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Synthesis of Ni Co-LDH by Microwave as the Electrode Material of Supercapacitor

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Abstract. In order to deal with energy and environmental problems, more and more researches have been made on electrode materials of supercapacitors in recent years. Among many electrode materials, layered double hydroxides (LDHs) is favored by researchers because of its high theoretical capacity. In this work, we report a facile route for synthesizing Ni Co-LDH, we choose the ZIF-67 as the template and the source of Co to synthesis Ni Co-LDH by microwave in the mixture of ethanol and DIwater. Through this route, the Ni Co-LDH can be synthesized in 3 min. The as prepared Ni Co-LDH exhibits outstanding specific capacitance of $2376\text{F}\cdot\text{g}^{-1}$ at $1\text{A}\cdot\text{g}^{-1}$ and it can maintain 84.61% of its initial value after 1000 cycle. Asymmetric supercapacitor(M-3//GO) with a maximum voltage of 1.5V has demonstrated a high energy density of $39.28\text{Wh}\cdot\text{kg}^{-1}$, a high power density of $7513\text{W}\cdot\text{kg}^{-1}$ at $20.21\text{Wh}\cdot\text{kg}^{-1}$.

1. Introduction

Metallic organic framework (MOFs) is considered as a good template for nanomaterials due to its unique pore structure and high specific surface area [1-3]. ZIF-67 is one of ZIFs. The supercapacitance phenomenon is directly associated with surface properties, Because of its special structure, Layered double hydroxides (LDH) has been used in catalysis, electrochemistry, drug carrier and other fields [4]. However, traditional heating methods, such as reflux heating and solvent heating, have been reported for the synthesis of Layered double hydroxides (LDH), These methods have some inherent defects, such as slow heating, uneven and so on [5-7]. Therefore, we choose microwave-assisted hydrothermal, compare to traditional heating methods, it has many advantages, (1) there is no temperature gradient during heating process, (2) The source of heating and reactant don't contact directly and decrease the wall effect. (3) it's easy to setup parameter, so the accuracy is better than traditional heating methods. [8].

In this work, High performance bimetallic hydroxides were prepared by microwave assisted heating in a short time. After electrochemical characterization, its specific capacitance reached $2376\text{F}\cdot\text{g}^{-1}$ at $1\text{A}\cdot\text{g}^{-1}$ and it can maintain 84.61% of its initial value after 1000 cycle in 1M KOH electrolyte. This indicates that the prepared materials have great prospects in the field of energy storage. Asymmetric supercapacitor(M-3//GO) with a maximum voltage of 1.5V has demonstrated a high energy density of $39.28\text{Wh}\cdot\text{kg}^{-1}$, a high power density of $7513\text{W}\cdot\text{kg}^{-1}$ at $20.21\text{Wh}\cdot\text{kg}^{-1}$.



2. Experimental

2.1. Synthesis of ZIF-67 Polyhedrons and Ni Co-LDH

The ZIF-67 polyhedrons were synthesized through the reported method [9]. With a minor modification. In brief, 8.7309g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30mmol) and 9.8522g 2-methylimidazole (2-mIM, 120mmol) were respectively dissolved in 500mL ethanol, after stirring 30min, The 2- mIM was rapidly poured into the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, which was further stirred. After the solution was homogenated, the solution was allowed to stand for 24h. Then the solution was centrifuged and washed with water and ethanol alternately for three times, collect the purple product. Using ZIF-67 as a sacrificial template, the Ni Co-LDH was synthesized through microwave irradiation. In detail, firstly we prepare the solution of ethanol and DI water, in which the volume ratio of water is 10%. Then ZIF-67 was dissolved in 60 mL prepared solution under ultrasonication to obtain a homogeneous violet dispersion, and meanwhile $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 140mL prepared solution under stirring to obtain a homogeneous solution. In this work, we prepare 5 different mass ratio of The $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZIF-67 which are 1:1, 2:1, 3:1, 4:1 and 5:1. Then the violet dispersion was added into $\text{Ni}(\text{NO}_3)_2$ solution and keep stirring about 15min. After that the dispersion was put into microwave oven and react 3min at medium-low fire. Finally the product were collected and washed with ethanol and DI water alternately by centrifugation. We name the product M-X, X represent the mass ratio of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZIF-67.

