



Mesoporous Co_3O_4 anchored on the graphitic carbon nitride for enhanced performance supercapacitor

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ABSTRACT

The Co_3O_4 anchored on the graphitic carbon nitride ($\text{g}-\text{C}_3\text{N}_4$) was fabricated via a facile co-precipitation method with MOFs/ $\text{g}-\text{C}_3\text{N}_4$ as precursor. The as-prepared $\text{Co}_3\text{O}_4/\text{g}-\text{C}_3\text{N}_4$ composite delivers a high specific capacitance of 780 F g^{-1} at the current density of 1.25 A g^{-1} in 2 M KOH solution and the capacitance value retain 80% after 1000 cycles with the current density of 3 A g^{-1} . The capacitance of $\text{Co}_3\text{O}_4/\text{g}-\text{C}_3\text{N}_4$ composite is much greater than the bare Co_3O_4 with 419 F g^{-1} at the current density 1.25 A g^{-1} . The investigation suggests that the excellent performance of capacitance may be assigned to as-prepared $\text{Co}_3\text{O}_4/\text{g}-\text{C}_3\text{N}_4$ composite, which could be a potential and outstanding electrode material in electrochemical energy storage devices.

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1. Introduction

Recently, supercapacitors as energy storage devices have attracted much attention for its promising properties, such as greater power density, longer cycling life, faster recharge capability, friendly environmental features and so on [1–3]. According to the charge storage mechanism, supercapacitors can be divided to two groups with electrical double layer capacitors (EDLCs) and faradaic pseudocapacitors. The faradaic pseudocapacitors offer much greater capacitance than the EDLCs because of their feature of large capacitance and fast redox kinetics [4,5]. To date, numerous efforts have been made to research the pseudocapacitors based on transitional metal oxides due to their variable valence for pseudocapacitance generation [6–8].

Among several transitional metal oxides, cobalt oxide (Co_3O_4) has been defined as an outstanding candidate for supercapacitor materials due to the advantages of the environmental friendliness, natural abundance and high theoretical specific capacitance (3560 F g^{-1}). However, influenced by the intrinsic low electrical conductivity and the limited diffusion distance of electrolytes into pseudocapacitor electrode, the capacitance was only contributed to the part of the surface active sites in electrode materials. Thus, in

order to enhance the capacitance of Co_3O_4 , three effective strategies are usually performed: Firstly, design and synthesis of hierarchical nanostructures with large surface area, such as nanowires, nanocubes, nanotubes, nanosheets and so on [9–12], which could greatly enhance the activities of materials. Secondly, the current collectors were used as substrate, and the materials were directly grown upon the substrate, which can avoid the uses of binder and increase the active site in the materials [13–15]. Thirdly, preparation of nanocomposites, such as combination with carbon material, metal or metal oxides, which may increase the electrical conductivity to enhance their pseudocapacitance value [15–21].

To the best of our knowledge, carbon materials are regarded as a promising modifier with the advantage of the large surface area, good electron transport and excellent chemical stability. Thus, some carbon materials, including porous carbon, graphene and graphene oxide, have been introduced into Co_3O_4 to assemble nano-composite with enhanced the capacitive performance of Co_3O_4 [15–18,22]. For instance, Zheng et al. prepared hierarchical N-doped carbon with Co_3O_4 nanoarrays by lyophilization method, which shown a high specific capacitance of 978.9 F g^{-1} with a current rate of 0.5 A g^{-1} [4]. Fan prepared a ultrathin Co_3O_4 nano-sheet array on 3D porous graphene/nickel foam with a high specific capacitance of 3533 F g^{-1} at a current rate of 1 A g^{-1} [15]. All of the listed nano-composited Co_3O_4 materials show obviously better electrochemical performance compared to the corresponding to Co_3O_4 itself. The reason was speculated that the incorporation of

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carbon materials into Co_3O_4 can greatly improve the conductivity and ultimately reduce the volume change effect, so it can promote the rate of faradaic reaction and the penetration to the electrolytes in catalytic process.

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a layered structure, similarly to the structure of graphene, and possesses a strong chemical stability, large surface area and rich diversity of hierarchical nano-structures [23–25]. All of these features are considered as a preferred material for green carrier in catalysis field. In addition, up to now, the research of nano-composite between Co_3O_4 and $g\text{-C}_3\text{N}_4$ is almost blank in supercapacitor application. Therefore, inspired by based on discovery, $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ nano-composite was obtained by chemical coprecipitation method using MOFs/ C_3N_4 as precursor. The resulted $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ composite exhibits a high specific capacitance of 780 F g^{-1} at the current density of 1.25 A g^{-1} , which is significantly larger than the pure Co_3O_4 with 419 F g^{-1} at the same current density, indicating the incorporation of $g\text{-C}_3\text{N}_4$ into Co_3O_4 can greatly enhanced the capacitance performance.

2. Experimental section

2.1. Materials

The $g\text{-C}_3\text{N}_4$ was prepared through the method of literature [26], and all of the other chemical reagents were commercially purchased and used as received without further purification.

2.2. Preparation of Co_3O_4

1,2,3,4,5,6-cyclohexanhexacarboxylic acid (1.0 mmol) was added to a stirred aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) in 15.0 mL H_2O to form a clear light-red solution. Then the mixture solution was followed by the dropwise addition of 1.6 mL tetramethylammonium hydroxide, which produced a pink emulsion at first, and then the suspension has been gradually resolved to form perse solution. The solution was allowed to stand at room temperature to obtain a purple-black gelatinous substance. The gel-substance was heated from 30°C to 400°C in furnace with a heating rate $1^\circ\text{C} \cdot \text{min}^{-1}$ and maintained at 400°C for 2 h to obtain black powder Co_3O_4 .

