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Original Article

Efficient and inexpensive MPCVD method to synthesize Co_3O_4/MoS_2 heterogeneous composite materials with high stability for supercapacitors

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ABSTRACT

Large-sized metal oxide particles have the potential to constitute cheap, high-performance, and high-stability supercapacitor electrode materials. Herein, the marketable large-sized Co_3O_4 particles (~6 μm) as the starting raw material, inexpensive Co_3O_4/MoS_2 core–shell heterogeneous composites have been one-step fabricated via an improvised MPCVD system modified by a domestic microwave oven. After that, the surface morphology, composition structure, and valence state of elements were analyzed to the confirmed successful synthesis of MoS_2 on the surface of Co_3O_4. Besides, the performance was tested by cyclic voltammetry and galvanostatic charge–discharge method. The results show that the synergistic effect of Co_3O_4 core and MoS_2 shell can effectively improve the material's electrochemical performance. The specific capacitance of Co_3O_4/MoS_2 composite can reach 337 F g^{-1} with a current density of 0.5 A g^{-1}, which is six times more than the raw Co_3O_4 powder. Furthermore, it could maintain 93.6% of the initial specific capacitance after 2000 charges and discharges. Finally, the mechanism of material performance improvement is proposed.

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1. Introduction

The global energy problem is increasingly prominent and has been one of the world [1,2]. Researchers have made great efforts in energy conversion and storage. As a new generation of energy storage devices, supercapacitors have been attracting continuous attention due to their high power density, fast charging/discharging rate, and long service life [3–5]. Co_3O_4 was used in pseudocapacitor due to its high theoretical specific capacity (3560 F g^{-1}) and ideal pseudocapacitance characteristics [6,7]. However, due to the massive volume expansion/contraction, low conductivity, and polarization, the practical efficiency of Co_3O_4 is far lower than the theoretical maximum, which hinders its application and development [8,9]. Also, people pay more attention to nanomaterials' research of nano-sized Co_3O_4 due to its high reactivity. However, the high cost and the instability in the reaction process have been hindering their practical application. In contrast, large-scale materials with low prices, high stability, and easier practical application have been ignored by researchers. This study is focused on the development of massive Co_3O_4 particles in the actual use of supercapacitors.

Building composite system is considered as an effective strategy to solve the problems of Co_3O_4 in energy storage [10–12]. As we all know, carbon materials are widely used in the research of building composite materials with Co_3O_4, such as carbon/Co_3O_4 [13–15], CNTs/Co_3O_4 [16,17], graphene/Co_3O_4 [18,19], etc. However, the theoretical capacity of carbon materials is low, which cannot meet large capacity requirements. Molybdenum disulfide (MoS_2), as a transition metal sulfide, exhibits higher capacitance and lower energy loss than carbon. Besides, like graphite, MoS_2 has a two-dimensional (2D) layered structure. The distance between adjacent layers is connected by weak van der Waals force, promoting ion insertion and extraction in charge and discharge cycle [20]. Therefore, MoS_2 is often reported to be used in the construction of composite materials in energy devices. For example, Liu et al. proposed a simple in-situ hydrothermal method to synthesize NiS_2/MoS_2 nanowires on nickel foam, which can be directly used as a binder-free electrode, thereby ensuring high conductivity. The electrode prepared by the 12 h hydrothermal reaction exhibited area capacitance of 4.46 F cm^{-2} at a current density of 5 mA cm^{-2} and excellent cycle stability with 8.6% capacitance loss after 3000 cycles [21]. Zhang et al. reported a new ultrasonic-assisted shearing physical method, prepared a large amount of c-MnO_2 into s-MnO_2 and then deposited MoS_2 composite material magnetron sputtering to form a heterojunction structure in s-MnO_2/MoS_2. The results show that the heterojunction structure in s-MnO_2/MoS_2 exhibits excellent performance, due to it has a large specific surface area and high conductivity. Also, an asymmetrical all-solid supercapacitor based on s-MnO_2/MoS_2 was fabricated. After 3000 charging and discharging processes, its specific capacitance can still maintain 90% of the cycle stability, which can better reflect the actual capacitor performance [22].