2.2. Electrochemical Characterization and Test

The materials were electrochemically characterized by a standard three-electrode system and 1M KOH as electrolyte, Saturated calomel electrode reference electrode, platinum electrode pair. After cyclic voltammetry (CV) or galvanostatic charge-discharge (GCD) test, Material specific capacity is calculated by the following formula[10].

$$C_s = \frac{1}{2mv\Delta V} \oint IdV \quad (1)$$

$$C_s = \frac{It}{m\Delta V} \quad (2)$$

3. Results and Discussion

3.1. Structure and Morphology Characterization

The surface morphology was observed by SEM characterization. As well displayed in Figure.1, the surface of ZIF-67 is a rhombohedral dodecahedral granular structure [11], After microwave treatment in the mixture of ethanol and water we obtain the Ni Co-LDH, from the SEM of the M-1 and M-2(Figure.1b,c), It is easy to observe that the surface of their particle are chaotic. Then it is obvious that the surface of M-3 is composed of numerous nanobelt (Figure.1d), this special morphology has high specific surface area which is good for the adsorption/desorption of conductive particle. With the increase of the mass ratio of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the morphology of M-4 and M-5(Figure.1e,f) are also composed of numerous nanobelt, but compared to M-3, their nanobelt are much more than M-3 but the thickness of each nanobelt is thinner than M-3. The formation mechanism of the structure can be described as: The reaction mechanism of this experiment is very simple, without adding any alkali or other additives Ni^{2+} adhere to the face of ZIF-67 and meanwhile the Ni^{2+} hydrolyze in the mixture of water and ethanol. Then the ZIF-67 particles are etched by the protons which is come from H_2O through hydrolyze and mean while the Co^{2+} starts hydrolysis reaction to form LDH structure. the water plays a crucial role during the reaction.

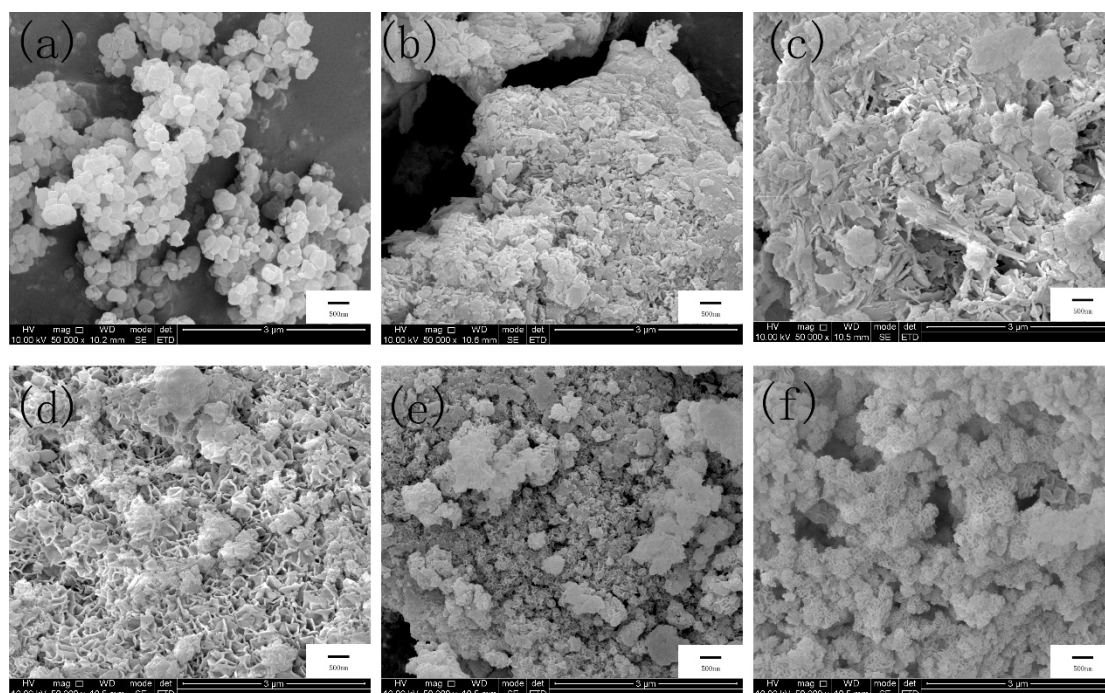


Figure 1. SEM of ZIF-67(a), M-1(b), M-2(c), M-3(d), M-4(e) and M-5(f).

