Hierarchical macro- and mesoporous assembly of metal oxide nanoparticles derived from metal-organic complex

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ARTICLE INFO

ABSTRACT

The hierarchical porous metal oxide combines the advantages of each class of hierarchical pores and has potential applications in different fields. Here we proposed an emulsion-calcination route for producing porous metal oxide. The porous metal-organic complex was first synthesized in CO_2-in-water emulsion, then the metal-organic complex was calcined to remove the organic linker and form porous metal oxide. The hierarchical macro- and mesoporous assemblies of Co_3O_4 nanoparticles were produced. The hierarchical macro- and mesoporous assemblies of Co_3O_4 nanoparticles were produced, with the macropores in size of hundreds of nanometers and the mesopores in 9−15 nm. The porosity properties and nanoparticle size of Co_3O_4 can be modulated by controlling CO_2 pressure. The as-synthesized Co_3O_4 is an excellent candidate catalyst for the methylene blue degradation. By taking advantages of the high porosity and small particle size, the Co_3O_4 have potential applications in catalysis, gas separation, and controlled drug release. The strategy proposed in this work can be applied to the synthesis of different kinds of porous metal oxides.

1. Introduction

Porous metal oxides with controlled morphology have shown application potential in catalysis, energy storage, conversion and gas sensing, owing to their large surface area, relatively mass reactive sites and good mass-transfer property [1,2]. Particularly, it is appealing to synthesize hierarchical porous metal oxides because such structures combine the advantages of each class of hierarchical pores, e.g. ultrahigh mass loading [3] and good mass transfer of macropores [4,5], good electronic [6], magnetic and catalytic properties of mesopores [4,7]. Diverse methods have been proposed for fabricating porous metal oxides, including template method [8], sol−gel processing [9], solvothermal technique [7,10], electrophoretic deposition method [11], nanocasting [12−14], and calcination from different precursors. Among these strategies, the calcination method has attracted much attention due to the easy control of process conditions, particle size, particle crystal structure and product purity. The commonly used precursors for producing porous metal oxides are metal oxalate [15], alkoxide [16], hydroxide [17], carbonate [18], inorganic-organic hybrid [19], and metal-organic framework [20,21].

Emulsion has been widely used in the preparation of porous polymers [22−24]. In general, water and oil are used as the two immiscible solvents for forming emulsions. Cooper et al. developed a CO_2-in-water emulsion (C/W emulsion) templating route for the synthesis of porous polymers [25−29]. In comparison with the traditional oil-in-water emulsions, the C/W emulsions have many advantages [30−35]. For example, the removal of the droplet phase is simple because CO_2 can revert to the gaseous state upon depressurization, which makes the post-process easier. Moreover, the emulsion properties can be modulated by controlling the pressure of CO_2. In addition, compressed CO_2 is a sustainable solvent because it is nontoxic, inexpensive, and non-flammable [36−43].

Here we proposed a C/W emulsion-calcination route for producing porous metal oxide. The porous metal-organic complex was first synthesized in C/W emulsion, followed by the calcination to remove the organic linker and form metal oxide. By this strategy, the hierarchical macro- and mesoporous Co_3O_4 and Mn_2O_3 were produced, with the macropores in size of hundreds of nanometers

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and the mesopores in 9−15 nm. Interestingly, the hierarchical macro- and mesoporous metal oxide is constructed by small nanoparticles (7−18 nm). The particle size and porosity properties of the metal oxides can be easily adjusted by CO_2 pressure. The combination of a hierarchical porous structure and small particle size makes the as-synthesized metal oxide excellent candidate catalyst for chemical reactions.

2. Experimental section

2.1. Materials

CO_2 (>99.95%) was provided by Beijing Analysis Instrument Factory. Pluronic F88 ($EO_{103}PO_{39}EO_{103}$) was a gift from BASF. $CoCl_26H_2O$ (99%) was provided by Tianjin Zongheng Industry and Trade Co., Ltd. 4,4′-(hexafluoroisopropylidene) bis(benzoic acid) (98%) and 3-methyl pyridine (98.5%) were purchased from J&K scientific Co., Ltd. Methylene blue was produced by TCI (>70% purity). $MnCl_2$ was purchased from Alfa Aesar. All these materials were used without further purification.

2.2. Metal oxide synthesis

For the Co_3O_4 synthesis, a desired amount of F88 was added into water (14 mL), which was loaded in a stainless-steel view autoclave (50 mL). Then $CoCl_2·6H_2O$ (0.1713 g), 4,4′-(hexafluoroisopropylidene) bis(benzoic acid) (0.392 g) and 3-methyl pyridine (1 mL) were added into the autoclave equipped with a magnetic stirrer. CO_2 was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at 30 °C for 48 h, the stirrer was stopped and CO_2 was released. The product was obtained after washing with ethanol for several times and drying at 30 °C under vacuum for 24 h. Then the metal-organic complex underwent thermolysis with a heating rate of 3.33 °C/min from room temperature to 400 °C in 2 h. After reaching the target temperature, the material was calcined for 2 h and then naturally allowed to cool down to room temperature. For the Mn_2O_3 synthesis, F88 (2.1 g), H_2O (14 mL), $MnCl_2$ (0.0906 g), 4,4′-(hexafluoroisopropylidene) bis(benzoic acid) (0.392 g) and 3-methyl pyridine (1 mL) were added into the autoclave. The other experimental conditions are the same with those for Co_3O_4 synthesis.