Herein, for the application of large-scale Co_3O_4 powder, we propose a novel material packaging method that uses the microwave plasma chemical vapor deposition (MPCVD) method to produce large-scale (~6 μm) Co_3O_4/MoS_2 core–shell composite. Firstly, the precursor was prepared by coating s and $MoCl_5$ on the surface of Co_3O_4 powder by the solution-drying method, and then the vertical sheet MoS_2 nanoshell was synthesized on the surface of Co_3O_4 by one-step MPCVD method. A domestic microwave oven modifies the experimental equipment. Compared with traditional methods, it has many advantages, such as low cost, fast speed, and simple operation. After that, the morphology, composition, and electrochemical performance of the composite materials were analyzed by various methods. The prepared Co_3O_4/MoS_2 composite material has a specific capacitance of 337 F g^{-1} when the current density is 0.5 A g^{-1}. It can still maintain an initial specific capacitance of 93.6% after 2000 cycles of charge and discharge. Finally, the effect of composite microstructure on electrochemical performance is discussed in detail. Our work provides a new possibility and innovation for the efficient utilization of large-scale transition metal oxide powder, especially for the electrode of a supercapacitor with high stability. The response diagram is shown in Fig. 1.

2. Experimental

2.1. Precursor preparation

Firstly, 50 ml of CS_2 solution was introduced into a mortar, and 200 mg of sulfur powder was quickly dissolved in the CS_2 solution. Then mix 200 mg of Co_3O_4 powder in a fully dissolved solution and stir in the air to dry. Because of the volatilization of CS_2, sulfur will be separated during the stirring process and evenly coated on the Co_3O_4 powder surface. After the powder sample was dried entirely, 400 mg of molybdenum pentachloride was dissolved in anhydrous ethanol and dropped into the powder sample for further grinding. Then put the sample into a vacuum drying oven and dissolve it at 60 °C for drying. Finally, the precursor system is ready.

2.2. Co_3O_4/MoS_2 composite material synthesis

The prepared precursor was put into the quartz boat and then into the MPCVD quartz tube's furnace cavity. Firstly, the furnace chamber is pumped to vacuum, and then Ar is injected according to the flow rate of 350 sccm. When the pressure in the furnace cavity is stabilized, the microwave source is turned on to generate plasma, and the sample can

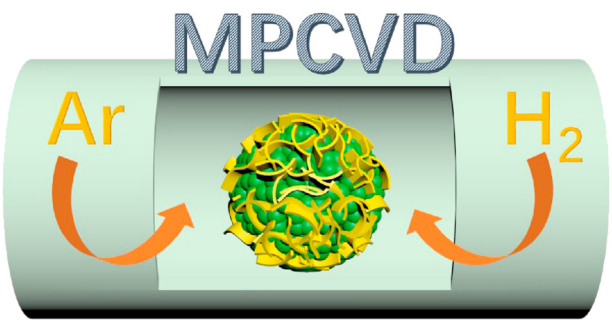

Fig. 1 – Schematic diagram of the coating growth mechanism for the Co_3O_4/MoS_2 composites.

react at 500 °C for 10 min in the Ar plasma. After the reaction, turn off the microwave source and cool the sample to room temperature in the Ar atmosphere. Then turn off the air source and pump to vacuum before taking out the sample.