The crystallinity and elements of the materials were analyzed by XRD, and the results were displayed in Figure.2. As we all see, the diffraction peaks of the synthesized ZIF-67 template matches well with the standard crystallographic spectrum [12]. After microwave treatment, The characteristic peaks of ZIF-67 have disappeared and new additional peaks at $2\theta=11.35^\circ$, 22.74° , 34.41° , and 60.34° , which match well with (003), (006), (012), and (110) reflections of a typical LDH materials are clearly observed, this indicates that the material has a good LDH crystal structure [11]. ZIF-67 and the Ni Co-LDH are also analyzed by energy dispersive spectroscopy (EDS, Figure.2(b,c)). After microwave treatment, only a trace quantity of C is detected in the Ni Co-LDH, Indicates that the ZIF-67 structure has been replaced, in addition, a quantity of Ni and O are detected, suggesting that the Ni Co-LDH has been synthesized, there is no H from the EDS spectroscopy because of its quantity is too light.

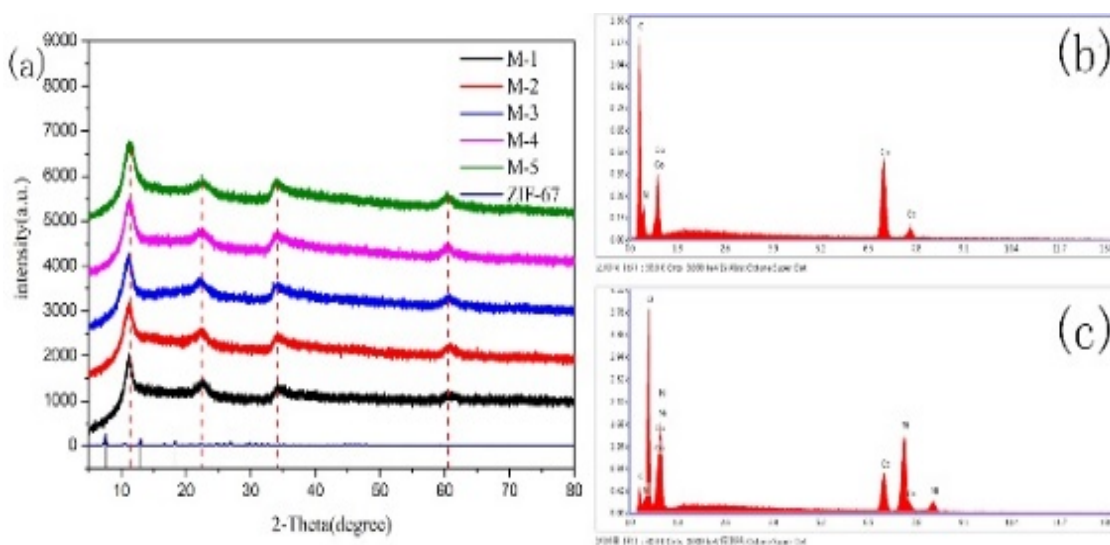


Figure 2. XRD pattern of ZIF-67 and Ni Co-LDH(a), EDS pattern of ZIF-67(b) and M-3(c)..

3.2. Electrochemical Evaluation of the Ni Co-LDH

In order to explore Ni Co-LDH as electrode material in supercapacitors in the application of prospects, the pseudocapacitive properties of the synthesized Ni Co-LDH were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD). Figure 3a gives the CV curves of the prepared Ni Co-LDH. CV curves were measured in a potential window of -0.2 to 0.8V. A pair of redox peaks can be observed in all curves, suggesting the pseudocapacitive characteristics of the Ni Co-LDH. Furthermore, the peaks are located at the two poles of potential window, that is because the low polarization. Figure 3b display the GCD plots of the Ni Co-LDH at current density of $1\text{A}\cdot\text{g}^{-1}$ within the potential window of 0 to 0.5V. It is obvious that the plateaus can be observed in the in the charge/discharge curves, which is consistent with the redox peaks of CV curves. The specific capacitance of M-1, M-2, M-3, M-4 and M-5 are 1344, 1544, 2376, 2232 and $1501.2\text{ F}\cdot\text{g}^{-1}$. Figure 3c shows the EIS plot, typically, in the low-frequency and high-frequency region, the impedance of M-3 is the lowest among the 5 materials. Furthermore, the cycle performance was shown in the Figure 3d, after 1000 cycles at current density of $5\text{A}\cdot\text{g}^{-1}$, the specific capacitance of M-1 to M-5 can maintain 73.13%, 92.80%, 84.61%, 85.61% and 76.10% of their initial value. Figure 3e,f show the CV curves and GCD plots of M-3. All curves had a pair of redox peaks, and all charge-discharge curves had a REDOX peak, which was consistent with CV results.

