fig.5 EDX patterns of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with 1 CMC of DDPDS

microspheres, indicating their elemental composition. The EDX profile (Fig.5) of the DDPDS system revealed that the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres were composed of Ni, S, and O. The peak arising from S arose from trace NiSO₄ · 6H₂O.

The XRD patterns of the prepared β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres with different concentrations of DDPDS are shown in Fig.6. Ni(OH)₂ with 3D hierarchical structure was synthesized via a simple and straightforward method. When the DDPDS concentration was increased, the XRD patterns of the Ni(OH)₂ exhibited typical features corresponding to β -Ni(OH)₂ and γ -Ni(OH)₂. For β -Ni(OH)₂, the six major characteristic diffraction peaks at 2θ of 19.5°, 33.0°, 38.8°, 52.1°, 59.0°, and 62.0° correspond to the (001), (100), (101), (102), (110), and (111) planes, which is in good agreement with the standard power diffraction patterns (JCPDS No: 38-0117)^[34-35]. In addition, the other peaks could be assigned to the (001) and (100) planes of γ -Ni(OH)₂ (Fig.6). These results identified the composite crystal structure that is expected to comprise

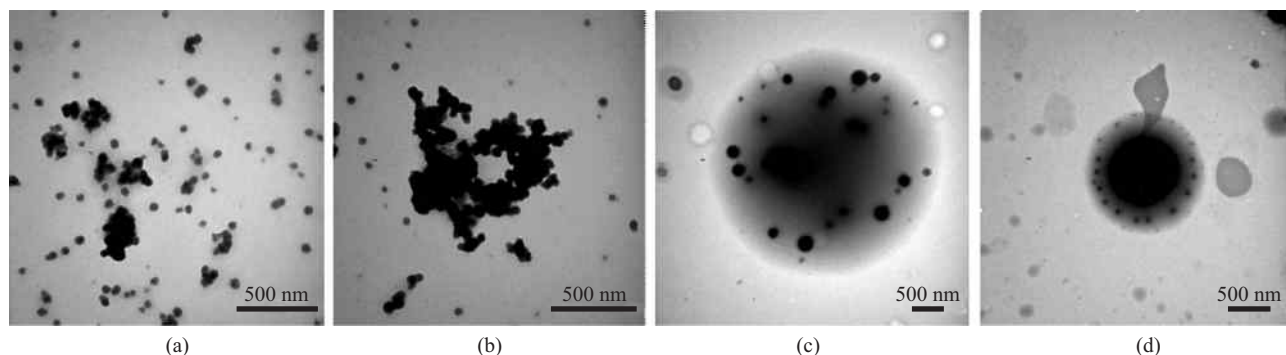


Fig.4 TEM images of ionic self-assembly systems: (a) DDPDS, 1 CMC; (b) DDPDS, 2 CMC; (c) DDPDS, 5 CMC; (d) DDPDS, 15 CMC

the new nickel-metal hydride material. In Fig.6, it is clear that all diffraction peaks of β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres showed stronger and sharper intensities with increasing DDPDS concentration, indicating that the addition of DDPDS improved the crystallinity of the composite nano-microspheres.

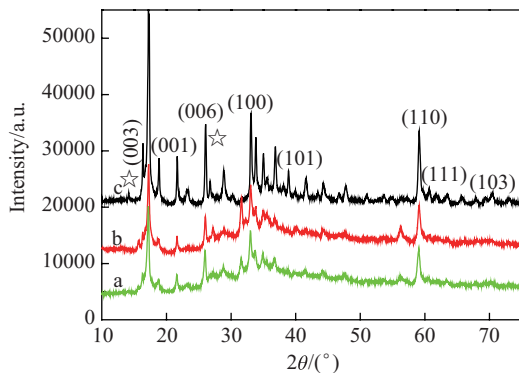


Fig.6 XRD patterns of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with different DDPDS concentrations: (a) 1 CMC; (b) 2 CMC; (c) 5 CMC