Under the heating effect of microwave plasma, S reacts with $MoCl_5$ and eventually generates MoS_2 on the surface of Co_3O_4. Simultaneously, free radicals and active groups in microwave plasma can increase reaction and accelerate the reaction rate. The chemical reaction equation for generating molybdenum disulfide is as follow:

$$2MoCl_5 + 4S \rightarrow 2MoS_2 + 5Cl_2 \quad (1)$$

2.2. Characterization method

The field emission scanning electron microscopy (FE-SEM, JSM-7800F, JEOL, Japan) was employed to observe the samples' morphology. The microstructure of the sample was expressed over the range 20°–90° by X-ray diffraction spectrum (XRD, X'Pert3 Powder, Panalytical, Netherland), Cu Kα radiation (λ = 1.5418 Å). The X-ray photoemission spectroscopy (XPS, Kratos Analytical Ltd., U.K.) was used to exhibit the samples' elemental composition and valence state.

2.3. Fabrication of electrodes and performance measurement

The electrode's preparation process was as follows: firstly, the prepared active material, acetylene black and polyvinylidene fluoride were mixed in a ratio of 8:1:1, and then ground into slurry after adding NMP. After that, the slurry was coated on the ultrasound-treated nickel foam substrate (1 cm × 1 cm) and dried in a vacuum oven at 60 °C for 8 h. The mass of active substance on the nickel foam collecting fluid should be higher than 1 mg cm^{-2}.

The working electrode, Pt counter electrode, and Hg/HgO reference electrode constitute a three-electrode system. Cyclic voltammograms (CV), galvanostatic charge/discharge (GCD), and cycle life were tested in 6 mol/L KOH electrolyte.

3. Result and discussion

SEM analyzed the surface structure of the composite. Fig. 2a and b shows the SEM images of the raw Co_3O_4 and Co_3O_4/MoS_2 powder, raw Co_3O_4 is a spherical powder with a diameter of about 6 μm and is composed of small particles with a diameter of about 300 nm. Moreover, there are small pores between the tiny particles. When the surface of Co_3O_4 powder is coated with MoS_2 shell through experiments, the morphology of composite powder becomes the appearance in Fig. 2b. The powder's surface is covered with an upright lamellar structure, namely the MoS_2 shell that we synthesized on the surface of Co_3O_4. It can be observed from the specific surface area of the powder significantly increases after the flake MoS_2 coated, which provides much more active sites for the energy storage, enabled the material to carry out the redox reaction more thoroughly, thus improving the electrochemical performance. Element mapping was used to analyze the distribution of elements in the Co_3O_4/MoS_2 composite and the mapping results of the illustration in Fig. 2b is shown in Fig. 2c-f. It is observed that the elements of Mo, S, Co, and O are evenly distributed. Thus, we can confirm that the MoS_2 layer is uniformly wrapped on the surface of Co_3O_4.

To verify the composite material's composition, the sample of Co_3O_4/MoS_2 composite material was tested by X-ray diffraction to analyze its composition and crystal structure. Fig. 3 shows the XRD pattern of Co_3O_4/MoS_2 composite powder in the scanning range of 10–90°. The results showed that the samples were mainly composed of three components: the diffraction peaks at 14.3° and 39.6° were corresponding to the (002) and (103) crystal planes of MoS_2 (JCPDS: 37-1492). Moreover, the diffraction peaks at 31.3°, 36.8°, 44.8°, 59.3°, and 65.2° correspond to the (220), (311), (400), (511) and (440) crystal

