Ordered Mesoporous Carbon Embedded with Cu Nanoparticle Materials for Electrocatalytic Synthesis of Benzyl Methyl Carbonate from Benzyl Alcohol and Carbon Dioxide

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ABSTRACT: We prepared a series of ordered mesoporous carbons embedded with different contents of Cu nanoparticles (Cu/OMC-X) and applied them to electrocatalytic synthesis of benzyl methyl carbonate. The materials were characterized by many measurements, which showed that Cu/OMC-X materials maintain highly ordered mesoporous structures with high surface area and highly dispersed Cu nanoparticles. As expected, the materials exhibit good electrocatalytic performance. The optimal yield of benzyl methyl carbonate reaches 69.7% on Cu/OMC-3.

INTRODUCTION

Carbon dioxide (CO₂) is considered as the main contributor to greenhouse gases. At the same time, it is a cheap, nontoxic, and recyclable carbon source, so that considerable attention has been focused on the fixation and utilization of CO₂.¹,² From that we can not only improve energy efficiency, reduce greenhouse gas emissions, and air pollution to achieve a virtuous cycle of energy utilization, but also can synthesize important chemical products.³−⁷ Electrocarboxylation is an effective method for fixing CO₂, which could synthesize organic carbonates and organic carboxylates by combining CO₂ with epoxides,⁸ aldehydes,⁹ ketones,¹⁰,¹¹ olefins,¹²−¹⁴ alkenes,¹⁵ halides,¹⁶−¹⁸ alcohols,¹⁹,²⁰ and so on. In the previous investigations of electrochemical synthesis of aromatic carbonates, Pt,²¹ Hg,²² and Cu¹⁹ are normally used as cathodes. Among them, Cu is the most recommended, as Pt is a noble metal and Hg is a toxic metal. Yamamoto et al.²³ examined various metals including Cu supported on activated carbon fibers as electrocatalyst, which all show high current density and selectivity compared to the planar electrodes. Thus, dispersing the metal on a high surface area support could well result in increasing the activity of the electrocatalyst.

Ordered mesoporous carbon (OMC) has attracted much attention as the substrate for metal nanoparticles and metal oxide nanoparticles.²⁴−²⁷ Compared with traditional carbon material, it has high specific surface area, large pore volume, uniform and adjustable pore size, and regularly arranged pore structure, so that the nanoparticles can be highly dispersed on its surface and it can facilitate mass transfer of reactants and products.²⁸−³² Moreover, its good conductivity makes it an excellent candidate for electrode materials.

In this paper, we prepared the OMC embedded with Cu nanoparticles (Cu/OMC) by a simple one-pot method using phenolic resins as the carbon source, triblock copolymer Pluronic F127 as the template, Cu(NO₃)₂·3H₂O as the metallic precursor, and acetylacetone as the coordination agent. The Cu/OMC composites were applied in electrosynthesis of benzyl methyl carbonate from benzyl alcohol and CO₂ which exhibits high electrocatalytic activity.

RESULTS AND DISCUSSION

Characterization of Cu/OMC. A series of Cu/OMC materials were prepared by a one-pot synthesis process (see the Experimental Section for details). The wide-angle X-ray diffraction (XRD) patterns of Cu/OMC with different Cu contents are shown in Figure 1A. The broad diffraction peak at 2θ = 20−28° is a characteristic reflection of amorphous carbon. All curves except curve f have diffraction peaks at 2θ = 43.3, 50.4, and 74.1°, which correspond to the (111), (200), and (220) reflections of Cu with the face-centered cubic structure according to the JCPDs card no. 04-0836. It means that the Cu precursor was completely reduced to metallic Cu.
during the carbonization.\textsuperscript{33} According to the Scherrer equation, the sizes of the Cu nanoparticles are 17–30 nm for Cu/OMC-X.

Small-angle XRD diffraction was utilized to obtain the structural information of the composites. Figure 1B shows small-angle XRD patterns of OMC and Cu/OMC-X, in which a diffraction peak of 2θ at about 1.0° can be observed. It illustrates that OMC has a high-quality mesostructure. In addition, when Cu was embedded into OMC, no obvious spectral characteristic changes were observed at low 2θ angles, indicating that the ordered mesoporous structure remained unchanged after the incorporation of Cu.