The specific surface area of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres significantly influenced their electrochemical properties. With larger specific surface area, the activation point becomes higher and the electrochemical reaction proceeds more easily, resulting in better electrochemical performance. Therefore, the specific surface area of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with different concentrations of DDPDS (1, 2, 5, and 15 CMC) was determined (Table 2). The specific surface area of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres was 10.50 m²/g when prepared at 180°C without DDPDS addition. Upon adding DDPDS, the specific surface area of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres increased significantly, and the specific surface area further increased with increasing DDPDS concentration. At 5 CMC of DDPDS, the specific surface area of nano-microspheres was stable at 23.86~23.88 m²/g. This may be because the addition of surfactants caused the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres to change from irregular shaped to a more regular spherical structure, resulting in a more uniform dispersion.

Table 2 The specific surface areas of β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres determined by the BET technique

DDPDS concentration/CMC	Specific surface area/(m ² · g ⁻¹)
0	10.50
1	14.65
2	16.94
5	23.86
15	23.88

3.2.2 SEM analysis

The shape of the Ni(OH)₂ crystals can be controlled by adding chemical capping reagents to the solution. The DDPDS likely serves as an adsorbing species on the faces of the nano-microspheres, changing the properties of the crystal planes and promoting the growth of β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres with a 3D structure. To investigate the effect of DDPDS concentration on the shape evolution, a controlled experiment was performed using different DDPDS concentrations, while other parameters were held constant. SEM was used to observe the grain morphology and size of the resulting β -Ni(OH)₂/ γ -Ni(OH)₂ composites nano-microspheres. Fig.7 shows the SEM images of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres synthesized with different DDPDS concentrations at 180°C for 8 h.

Fig.7(a) shows the SEM images of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared without DDPDS, and it is clear that they were composed of a large number of irregularly shaped sheets. Some incomplete nano-microspheres with a flowerlike structure formed at 1 CMC DDPDS, and could be seen in Fig.7(b) ~ Fig.7(c). The β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres mostly consisted of irregular and adhesion microspheres. In the presence of DDPDS, the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres formed different size microspheres with a diameter of 1~2 μ m. The SEM image of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with 2 CMC of DDPDS is shown in Fig.7(d), and the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres exhibited irregular hollow microspheres consisting of