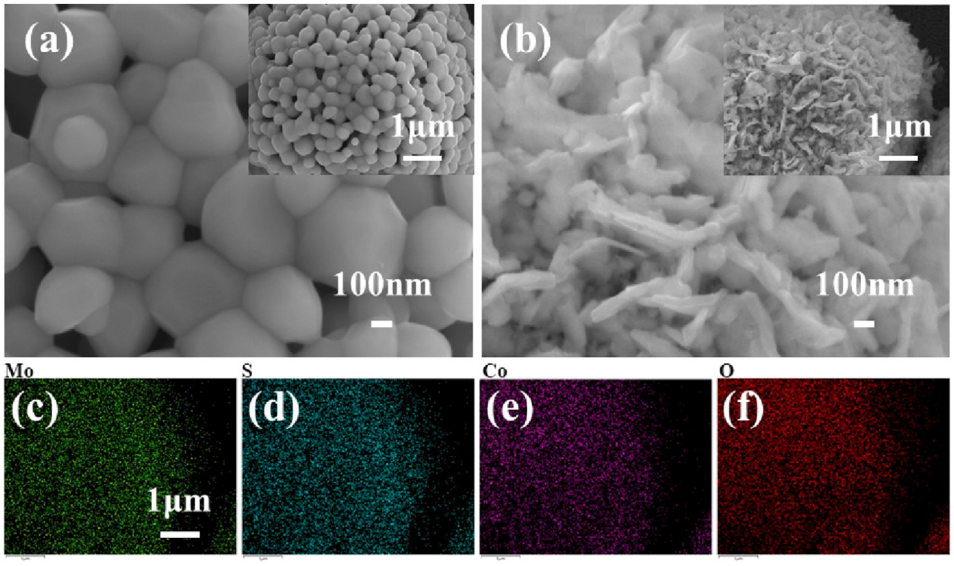

Fig. 2 – SEM images of raw Co_3O_4 powder (a), Co_3O_4/MoS_2 composite (b), and the corresponding element mappings of molybdenum (c), sulfur (d), cobalt (e) and oxygen (f).

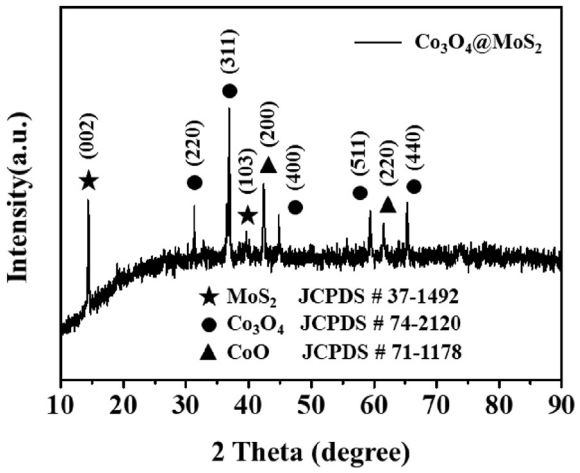

Fig. 3 – (a) XRD pattern of the Co_3O_4/MoS_2 composite.

planes of Co_3O_4 (JCPDS: 74-2120). Furthermore, the remaining diffraction peaks at 42.4° and 61.5° were consistent with the (200) and (220) crystal planes of CoO (JCPDS: 71-1178). The XRD diffraction peaks proved that MoS_2 nanosheet was successfully generated on the surface of spherical Co_3O_4 powder. On the other hand, the presence of CoO in the composite may be due to the collision of active groups in the microwave plasma, which accounts for only a small fraction of the composition.

X-ray photoelectron spectroscopy is another essential method to analyze the composition of materials. The XPS spectra of the Co_3O_4/MoS_2 composite is exhibited in Fig. 4. The result shows the presence of molybdenum, sulfur, cobalt, and oxygen elements. Firstly, the spectrum of Co 2p is shown in Fig. 4a, which shows two dipoles with a binding capacity of 779.3 eV and 795.4 eV, corresponding to the spin–orbit coupling levels of Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively [23–25]. Secondly, Fig. 4b shows the combined energy spectrum of O 1s, where the peak value of 529.9 eV can be attributed to the surface lattice O^{2-} of the metal oxide. Besides, the peak value of 531.1 eV corresponds to the adsorption of oxygen and hydroxyl. These results confirm that Co_3O_4 is the primary cobalt source in the composite rather than CoO. Fig. 4c shows the Mo 3d spectrogram of the composite material, which has three peaks corresponding to Mo and S species existing in the sample. The peaks at 233.05 and 229.9 eV are Mo $3d_{3/2}$ and Mo $3d_{5/2}$ binding energies, respectively. These peaks can be attributed to the Mo^{4+}, which confirms MoS_2 nanowires' formation. The peak at 227.05 eV can be attributed to the S element's 2s binding energy in MoS_2. Finally, the high-resolution S 2p spectrum shows the analytical peaks at 161.9 eV and 163.3 eV in Fig. 4d, which can correspond to the spin orbits of S $2p_{3/2}$ and S $2p_{1/2}$, respectively. These binding energies are consistent with the other reported MoS_2 crystal data [26,27].