Thermogravimetric analysis (TGA) curves were recorded in air for all composites (Figure 2). The curve of OMC (curve f) has a significant weight loss at about 500 °C, suggesting carbon combustion, which is higher than those of Cu/OMCs. Weight-invariant phenomena were visible above 460 °C for Cu/OMCs. The weight percentages of Cu obtained by combusting the carbon components in the composites were 3.3, 5.3, 7.9, 10.0, and 12.6 wt % for Cu/OMC-1, Cu/OMC-2, Cu/OMC-3, Cu/OMC-4, and Cu/OMC-5, respectively.

The N\textsubscript{2} adsorption–desorption isotherms are shown in Figure 3A. It can be clearly seen that Cu/OMC-Xs exhibit typical type IV isotherms with H1 hysteresis loops, whereas the N\textsubscript{2} adsorption–desorption isotherm of OMC (Figure S1A) also have the same characteristics, indicating the mesoporous structure of the composites, which is consistent with the result of small-angle XRD. The pore size distribution curves (Figures 3B and S1B) derived from adsorption branches using the Barrett, Joyner, and Halenda (BJH) model revealed the narrow pore size distribution in all samples. The corresponding textural properties are summarized in Table 1. It was observed that a certain amount of Cu nanoparticles embedded in OMC helped increase the Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore size of OMC. It may be because Cu embedded in OMC prevents the carbon matrix from shrinking during carbonization. However, with the increase of Cu content, both the BET surface area and the pore volume tend to increase first and then decrease. During the process of Cu\textsuperscript{2+} to metallic Cu, carbon is consumed on the one hand, and the pores may be slightly blocked on the other hand.

In order to characterize the mesostructure and the dispersion of nanoparticles of OMC and Cu/OMC, the typical transmission electron microscopy (TEM) images are shown in Figure 4. The well-ordered arrangement of mesopores was clearly observed for OMC (Figure 4f), giving evidence for the presence of an ordered hexagonal mesostructure. For the Cu/OMCs (Figure 4a–e), directional and hexagonally arranged pores can be clearly observed, which implied that the incorporation of Cu nanoparticles does not destroy the ordered mesoporous structure, which is consistent with the results from small-angle XRD (Figure 1B). Dark spots were observed for the Cu nanoparticles, which were highly dispersed in the carbon matrix. According to the particle size distribution histograms (Figure 4, inset), the average particle size of Cu nanoparticles is about 27, 27, 31, 34, and 39 nm for Cu/OMC-1, Cu/OMC-2, Cu/OMC-3, Cu/OMC-4, and Cu/OMC-5, respectively. The particle sizes of nanoparticles obtained from TEM are slightly larger than those obtained from XRD, which is similar to others’ research.\textsuperscript{35} The unit-cell parameters (a\textsubscript{0}) calculated from XRD are about 10 nm (Table 1). As a result, some particles penetrate the carbon wall and become stuck in two to four mesopores.
Electrochemical Catalysis. According to the above characterization, the Cu/OMC-X materials have good characteristics, such as highly ordered mesoporous structures, high surface area, and highly dispersion of Cu nanoparticles. Next, in order to explore their electrocatalytic performance, Cu/OMC-X materials were used in electrocatalytic reaction of benzyl alcohol and CO₂ to synthesize benzyl methyl carbonate.

It can be seen from Figure 5 that the electrode material has a great influence on the yield. On the OMC electrode, only 12.0% of benzyl methyl carbonate could be obtained (Table 2 entry 1), which is much lower than those on Cu/OMC (Figure 5) and Cu (Table 2 entry 2), illustrating that Cu plays an important role in the catalytic reaction. By comparing electrode materials with different Cu contents at the same current density (Figure 5), we can see that as the Cu content in Cu/OMC-X increases, the product yield of the present increases first and then decreases, of which Cu/OMC-3 shows the best electrocatalytic effect. This law is consistent with the

Table 1. Textural Properties of Cu/OMC-X

| sample        | Cu contenta (wt %) | S BETb (m²/g) | V pc (cm³/g) | D pd (nm) | unit cell parameter a ad (nm) | particle size e (nm) | ECSAf (cm²/g) |
|---------------|--------------------|---------------|--------------|-----------|-------------------------------|----------------------|---------------|
| OMC           | 542                | 0.266         | 1.67         | 9.99      |                               |                      |               |
| Cu/OMC-1      | 3.3                | 588           | 0.438        | 4.36      | 9.99                          | 27                   | 3.71          |
| Cu/OMC-2      | 5.3                | 597           | 0.438        | 4.36      | 9.80                          | 27                   | 7.55          |
| Cu/OMC-3      | 7.9                | 690           | 0.507        | 4.64      | 10.40                         | 31                   | 23.73         |
| Cu/OMC-4      | 10.0               | 561           | 0.403        | 4.36      | 9.99                          | 34                   | 18.34         |
| Cu/OMC-5      | 12.6               | 510           | 0.368        | 4.36      | 10.40                         | 39                   | 6.82          |