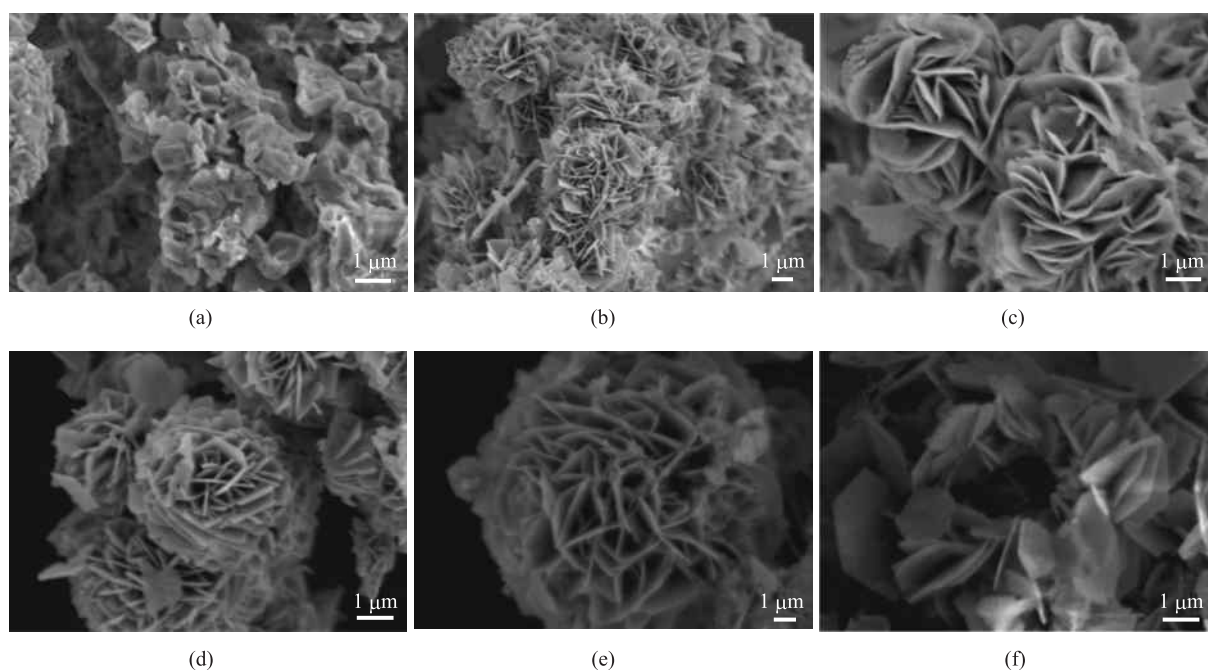


Fig.7 SEM images of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with different DDPDS concentrations: (a) without DDPDS; (b), (c) 1 CMC; (d) 2 CMC; (e) 5 CMC; (f) 15 CMC

nanosheets with a diameter of 2~4 μm . The β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres presented different-sized flowerlike structures composed of regular nanosheets. Moreover, a much higher DDPDS concentration (5 CMC) resulted in larger microspheres (Fig.7(e)). The phosphate groups in the molecular chain of DDPDS had a strong tendency to attract positively charged ions or attach to positively charged surfaces. When the concentration of DDPDS was further increased to 15 CMC, the interaction between DDPDS and Ni^{2+} led to the increase of free Ni^{2+} and regular nanosheets, and the nano-microspheres tended to conglutinate. In the SEM image shown in Fig.7(f) hexagonally shaped β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres can clearly be observed.

In Fig.7, it can be seen that the morphology of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres became more regular and the nanosheets showed bigger flakes with increasing DDPDS concentration. The results indicated that the DDPDS concentration had a significant influence on the morphology and size of the prepared β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres. In the presence of DDPDS, the

nanostructure agglomerated easily, the 3D flowerlike nanostructure was more regular, and the particle size increased.

3.2.3 Electrochemical measurements

The electrochemical performance of the prepared materials in basic media (6 mol/L KOH) was characterized. The SEM images showed that the shape of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres tended to stabilize when the concentration of DDPDS was increased over 5 CMC. Thus, we performed the electrochemical characterization experiment at 1, 2, and 5 CMC. As shown in Fig.8(a), except for the control group, the specific capacity of all samples was very similar. When the scavenging speed was increased, specific capacity differences between several samples became more obvious. The specific capacity of the sample prepared with 5 CMC of DDPDS was higher than that of the samples prepared with 1 CMC and 2 CMC of DDPDS. Regardless of the scavenging speed, the specific capacity of the control group was the lowest. This was because with the addition of DDPDS, the shape of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-

microspheres became increasingly uniform.

CV scans can be used to probe the electrochemical behavior of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres of the electrode surface and internal electrode directly. In Fig.8(b), it can be seen that the curves of the samples had several obvious oxidation-reduction peaks, and the positions of the peaks are largely identical, indicating that the specific capacity is derived from the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres. The reduction peak was observed at 0.1 V, which corresponded to the reduction of NiOOH to β -Ni(OH)₂/ γ -Ni(OH)₂. Under the same scanning speed, the area of the cyclic voltammetry curve of the samples prepared with 5 CMC of DDPDS was the largest, indicating that its specific capacity was also the largest. The areas of the samples prepared with 1 CMC and 2 CMC of DDPDS were similar, and the area of the control sample was the smallest.