The electrochemical properties of the Co_3O_4/MoS_2 composite were evaluated by three-electrode electrochemical tests in the range of 0–0.4 V potential. Fig. 5a shows cyclic voltammetry (CV) curves of Co_3O_4/MoS_2 composites at different scanning rates (5–100 mV s^{-1}). As can be seen from the figure, with the increase of the scanning rate, the CV curve of the composite material shows a strong current response, indicating that the Co_3O_4/MoS_2 composite material has excellent capacitance characteristics. CV curve has a large deviation from the rectangle, and there are obvious redox peaks. It reflects that the redox reaction occurred in the charging and discharging process, and the composite has typical pseudocapacitance property. Simultaneously, when the electron flow rate is greater than the reaction rate, the polarization effect will be generated. With the increase of the scanning rate, the CV curve will move the anode peak to the direction of high potential and the cathode peak to low potential [28]. Other literature has reported similar curve shapes [29–31]. Compared with the CV curve of raw Co_3O_4 material, as shown in supporting information Fig. S1, its effective area has been significantly increased, which proves that the specific capacitance of the material has been greatly improved. According to the report, the redox reaction peak in Fig. 5a corresponds to the redox reaction of Co_3O_4 and MoS_2 with OH^- in electrolyte. The Co_3O_4 reaction equations were as follows:

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^- \quad (2)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (3)$$

And according to recent reports by Barik et al. [32,33], MoS_2 may react with the electrolyte as follows:

$$MY_x + OH^- \leftrightarrow MY_xOH + e^- \quad (4)$$

$$MY_xOH + OH^- \leftrightarrow MY_xO + H_2O + e^- \quad (5)$$

Where MY_x is layered sulfide and non-layered sulfide (including: MoS_2, WS_2, FeS_2, etc.). Fig. 5b displays the galvanostatic charge/discharge (GCD) test results of Co_3O_4/MoS_2 composite powder with different current densities in KOH solution (6m) at 0–0.4 V (relative to SCE). These curves have distinct slopes at different current densities. Therefore, the material exhibits typical pseudocapacitance characteristics. Moreover, compared with the GCD curve of raw Co_3O_4 (shown in supporting information Fig. S2), the discharge time at the same current density is significantly prolonged, which confirms the increase of material capacitance and is consistent with the test results in Fig. 5a. Formula $C = It/\Delta Vm$ was used to calculate the specific capacitance at different current densities. I is the discharge current, t is the total discharge time, ΔV is the potential drop in the discharge process, and m was the mass of Co_3O_4/MoS_2. The calculated results are shown as well as the specific capacitance of raw Co_3O_4 and coulombic efficiency of Co_3O_4/MoS_2 in Fig. 5c. When the current density is 0.5, 1, 2, 5 and 10 A g^{-1}, the specific capacitance of the Co_3O_4/MoS_2 composite material is 337, 335, 332, 320.5 and 310.3 F g^{-1}, and the coulomb efficiency is 97.48%, 98.12%, 98.57%, 99.12% and 99.45%, respectively. However, when the current density is the same, the original Co_3O_4 material's specific capacitance is only 53.25, 46.25, 41.25, 37.5, and 33.5 F g^{-1}, respectively. The data showed that by coating the Co_3O_4 powder with an outer layer of MoS_2, the material's specific capacitance increased more than six times. Besides, cyclic stability is another important property of electrode materials for supercapacitors. Finally, the cyclic stability of Co_3O_4/MoS_2 composite material, 2000 charge, and discharge cycles were performed at the current density of 10 A g^{-1}. The cyclic test results are shown in