The Cu weight percentage obtained by combustion of the carbon components, by TGA. b Calculated by the BJH model from the sorption data in a relative pressure range from 0.01 to 0.15. c Calculated by the BJH model from the adsorption branches of the isotherms. d Calculated from the XRD results. e Average crystal size estimated by TEM. f The electroactive area measured by the method of Pb-UPD and calculated with charge density of 280 μC/cm².

Figure 3. Nitrogen adsorption–desorption isotherms (A) and BJH pore size distribution curves (B) of Cu/OMC-X: (a) Cu/OMC-1, (b) Cu/OMC-2, (c) Cu/OMC-3, (d) Cu/OMC-4, and (e) Cu/OMC-5.

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The yield of benzyl methyl carbonate is also strongly dependent on the current density. As shown in Figure 5, the yield increased first and then decreased with the increase of current density on all five Cu/OMC materials. The highest yield of 69.7% was obtained on Cu/OMC-3 at a current density of 6.11 mA/cm². When the current density is low, the electrode potential is positive, so it is difficult to reduce the chemicals, resulting in low yield. Conversely, when the current density is large, the electrode potential is negative, so side reactions, such as electroreduction of electrolyte or CO₂, will occur, which reduce the yield. There are many other important factors that influence the electrochemical reactions, such as the concentration of benzyl alcohol and charge amount (Table S2). The yield of the products increases first and then decreases, with the increase of the concentration of benzyl alcohol and charge amount. Under the optimized condition, the yield was 69.7%.

**Table 2. Yields of Benzyl Methyl Carbonate on Different Electrodes**†

| entry | working electrode | yield (%) |
|-------|-------------------|-----------|
| 1     | OMC               | 12.0      |
| 2     | Cu                | 31.0      |
| 3     | Cu/OMC-3          | 69.7      |
| 4     | Cu/AC             | 29.8      |
| 5     | Cu/CNT            | 40.2      |

† General conditions: two-department cell, V_MeCN = 15 mL, C_benzylalcohol = 0.15 mol/L, j = 6.11 mA/cm², C_TBAI = 0.2 mol/L, Q = 1 F/mol, anode = graphite, CO₂ pressure = 1 atm.

In summary, we used a simple one-pot method to synthesize OMC embedded with Cu nanoparticles, which showed good electrocatalytic activity for preparation of organic carbonate from alcohol and CO₂. The content of Cu affects the specific surface area and electrocatalytic activity of the material. The yield of benzyl methyl carbonate reaches 69.7% under optimized conditions on Cu/OMC-3. This work expands the application of Cu/OMC composites as catalytic materials for electrochemical fixation of CO₂ to synthesize high value-added organic chemicals under mild conditions. It may provide some new ideas for designing cheaper and more efficient electrocatalysts.

**EXPERIMENTAL SECTION**

**Chemicals.** Poly-(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide) triblock copolymer Pluronic F127 (M_w = 12,600, PEO_{106}PPO_{70}PEO_{106}) was purchased from J & K Chemical. Phenol, formaldehyde (37 wt %), ethanol, Cu(NO₃)₂·3H₂O, acetylacetone, acetonitrile (MeCN), tetra-butylammonium iodide (TBAI), benzyl alcohol (PhCH₃OH), potassium carbonate anhydrous, methyl iodide, ether, hydrochloric acid, magnesium sulfate anhydrous were purchased from Sinopharm Chemical. All the chemicals were used as received.