2.3. Preparation of $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$

A procedure similar to that of Co_3O_4 was applied to prepare $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ except that the resulted perse solution has been added 30 mg $g\text{-C}_3\text{N}_4$ and stirred for 10 min to form dark-green suspension. The resulting mixture was allowed to slowly evaporate to give blackish-green gels. The gels were placed in a muffle and heated at 400°C for 2 h in air with a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$ to produce black $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ particles.

3. Results and discussion

Fig. 1 shows the XRD pattern of the graphitic carbon nitride, Co_3O_4 and Co_3O_4 /graphitic carbon nitride composite. The peaks of carbon nitride presented a sharp diffraction peak centered at 27.5° , corresponding to a characteristic peak (002), which can be ascribed to the interlayer stacking of aromatic systems in graphitic carbon nitride [27]. For the XRD patterns of Co_3O_4 , the diffraction peaks located at 31.2° , 36.7° , 44.8° , 59.2° and 65.1° can be easily indexed to the (220), (311), (400), (511) and (440) planes in the standard Co_3O_4 pattern [28]. Besides, the diffraction peak of Co_3O_4 /graphitic carbon nitride composite at 27.7° can be attributed to the (002) plane of graphitic carbon nitride, indicated that the graphitic carbon nitride has been successfully existed in composite.

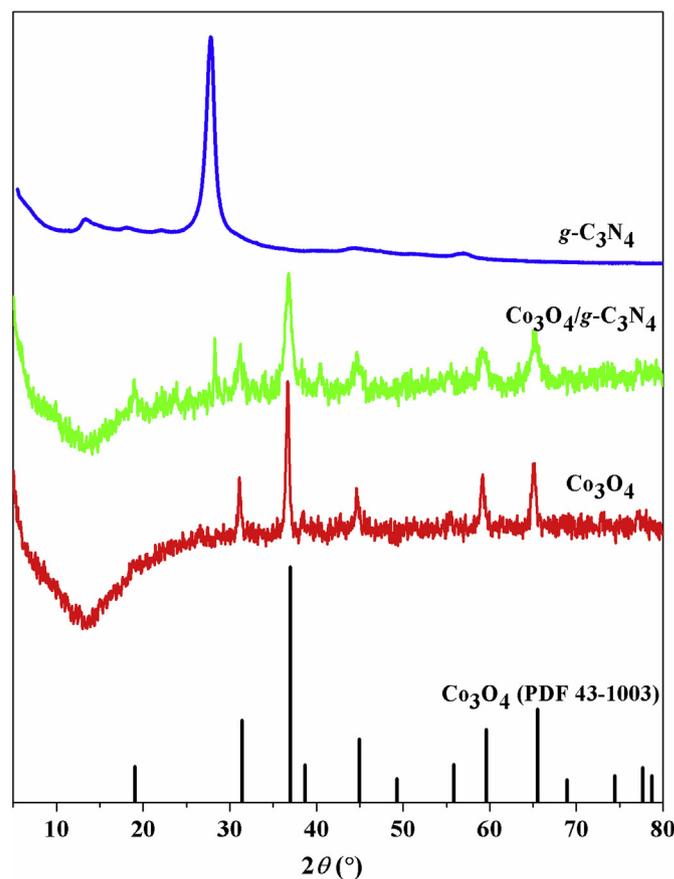


Fig. 1. XRD patterns of $g\text{-C}_3\text{N}_4$, Co_3O_4 and $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ composites.

The FT-IR spectra further confirm the presence of graphitic carbon nitride in Co_3O_4 /graphitic carbon nitride composite as shown in Fig. 2. For graphitic carbon nitride, the broad band at 3165 cm^{-1} was attributed to the stretching mode for the group of $-\text{NH}$ or $-\text{NH}_2$. The $\text{C}=\text{N}$ stretching vibration resulted in a strong absorption peak at 1648 cm^{-1} and the s -triazine ring vibration mode was absorption at 808 cm^{-1} . However, as regard to the $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ composite, the peak at 3329 cm^{-1} and 3170 cm^{-1} may assign to the $\text{O}-\text{H}$ bands and $\text{N}-\text{H}$ group, which associated with a larger of surface-absorbed H_2O molecules and uncondensed amino groups. The bands peak at 1641 cm^{-1} can be corresponding to the $\text{C}=\text{N}$ stretching vibration mode of $g\text{-C}_3\text{N}_4$, and the stretching vibration mode of $\text{Co}-\text{O}$ bond of Co_3O_4 were verified at 660 and 569 cm^{-1} , respectively, indicating the surely presence of graphitic carbon nitride and Co_3O_4 in composite, and the spectra information agrees well with the X-ray diffraction analyses described above.

Moreover, to further confirm the chemical state of the elements in the composites of Co_3O_4 and $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ composite, the x-ray photoelectron spectroscopy (XPS) measurement was performed. The Co 2p XPS spectra as shown in Fig. 3 indicates two main binding energy band at 780.6 eV (Co 2p_{3/2}) and 796 eV (Co 2p_{1/2}) with two shakeup satellite peaks at 786.6 and 802.4 . In comparison to the XPS peak of $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ composite, the shift of the corresponding Co 2p_{3/2} and Co 2p_{1/2} peak of $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ to 781.0 and 796.8 eV , respectively, implied the strong interactions between Co_3O_4 and graphitic carbon nitride. The peak O 1s at 529.7 eV corresponds to the typical metal-oxygen bond and the peak at 531.9 eV are the defects with low oxygen. The high peak area ratio of peak $531.9 \text{ eV}-529.7 \text{ eV}$ for Co_3O_4 and $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4$ composite is significantly different other O 1s XPS spectra of Co_3O_4 in

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