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Cyclic voltammetry analysis of copper electrode performance in Na_2WO_4 solution and optical property of electrochemical synthesized $CuWO_4$ nanoparticles

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ABSTRACT

The electrochemical behavior of copper electrode in sodium tungstate (Na_2WO_4) solution has been studied through cyclic voltammetry (CV). CV results informed that $CuWO_4$ was formed in kinds of electrochemical processes followed with chemical reaction. A cationic exchange membrane-assisted electrolysis method was developed to synthesize optical nanoparticle $CuWO_4$ for the first time. Anode chamber collected $CuWO_4$ was calcined at 500 °C based on the thermogravimetry test result. The X-ray diffraction (XRD) pattern of calcined $CuWO_4$ showed no impurities. Microstructure of $CuWO_4$ was characterized by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM). The fourier transform infrared spectroscopy (FTIR) of the sample further confirmed the formation of pure $CuWO_4$ nanoparticle. Furthermore, the optical property of the nanomaterial was studied by ultraviolet visible diffuse reflectance spectrophotometer (UV–vis) and photoluminescence (PL).

1. Introduction

Tungstate is a main type of inorganic functional materials, the wide applications illustrated as follows, photoluminescence applications [1,2], magnetic property applications [3,4], supercapacitors [5,6], laser hosts [7,8], gas-sensing applications [9,10], catalysts [11,12], photocatalysts [13–15], scintillator materials [16,17], humidity sensors [18,19], microwave applications [20,21], optical fibers [22,23], lithium batteries [24,25], etc. Developed tungstate synthetic methods include microwave-assisted synthesis [5,26], sol-gel method [27,28], hydrothermal method [29–32], solid state reaction [33,34], microemulsion-based synthesis [35,36], molten salt method [13,37], coprecipitation method [38–42], solvothermal method [43,44], mechanochemical synthesis [45,46], polymerized precursor method [47,48], electrochemical synthesis [49,50], sonochemical method [51,52], etc.

In the present paper, the electrochemical behavior of copper in Na_2WO_4 solution was explored and the synthesis method for $CuWO_4$ nanoparticle by cationic exchange membrane-assisted electrolysis was studied for the first time. The TG, XRD, TEM, FTIR, UV and PL techniques were utilized to characterize the basic properties of $CuWO_4$ nanoparticles.

2. Experimental

$Na_2WO_4 \cdot 2H_2O$ and hydrochloric acid were of analytical purity and used as received without further purification. Anode copper foil (in 99.99% purity) and cathode titanium mesh both degreased by acetone (C_3H_6O) and anhydrous ethanol (CH_3CH_2OH). Electrodes area is 8 cm^2. The anolyte is 0.1 M Na_2WO_4 solution and the catholyte is 0.1 M hydrochloric acid.

2.1. Cyclic voltammetry analysis of copper electrode in Na_2WO_4 solution

The electrolytic cell depicts in Scheme 1 that consists of anode chamber and cathode chamber partitioned with the cationic

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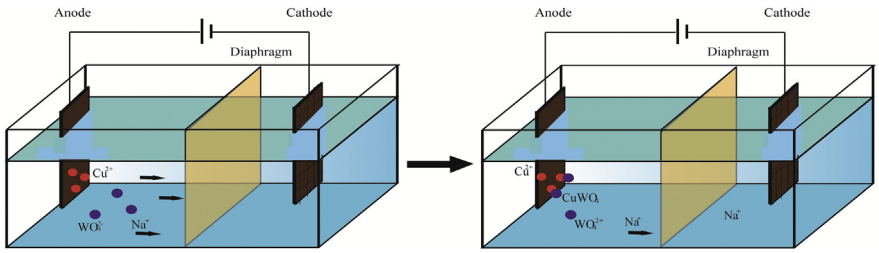

Scheme 1. The electrolytic cell with cationic exchange membrane used for CV test and $CuWO_4$ preparation. Hydrated $CuWO_4$ precipitated in anode chamber.

exchange membrane (Nafion cationic exchange membrane made by DuPont Co.). Put the copper electrode in anode chamber with Na_2WO_4 solution, the titanium mesh in cathode chamber with diluted hydrochloric acid and the Ag/AgCl reference electrode in the same chamber with the copper electrode. Cyclic voltammetry analysis was performed with CHI 760D by Shanghai Chenhua.

2.2. Preparation of $CuWO_4$ nanoparticles

Constant voltage (1 V) was applied to the electrolytic cell, after a few minutes, $CuWO_4$ hydrate precipitate was formed on copper anode surface and then dispersed in anode chamber. The products on the anode chamber were collected, washed and dried, then calcined by muffle furnace in air at 500 °C (at a rate of 5 °C/min) for 2 h before characterization and measurement.