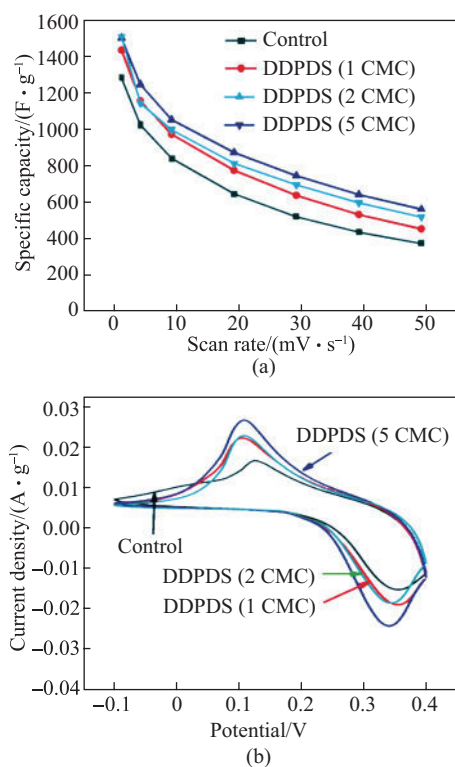


Fig.8 Comparison of the specific capacity of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with different concentrations of DDPDS (a); the CV scans of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres prepared with different concentrations of DDPDS at a scan rate of 10 mV/s (b)

3.3 Formation mechanism of β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres

To understand the growth mechanism of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite architectures, systematic time-dependent experiments were performed at 2 CMC DDPDS and 180°C. SEM images (Fig.9) of the products obtained at 1, 2, 3, 5, and 8 h during the hydrothermal process were collected, and they illustrated the morphology evolution of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite architecture.

In Fig.9(a), the sample collected at 1 h mostly consists of very thin metastable broken nanosheets. Moreover, nanosheet assemblies of approximately 2 μ m could be observed as a result of aggregation and growth of the particles. The sample obtained at 2 h (Fig.9(b)) showed that the aggregation of the nanosheets formed a ball-flower microsphere, and the nanosheets became thicker in Fig.9(c). At 3 h, the nanosheets of the 2 μ m flowerlike microsphere arranged closely and the hollow interior was clearly reflected by the open mouth on the microsphere in Fig.9(d). With the increase of reaction time, besides the flowerlike hollow spheres, some underdeveloped ball-flower hollow architectures also can be observed in Fig.9(e), indicating that oriented attachment is still occurring. Simultaneously, the nano-microspheres became more structured and increased in size to 3~5 μ m. At 8 h, the underdeveloped flowerlike hollow architectures continued to grow by combining the remaining primary nanosheets, finally forming the flowerlike structure, as shown in Fig.9(f). As a result, the nanosheets were completely changed to pompom-like microspheres and fully developed 3D flowerlike hierarchical hollow architectures were obtained.

In previous studies, the formation mechanism of β -Ni(OH)₂ composites was explained by soft templates of CO₂ bubbles formed by the decomposition of CO(NH₂)₂ [36-38]. From CO(NH₂)₂, many micrometer/sub-micrometer CO₂ bubbles were produced at 180°C. The self-assembly process occurred around the gas/liquid interface of CO₂, and finally the 3D flowerlike hierarchical hollow architectures were formed using