**MATERIALS SYNTHESIS**

**Synthesis of Resol Precursors.** Resol, a low weight molecular phenolic resin as the carbon resource, was prepared according to the previous report work. The process was as follows: 8.0 g of phenol was melted at 40–42 °C in a round-bottomed flask; then 1.7 g of 20 wt % sodium hydroxide (NaOH) aqueous solution was added under stirring; 10 min later, 13.8 g of formaldehyde solution (37 wt %) was added dropwise under 50 °C; then the reaction solution was heated up to 70–75 °C and kept for 1 h. After that, the reaction solution was cooled down to room temperature and the pH value adjusted to about 6–7 by using a 2.0 M HCl solution. Then, water was removed by vacuum evaporation at 50 °C. At last, the resol precursor was dissolved in ethanol (20 wt %) for future use.

**Synthesis of the Cu/OMC Composite.** The Cu/OMC composite was prepared by coassembly of the resol precursor, triblock copolymer Pluronic F127, Cu(NO₃)₂·3H₂O via evaporation-induced self-assembly strategy. The process was as follows: 1.0 g of Pluronic F127 was dissolved in 16.5 g of ethanol; then 5.0 g resol precursor solution (20 wt %) was added and stirred for 10 min. Subsequently, a certain of Cu(NO₃)₂·3H₂O dissolved in 3.5 g of ethanol was dropped in and acetylacetone with a molar ratio with Cu of 1:1.5 was added. After further stirring for 12 h, the mixture was cast onto glass pans, followed by evaporation of ethanol for 8 h at room temperature.
temperature and then thermopolymerized in an oven at 100 °C for 24 h. After that, the obtained composite film was scrapped off and then carbonized in a tubular furnace at 800 °C for 3 h under N2 flow at the ramp of 1 °C/min below 600 °C and 5 °C/min between 600 and 800 °C. The obtained material was denoted as Cu/OMC-X, where X = 1, 2, 3, 4, and 5, and the contents of Cu are listed in Table 1.

Electrocatalytic Synthesis. The electrocatalytic synthesis process was performed by galvanostatic electrolysis with a direct-current-regulated power supply (HY3003M, HYelec, China). Cu/OMC-X (60 mg) was mixed with 148 μL of sodium carboxymethylcellulose aqueous solution (1 wt %), then coated on carbon paper (2 cm × 2 cm) and used as a cathode. Galvanostatic electrolysis was carried out in a twodepartment cell with a solution of 0.2 mol/L TBAI catholyte and 0.2 mol/L TBAI−CH3CN-0.15 mol/L PhCH3OH saturated with CO2 in a cathode chamber and 0.2 mol/L TBAI−CH3CN in anode chamber, equipped with a Cu/OMC cathode and a graphite anode, until 1.0 F/mol of charge passed. At the end of the electrolysis, the catholyte was esterified by 0.3 mL of methyl iodide and 0.3 g of anhydrous potassium carbonate at 55 °C for 5 h. After that, the solution was extracted with ether, and the combined organic layer was dried over anhydrous magnesium sulfate. At last, the yields based on the starting materials was analyzed by gas chromatography [Shimadzu GC-2014 GC equipped with a flame ionization detector and a Rtx-5 column (30 m × 0.25 mm × 0.25 μm)].

Characterization. The XRD patterns were collected on a Bruker D8 ADVANCE instrument using Cu Kα radiation (λ = 1.5418 Å) at 35 kV and 25 mA. TGA was carried out using a Metzsch TGA-STA449F3 analyzer from 25 to 800 °C in an air flow of 80 mL/min at a heating rate of 10 °C/min. TEM images were captured by an FEI Tecnai G2 F30 microscope operated at 300 kV. Nitrogen adsorption–desorption isotherms were measured on a Quantachrome Autosorb-3B instrument after evacuating the samples at 573 K for 6 h. The specific surface areas were evaluated using the BET method and the pore distribution was calculated by the BJH method from adsorption branches of isotherms.

Measurement of ECSA. ECSA of Cu/OMC-X was determined by measuring the charge associated with the stripping of an underpotential deposited Pb monolayer with a CHI 650a Electrochemical Station (Shanghai Chenhua Instruments Company). The saturated calomel electrode and a Pt net were used as the reference electrode and the counter electrode, respectively. The cyclic voltammograms were obtained at a scan rate of 10 mV/s in a N2-saturated aqueous solution of 0.1 mol/L KNO3−1 mmol/L Pb(NO3)2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03651.

BET analysis of OMC, TGA curves, SEM images of Cu/C, ECSA of Cu/OMC, the influence of benzyl alcohol concentration, the influence of charge that passed the electrode, and ECSA of Cu/CNT and Cu/AC (PDF)

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Notes

The authors declare no competing financial interest.

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