2.3. Characterization

The morphologies of metal oxides were characterized by scanning electron microscope (SEM, HITACHI S-4800), transmission electron microscope (TEM, JEOL JEM-1011) and Field Emission Transmission Electron Microscopy (JEOL JEM-2100F). X-ray diffraction (XRD) was performed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 200 mA. The porosity properties were gained from nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 2020 (M + C) system. The FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer. The thermogravimetric measurements were carried out using HITACHI-STA 7300 with air flow of 100 mL/min.

2.4. Photocatalytic test

The catalytic experiment was carried out in a 100 mL glass flask containing an aqueous MB solution (2 mg/L, 50 mL) and Co_3O_4 (1.2 mg) at room temperature. The solution was stirred with a magnetic stirrer in dark for 30 min to establish adsorption equilibrium between the solution and the catalyst before exposure to the irradiation of a 100 W Tungsten Halogen Lamp consisting of visible light spectrum. The light irradiation experiment was conducted after adding H_2O_2 (100 mM). 1 mL MB aqueous solution was filtered out from the reactor vessel at different time intervals. The UV−vis adsorption spectrum of the filtered solution was measured using a spectrophotometer (Shimadzu, UV-2550), and the MB concentration was estimated by the absorbance at a wavelength of 664 nm. The variation of the relative concentration of the remaining MB in solution vs irradiation time was obtained from the optical absorbance at 664 nm. The MB degradation ratio was determined by $(1-[A/A_0])$ where A_0 is the absorbance at t = 0 and A is the absorbance at given reaction time.

2.5. Adsorption test

The adsorption experiment was carried out in a 100 mL glass flask containing an aqueous MB solution (2 mg/L, 50 mL), H_2O_2 (100 mM) and Co_3O_4 (1.2 mg) at room temperature. The Co_3O_4 is synthesized at CO_2 pressure of 10.65 MPa. The solution was stirred with a magnetic stirrer in dark. 1 mL MB aqueous solution was filtered out from the reactor vessel at different time intervals. The UV−vis adsorption spectrum of the filtered solution was measured using a spectrophotometer (Shimadzu, UV-2550), and the MB concentration was estimated by the absorbance at a wavelength of 664 nm. The variation of the relative concentration of the remaining MB in solution vs irradiation time was obtained from the optical absorbance at 664 nm. The MB adsorption rate was determined by $(1-[A/A_0])$ where A_0 is the absorbance at t = 0 and A is the absorbance at given time.

3. Results and discussion

Co_3O_4 has received an increased research interest in a wide range [44,45] because of its excellent electrochemical [46], semiconductor [47], and magnetic properties [48], etc. The procedure for synthesizing porous Co_3O_4 is illustrated in Fig. 1. The foam emulsion was prepared (Fig. 1b) by charging compressed CO_2 into 15 wt% F88 aqueous solution (Fig. 1a) under stirring. The surfactant F88 was used to stabilize the C/W emulsion. The purple metal-organic complex was obtained in the foam emulsion from the reaction of $CoCl_2·6H_2O$ with ligand 4,4′-(hexafluoroisopropylidene) bis(benzoic acid) (H_2hfbba) and coligand 3-methyl pyridine (3-mepy) (Fig. 1c) [49,50]. Then the metal-organic complex was calcined at 400 °C for 2 h to remove the organic linkers and obtain the cobalt oxide (Fig. 1d), based on the thermogravimetric analysis (Fig. S1).

Fig. 2 shows the XRD pattern of the cobalt oxide synthesized at 10.65 MPa. The diffraction peaks correspond to spinel-type Co_3O_4 (JCPDS Card No. 43−1003). No impurity diffraction peaks from other cobalt oxides like CoO and Co_2O_3 were observed, indicating the product is composed of pure Co_3O_4. The FT-IR spectra provide further evidence for the formation of Co_3O_4 (Fig. S2).

The morphologies of the Co_3O_4 were characterized by SEM and TEM images (Fig. 3 and Fig. S3). Clearly, Co_3O_4 presents a morphology of rectangle plate (Fig. 3a and Fig. S3). From Fig. 3b, it can be seen that the Co_3O_4 plates are highly porous, with a macrocellular structure. The macropore size is as large as hundreds of nanometers. The TEM image further proves that the Co_3O_4 adopts a macroporous structure (Fig. 3c and d). From the magnified TEM images, it is evident that the Co_3O_4 plate is composed of small nanoparticles about 7 nm, forming mesopores about 10 nm (Fig. 3e and f).

High-resolution TEM (HRTEM) observation was carried out to study the crystal orientation of the synthesized Co_3O_4. As shown in Fig. 4, a set of {111} planes with a lattice space of 0.46 nm, a set of {220} planes with a lattice space of 0.29 nm, a set of {222} planes with a lattice space of 0.23 nm and a set of {331} planes with a