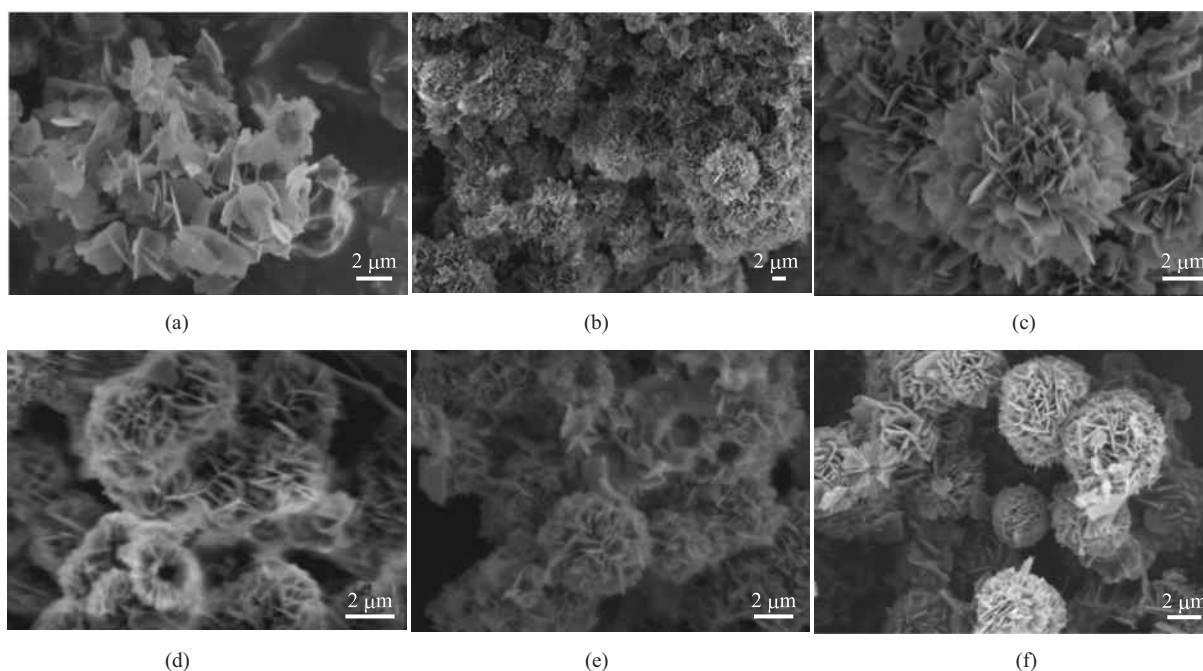


Fig.9 SEM images of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres at different reaction time: (a) 1 h; (b), (c) 2 h; (d) 3 h; (e) 5 h; (f) 8 h

the CO₂ bubbles as a template. At this point, the hollow inner diameter of the nano-microspheres likely correspond to the diameter of the CO₂ bubbles, which were approximately 2~3 μ m, and the outer diameter was approximately 2~5 μ m.

However, in this study nano-microspheres were not formed in the absence of DDPDS. Here, the surfactant must have played a key role in the structural evolution. In addition, the inner diameter of the hollow microsphere was determined to be approximately 500 nm (Fig.9(d)). The inner diameters of the hollow spheres were smaller than the diameters of the CO₂ bubbles measured in previous studies^[39]. The inner diameters of the hollow spheres corresponded to the diameters of the surfactant micelles. Hence, the formation mechanism of the 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres assisted by the DDPDS is proposed to involve a micelle-template instead of a bubble-template, as shown in Fig.10. First, the DDPDS self-assembled to form spherical micelles in the ethanol-water solution. Thus, when the spherical DDPDS micelles were thoroughly dispersed, they are separated from each other by electrostatic repulsion. Under these conditions, if positively charged species

like Ni²⁺ are present, the ion adsorption process occurs as a consequence of mutual electrostatic attraction between Ni²⁺ and DDPD⁻. Afterwards, the urea was decomposed and released NH₃ to provide OH⁻ for the formation of Ni(OH)₂ composites, and the initial precipitates provided the numerous Ni(OH)₂ nucleation sites. The freshly formed crystalline nanoparticles were unstable because of their high surface energy and aggregated to form increasingly larger nanoparticles. As the reaction proceeds, the nanosheets gradually formed because that each crystal was oriented in a certain direction, and were easily attached to DDPDS. The piled sheets gradually grew together and a large number of nanobars intertwined with each other to form the flowerlike structure. Here, DDPDS acted as a soft template to induce the self-assembly of the nanosheets on its surface^[40-41]. The addition of DDPDS increased the rate of nanosheet aggregation, flowerlike structure formation, and increased size of the microspheres.

