From bulk to nano metal phthalocyanine by recrystallization with enhanced nucleation

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ABSTRACT

A recrystallization process with enhanced nucleation by a dilute KOH aqueous solution is used to create nano from bulk metal phthalocyanines (MPcs). Cobalt phthalocyanine (CoPc) nanorods (~20 nm in width and ~60 nm in length) and copper phthalocyanine (CuPc) nanorods (~30 nm in width and several hundred nano meters in length) are prepared from bulk CoPc and CuPc, respectively. It indicates the strength of the interaction force between MPcs and H_2O molecules possibly affects the size of the nano particles. The formation of nano MPcs and purification were accomplished simultaneously, providing a facial way to turn bulk MPcs into nano with high purity.

1. Introduction

Metal phthalocyanine (MPc) compounds, as two dimension planar macromolecule compounds with π-π conjugated systems, have applications in many fields including solar cells [1—4], sensors [5,6] and catalysts [7,8]. Recently, with increasing demands for electronic devices [9], sensitive sensors [10], medical instruments [11—13], energy electrodes [14—17], as well as carbon capture systems [18,19] nanosized MPcs attract much interest. The preparation of MPc nano materials is of utmost importance in their applications. Nano MPcs have been achieved by vapour-phase deposition [20], electrochemical deposition [21], template method [22] and hydrothermal process [23,24]. However, in most cases, the synthesis processes take a long time and high energy consumption. In addition, lots of impurities appear in the as prepared nanoscale MPcs. There is a great challenge to the preparation of MPc nano materials with high purity economically.

The commercial synthesis of bulk MPcs have lasted for decades.

The bulk MPcs have been produced at low cost by the optimised industrial process. However, with the requirements of nanosized MPcs, a facial way to turn the bulk MPcs into nano materials with high purity should be very interesting and useful. Recrystallization has been used for the purification of MPcs [5,25]. As a typical purification process, the bulk MPcs are dissolved in concentrated H_2SO_4, and filtered. The filtrates were transferred to water, the pure MPcs formed by a recrystallization process. On the other hand, nucleation plays a key role in the formation of nano materials. In our present work, in order to prepare nanosized MPcs, a dilute basic aqueous solution replacing pure water was used to enhance the nucleation of MPcs from its concentrated H_2SO_4 solution. In brief, the bulk cobalt phthalocyanine (CoPc) and copper phthalocyanine (CuPc) prepared by microwave synthesis were employed as the examples to show that how to turn bulk MPcs into nano. They were dissolved in concentrated H_2SO_4, and filtered. Then the filtrates were transferred to a much larger amount of dilute basic aqueous solution (2×10^{-4} mol L^{-1} KOH). Nanosized CoPc and CuPc formed via a recrystallization process with enhanced nucleation by the neutralization reaction between H_2SO_4 and KOH.

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2. Experiment

2.1. Measurements

The morphologies of the samples were characterized by a scanning electron microscope (SEM, JEOL, JSM-6700F). The microstructure of the products was obtained by a transmission electron microscope (TEM, JEOL, JEM-3010, 300 kV). For TEM observation, the samples were dispersed in alcohol with the aid of ultrasonic agitation for several minutes, and then, a drop of solution was dropped onto a copper grid covered by porous carbon. The obtained products were confirmed by Infrared absorbance spectrum (IR) (Germany EQUINOX 55 spectrometer, KBr pellets) in the 400—4000 cm^{-1} range, and Uv—vis spectra Perkin-Elmer Lambda 40 UV—visible spectrometer, Elemental analysis (carbon, hydrogen, nitrogen) was performed on a Germany VarioEL III CHNOS analyzer. The overall structure of the samples was recorded using a Rigaku (Tokyo, Japan) D/max-2400 X-ray diffractometer (XRD) with Cu Kα radiation. Electrochemical experiments were performed with a CorrTest electrochemical work station (CS310 Wuhan CorrTest Instrument Company) in a conventional three-electrode cell using the loaded The glassy carbon electrode (3 mm in diameter) as the working electrode, a graphite rod as the auxiliary electrode, and a saturated calomel reference electrode. All potential data reported in this work were measured with respect to the reversible hydrogen electrode and all electrochemical data were obtained at room temperature.

2.2. Electrochemistry

2.2.1. For oxygen reduction reaction

The glassy carbon electrode (GCE, 3 mm in diameter) was polished with ~0.5 μm alumina slurry prior to modification; it was subsequently washed ultrasonically in distilled water for 3 min and in acetone for 3 min. The cleaned GCE was dried in air. The loading of MPcs was carried out with 10 μL of a loading density of 2 mg ml^{-1}. After evaporation of the solvent, 10 μL of a diluted Nafion solution (5 wt % in ethanol) was put on top of the resultant electrode which was then dried in air. Electrochemical experiments were performed with a CorrTest electrochemical work station (CS310 Wuhan CorrTest Instrument Company) in a conventional three-electrode cell using the loaded GCE (3 mm diameter) as the working electrode, a graphite rod as the auxiliary electrode, and a saturated calomel reference electrode (SCE). All potential data reported in this work were measured with respect to the reversible hydrogen electrode (RHE) and all electrochemical data were obtained at room temperature. CV measurements were done in O_2 saturated 0.1 M KOH solution, with the scan rate of 50 mV s^{-1}. Before CV measurements, the working electrodes were electrochemically cleaned by sweeping their potential between −0.2 V and 1.2 V at 50 mV s^{-1} in an oxygen-protected 0.1 M KOH until a steady voltammogram curve was obtained. All potentials in the RHE scale were converted from the SCE scale using E (RHE) = E (SCE) + 0.99 V in 0.1 M KOH [26]. All experiments were done at room temperature.