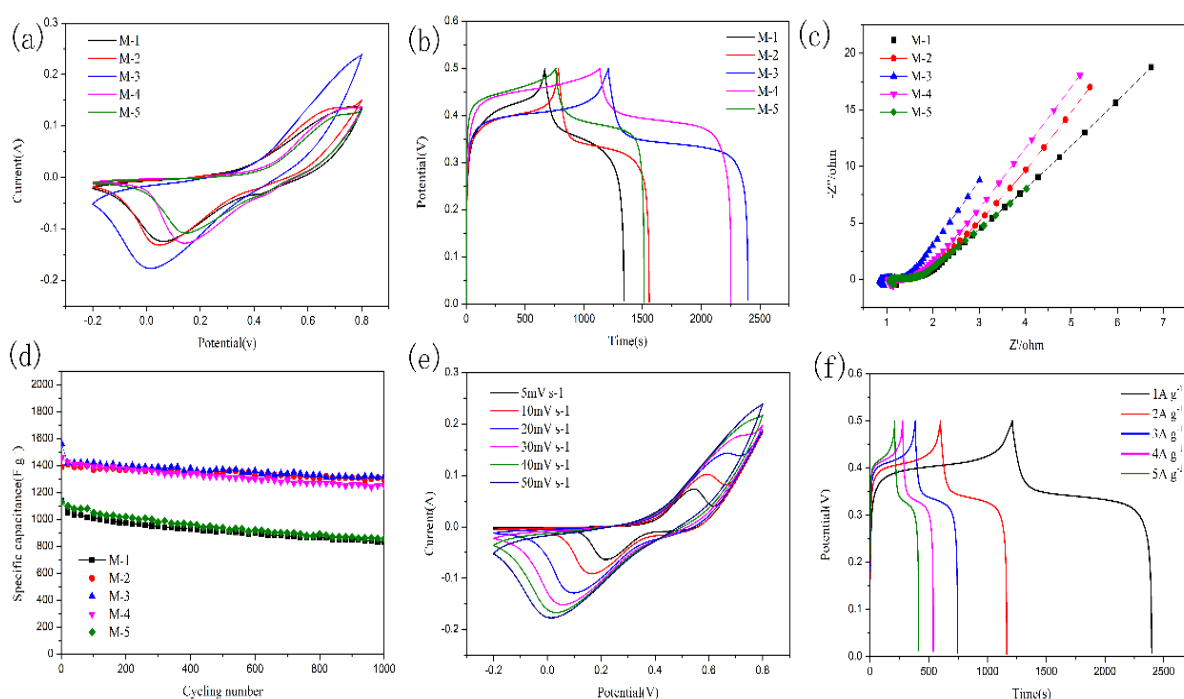


Figure 3. Electrochemical performance of Ni Co-LDH.

Table 1 is the compared table with other published paper:

Table 1. Comparison of electrochemical properties

Sample	Specific capacitance	Cycling number/Retention	Ref.
ZIF-L-Co nanoflake	894 C g^{-1} at 2A g^{-1}	3000 at $5\text{A g}^{-1}/82\%$	[4]
$\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$ Double-Shelled Nanocages	972 F g^{-1} at 5A g^{-1}	12000 at $5\text{A g}^{-1}/92.5$	[9]
LDH nanocages	1203 F g^{-1} at 1A g^{-1}	1000 at $8\text{A g}^{-1}/90.2\%$	[11]
Ni Co-LDH	2376 F g^{-1} at 1A g^{-1}	1000 at $5\text{A g}^{-1}/84.61\%$	This work

In order to further explore the actual performance of the material in the capacitor, an asymmetric supercapacitor was assembled by M-3 as the positive electrode material and graphene oxide (GO) as the negative electrode material. It is shown in the Figure 4a, the potential window of GO is from -1 to

0V, while M-3 is from -0.2 to 0.8V, thus the potential window of M-3//GO has been extended to 1.5V through constantly attempt. As for CV curves of M-3//GO in Figure4b, The charge-discharge potential window expanded from 1V to 1.5V, and all of them showed good performance. Then, a series of CV curves of different scan rate from 5mV to 35mV were shown in Figure4c, The results showed that the assembled ASC had electric double-layer capacity and redox capacity. even at high scan rates of 35 mv/s, the shape of CV curve still maintain, which indicates that the assembled M-3 //GO has low resistance and good rate performance. Figure6d shows the GCD of M-3//GO of different potential window which correspond with Figure4b. It is obvious that the GCD curves of ASC at various current densities was shown in Figure4e. The calculated specific capacitances are 125.7, 111.9, 100, 96, 89.87, 84 and 64.67F·g⁻¹ at current density of 0.5, 1, 2, 3, 4, 5, 10A·g⁻¹.Respectively, ragone plots relative to the corresponding energy density (E) and power density (P) were calculated and shown in Fig4f. The energy density of the assembled M-3//GO was 39.28Wh·kg⁻¹ at power density of 375.17W·kg⁻¹, As the power density increased to 7513 W·kg⁻¹ the energy density still remained 20.21 Wh·kg⁻¹. demonstrating high rate behavior (retention 51.45%) for the M-3//GO assembled with M-3 and GO. At high power density, this excellent rate characteristic is superior to most asymmetric supercapacitors based on LDH.