2.3. Characterization of materials

The thermogravimetric analysis (TG) was implemented by STA 449 F3 DSC/DTA-TG Simultaneous Thermal Analyzer (German NETZSCH). Using X-ray powder diffraction in D8 Advance X-ray diffractometer (German Bruker AXS) equipped with graphite monochromator and Cu target to analyze the phase of $CuWO_4$. The morphological structure was characterized by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) by JEOL JEM-2100F. Fourier transform infrared analysis (FTIR) was carried out by IRAffinity-1 Fourier transform infrared spectrometer (Japan's shimadzu). UV–vis spectrum of the obtained sample was tested by UV 3600 spectrophotometer and PL spectrum was tested by F-4600 fluorescence spectrophotometer (Japan).

3. Results and discussion

To get insight into the electrochemical performance of copper electrode in Na_2WO_4 solution, CV test was carried out in detail as follows.

Wide scan range CV result shown in Fig. 1(a). In Fig. 1(a), the peak A_1 (−0.129 V) was covered by rapid increase of the anodic current at the peak A_2 (0.047 V). We can see the peak A_1 clearly in Fig. 1(b) which is associated with the Cu oxidation to form Cu_2O. Cu_2O oxidized to form $CuO/Cu(OH)_2$ as potential increased. At peak A_2 (0.047 V), Cu is oxidized to $CuO/Cu(OH)_2$ directly. From 0.3 V to 1.1 V, bulk quantities of $CuWO_4$ hydrate precipitates grew in the anode chamber. As the potential decreased, $CuO/Cu(OH)_2$ reduced to Cu_2O at −0.389 V and Cu_2O or $CuO/Cu(OH)_2$ reduced to Cu directly at the peak C_1 (−0.653 V) [53].

Fig. 1(c) shows the CV test result of platinum (Pt) instead of copper in the same electrolytic process. It is conducive to understand the anion effect on the anode reaction process. Comparatively, there are only one anodic peak A_1 and one cathodic peak C_1. As we all know that Pt is stable, no soluble of it, whereas the WO_4^{2-} polymerized to form polyanion at 0.831 V and its depolymerized at −0.226 V. All the peaks of anion reaction at anode are different with the peaks of copper anode oxidation, it means that the anion has no direct effect on the copper anode oxidation. WO_4^{2-} reacted with $CuO/Cu(OH)_2$ to form $CuWO_4$ in the subsequent chemical reaction. In summarize, $CuWO_4$ formed in the consequent electrochemical/chemical reaction take place at anode surface or/and in anode chamber.

$$Cu \rightarrow Cu_2O \rightarrow CuO/Cu(OH)_2 \rightarrow CuWO_4 \text{ hydrate precipitate}$$

The cyclic voltammogram record of copper in different concentrations of Na_2WO_4 aqueous solution is shown in Fig. 2. When the concentration is 0.001 M, there are no formation of $CuWO_4$ but a broader anodic peak and a wide reduction wave. With the increase of concentration, the electrochemical behavior of copper in Na_2WO_4 aqueous solution is alike. The passivation layers contain the inner Cu_2O and $CuO/Cu(OH)_2$ and the outer $CuWO_4$ hydrate

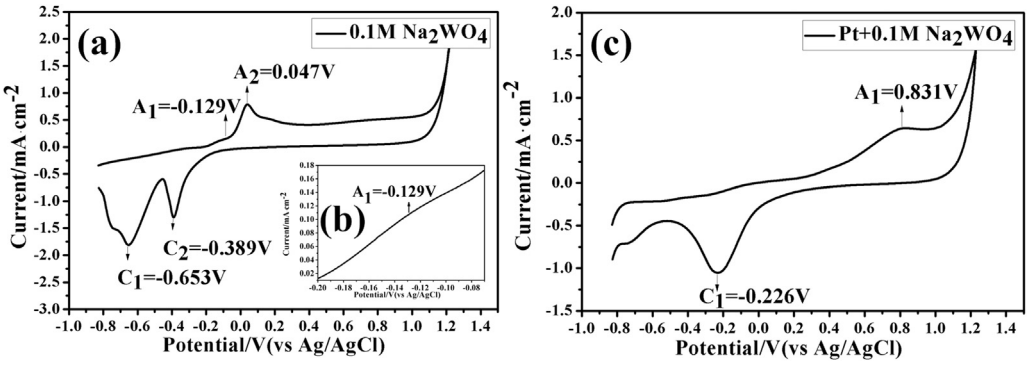

Fig. 1. Cyclic voltammograms recorded at copper working electrode in 0.1 M Na_2WO_4 aqueous solution (a), the inset (b) is the amplification of the peak A_1 in (a). Cyclic voltammograms recorded at platinum working electrode in 0.1 M Na_2WO_4 aqueous solution (c). Scanning range: −0.828 V–1.225 V, scanning rate: 50 mV/s.