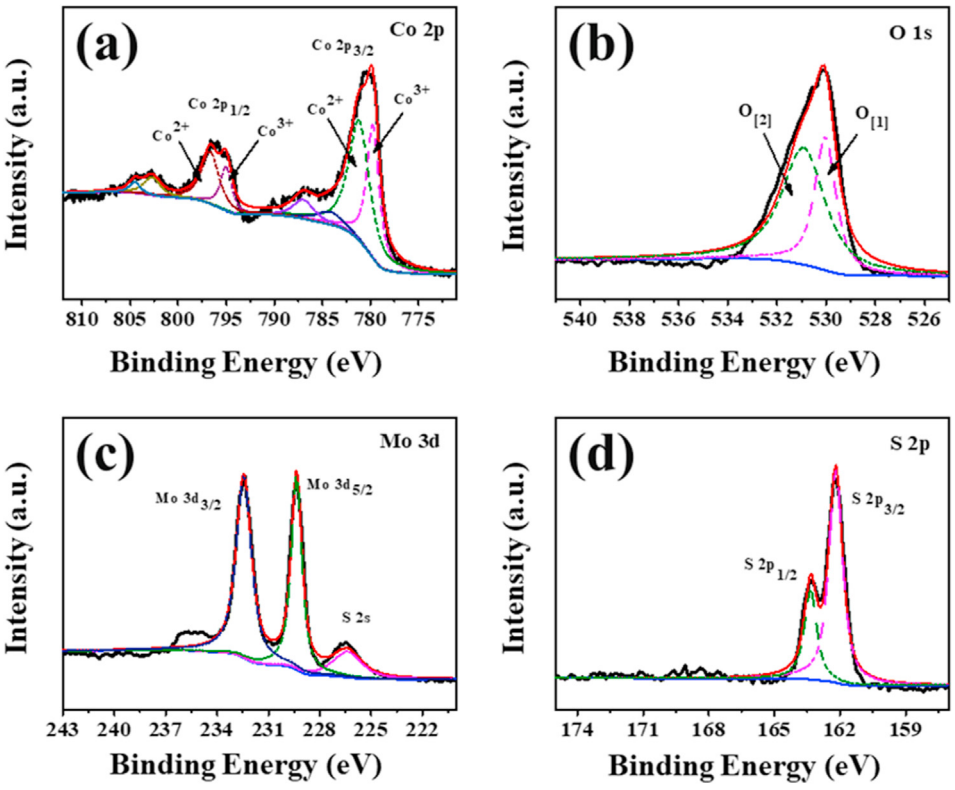

Fig. 4 – XPS survey spectra of Co_3O_4/MoS_2 composite; (a) Co 2p; (b) O 1s; (c) Mo 3d; (d) S 2p.

Fig. 5d. Moreover, it indicated that after 2000 cycles of charging and discharging, the material's specific capacitance is still 93.6%, so it has excellent cycle stability and long service life.

Through experiments and data analysis, Co_3O_4/MoS_2 with a core–shell structure has several times more noticeable performance improvement than the original Co_3O_4 powder. We analyze that this is not only due to the mechanical