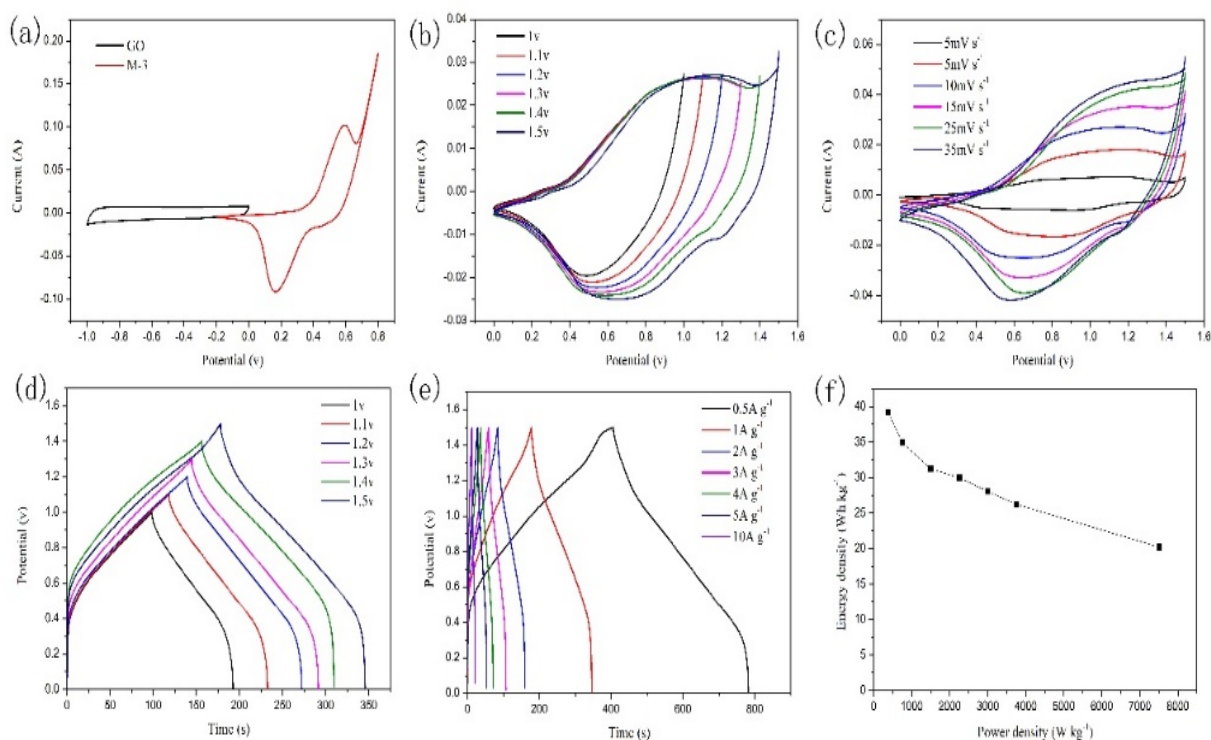


Figure 4. Electrochemical performance of asymmetric supercapacitor

4. Conclusion

In summary, Ni Co-LDH was synthesized by microwave in a mixture of water and ethanol using ZIF-67 as self-sacrificing template. And final product of Ni Co-LDHs(M-X) have different morphology because the different initial mass ratio of Ni(NO₃)₂·6H₂O, this indicate the mass ratio of Ni(NO₃)₂·6H₂O play a very important role during reaction. In addition, it showed a high specific capacitance of 2376F·g⁻¹ at the current density of 1A·g⁻¹ and it can maintain 84.61% of its initial value at current density of 5A·g⁻¹ after 1000 cycle. Asymmetric supercapacitor(M-3//GO) with a maximum voltage of 1.5V has demonstrated a high energy density of 39.28Wh·kg⁻¹, a high power density of 7513W·kg⁻¹ at 20.21 Wh·kg⁻¹.

5. Acknowledgement

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