4 Conclusions

In summary, dehydroabietic based phosphate diester sodium (DDPDS) was successfully prepared with 1 CMC (1 CMC of DDPDS is 1.35 g/L at 25°C),

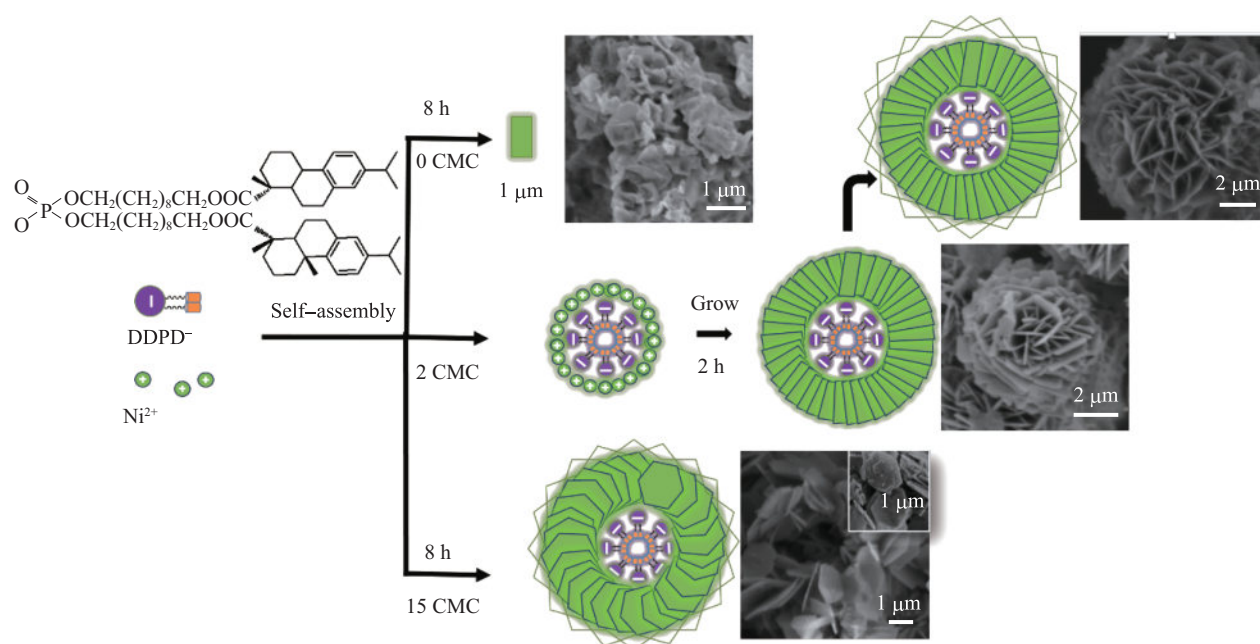


Fig.10 Formation mechanism of the flowerlike Ni(OH)₂ composite nano-microspheres in the presence of DDPDS

yielding a surface tension (γ_{CMC}) of 31.75 mN/m. The 3D flowerlike β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres were successfully synthesized via a facile hydrothermal method assisted by DDPDS at 180 °C for 8 h. The effect of DDPDS concentration on the crystal dimensions, structure, and morphology of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres was investigated in detail. The results showed that increasing the concentration of DDPDS intensified the diffraction peaks and improved the crystallinity of the products. The morphology and size of the prepared β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres could be strictly controlled by the addition of DDPDS. Furthermore, the addition of DDPDS improved the electrochemical performance of the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres. This synthetic strategy was facile, low-cost, eco-friendly, and was easily extended to produce the β -Ni(OH)₂/ γ -Ni(OH)₂ composite nano-microspheres.

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