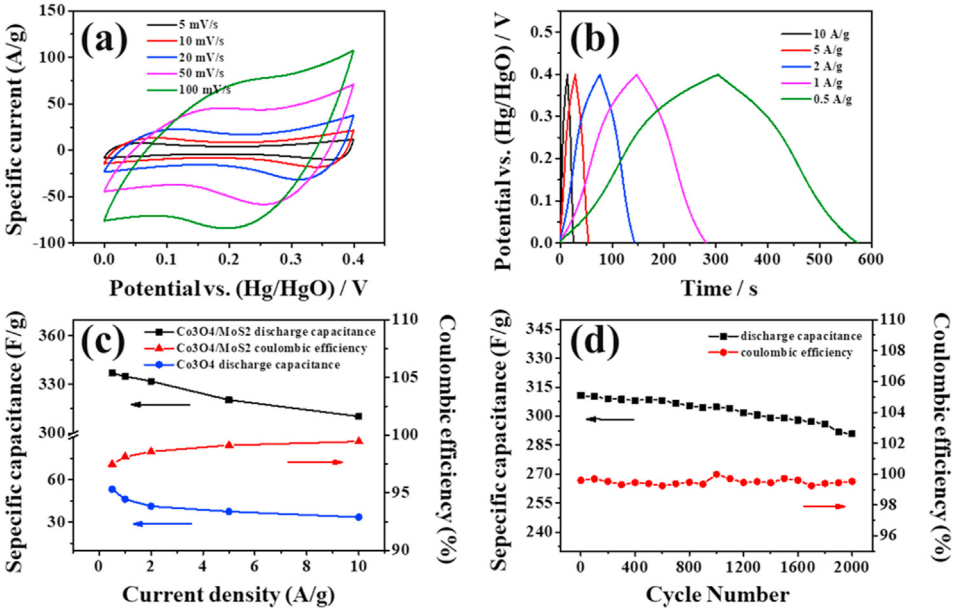

Fig. 5 – (a) CV curves of the Co_3O_4/MoS_2 composite at different scan rates; (b) Galvanostatic charge–discharge curves of the Co_3O_4/MoS_2 composite at various current densities; (c) Specific capacitance and Coulomb efficiency of Co_3O_4/MoS_2 composites at different current densities, and comparison with a specific capacitance of Co_3O_4 raw materials; (d) Capacitance retention of the Co_3O_4/MoS_2 composite electrodes after 2000 cycles at a current density of 10 A g^{-1}.

combination of Co_3O_4 and MoS_2, but also due to the following mutual enhancement effect:(a) The MoS_2 nanowires on Co_3O_4 shorten the transport/diffusion path of electrons and ions, resulting in a faster kinetic. (b) The lamellar structure of MoS_2 and the weak van der Waals interaction between layers facilitate the adsorption and desorption of electrons and provide a full reaction surface and a larger internal space, promoting the sufficient contact between active substances and electrolytes. (c) In charging and discharging, the outer layer of the MoS_2 nanometer sheet can buffer the volume expansion of Co_3O_4 powder inside. Therefore, the electrochemical properties of Co_3O_4/MoS_2 composites have been improved significantly.

4. Conclusions

In summary, Co_3O_4/MoS_2 core–shell composites with high electrochemical properties were prepared through a simple one-step MPCVD method by wrapping the MoS_2 nanometer sheet on the surface of spherical Co_3O_4 powder. The experiment equipment is refitted by the household microwave oven, which is simple to operate, low cost, short time consuming, and has a remarkable effect. A series of tests and analyses confirmed that the vertical flake MoS_2 nanometer sheet layer was synthesized on Co_3O_4 powder's surface and its surface morphology, composition structure, elemental valence state, and electrochemical performance were studied. The test results show that the specific capacitance of the Co_3O_4/MoS_2 composite material can reach 337 F g^{-1} at the highest, with excellent multiplier performance and cycle stability. It could maintain 93.6% of the initial specific capacitance after 2000 following charges and discharges. Finally, according to the test results, the composite material's performance improvement compared with the raw material is analyzed. This paper presents an idea of combining extensive particle powder with nanometer sheet material, which can achieve high specific capacitance and maintain excellent cycling stability.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled "Efficient and inexpensive MPCVD method to synthesize Co_3O_4/MoS_2 heterogeneous composite materials with high stability for supercapacitors".

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2020.12.101.

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