2.3. For Li/SOCl₂ batteries

The electrochemical measurements were carried out in specially designed test cells. The compartment of the cells is made from polytetrafluoroethylene (PTFE) material. The preparation of carbon cathode started from a mixture of 92 wt % acetylene black and 8 wt % Teflon binder. Then the pastes were formed by adding water and iso-propyl-alcohol into the mixture. Subsequently, the mixture pastes were dried at 120 °C for 4 h. These carbon electrodes were used as cathode with the apparent (exposed) area of 1 cm^2, and lithium foils were used as the counter electrodes. A 1.47 mol L^{-1} $LiAlCl_4$-$SOCl_2$ solution was used electrolyte. 2 mg of MPcs was added to the electrolyte for each cell. The discharge tests for Li/$SOCl_2$ batteries were evaluated at a constant resistance 40 Ω, and were stopped until the voltage reached 2 V. All the experiments were conducted in a glove box under an argon atmosphere.

The relative energy(X) of Li/$SOCl_2$ battery is used to evaluate the catalytic performance of MPcs to Li/$SOCl_2$ battery [27].

The energy of Li/$SOCl_2$ battery is

$$E = \int Pdt = 1/Re \sum U^2 \Delta t \qquad (1)$$

where P is the discharge power of the battery, Re is the constant external resistance, U is the discharged voltage in the test.

The relative energy of the battery is:

$$X = E/E_0 \times 100\% \qquad (2)$$

where E stands for the energy of the battery, E_0 stands for the energy of the battery in the absence of catalysts.

2.4. Synthesis of nanoscale CoPc and CuPc

0.50 g of the bulk MPc (M = Co^{2+}, Cu^{2+}) was dissolved in 10 ml concentrated H_2SO_4, and then was filtered. The filtrate was added to 1000 ml 2 × 10^{-4} mol L^{-1} KOH, and stirred at 120 r min^{-1} for about 10 min. The precipitate was washed by deionized water for three times. Then the precipitate was dried under vacuum at 70 °C overnight. CoPc nanorods: 64% yield; m. p.> 300 °C; IR(KBr pellet, cm^{-1}: 3422(vs), 1612 (s), 1523 (m), 1092 (s), 913 (m), 731 (s); s); UV/Vis (DMSO): λ_{max} = 328, 656 nm. Anal. Cald for $C_{28}H_{12}N_{12}Co$: C, 66.26; H, 2.82; N, 19.61; Found: C, 66.28; H, 2.86; N, 19.79%. CuPc nanorods: 69% yield; m. p.>300 °C; IR (KBr pellet, cm^{-1}): 3421(vs), 1610 (s), 1505 (m), 1090 (s), 899 (m), 722 (s); UV/Vis (DMSO): λ_{max} = 362, 624, 720 nm. Anal. Cald for $C_{32}H_{16}N_8Cu$: C, 66.72; H, 2.80; N, 19.26; Found: C, 66.49; H, 2.63; N, 19.31%.

3. Results and discussion

3.1. The morphology of CoPc and CuPc crystals

The CoPc obtained by the recrystallization process without KOH shows bulk morphologies (Fig. 1a). By contrast, the CoPc treated using a dilute KOH aqueous solution to enhance nucleation displays uniform nano nanorod structure (Fig. 1b and 1c). The CoPc nanorods are ~20 nm in width and ~60 nm in length (Fig. 1c). Similar as CoPc, the CuPc obtained by the recrystallization process without KOH shows bulk morphologies (Fig. 1d). While the CuPc treated by the recrystallization process with KOH displays uniform nanorod structure (Fig. 1e and 1f). The CuPc nanorods are ~30 nm in width and several hundred nano meters in length (as shown in Fig. 1f).

3.2. The phase characterization of CoPc and CuPc

The comparison of XRD patterns of nano and bulk MPcs are shown in Fig. 2. The XRD patterns of CoPc bulk show seven peaks at 2θ = 7.19, 10.02, 15.58, 24.23, 25.29, 26.74 and 27.93°. The CoPc nanorods show seven peaks at approximately the same positions while they are weaker and wider than that of CoPc bulk. This is attributed to that CoPc nanorods can stack in a very limited range of ordered state caused by the limitation of the number of CoPc molecules in every CoPc nano particles [18]. The XRD patterns of bulk CuPc and nano CuPc are similar, showing eight peaks at