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Zinc oxide quantum dots synthesized by electrochemical etching of metallic zinc in organic electrolyte and their electrochemiluminescent properties

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ABSTRACT

A universal and facile electrochemical etching method for synthesizing nanosized metal oxide semiconductors has been presented by taking the synthesis of ZnO quantum dots (QDs) from metallic zinc as an example. By applying an appropriate potential, metallic zinc was controllably oxidized to Zn^{2+} ion, the latter (Zn^{2+}) was released into an organic electrolyte and hydrolyzed by trace dissolved water therein, giving rise to ZnO QDs. The electrochemically synthesized ZnO QDs were uniform particles with an average diameter of 5.0 nm, and exhibited good photoluminescent and electrochemiluminescent activities. The effects of applied potential window, amount of water and dissolved oxygen on the formation of ZnO QDs were investigated and discussed in detail. The presently proposed electrochemical etching method not only has provided a facile, low-cost and controllable way to obtain ZnO QDs, but also would be applicable as a universal method in synthesizing other kinds of nanosized metal oxide semiconductors from related metals.

1. Introduction

Nanosized metal oxide semiconductors have been hot research issues during the past years, because they not only inherit the excellent properties from their bulk, but also posses special properties originating from their size confinement and anisotropic geometry [1]. Nanosized metal oxide semiconductors exhibit novel piezoelectric [2], optoelectric [3], photochemical [4], magnetic [5], and catalytic [6], properties, which can be easily modulated by the sizes of nano-structures. Therefore, these excellent properties of nanosized metal oxides have led to very attractive applications in various fields, for examples, many kinds of metal oxide nanocrystals have been used for photochemical reagents [7], solar cell [8], light emitting diodes [9], catalysis [6,10], and biomedical applications [11], e.g. they can be used as fluorescent probes in biological staining and diagnostics [12], as biological labeling in cellular imaging [13], and can be used in magnetic resonance imaging contrast enhancement [5,14], drug targeting [15], and drug delivery [16].

Due to their large potential applications, the syntheses of nanosized metal oxide semiconductors have attracted broad attention from researchers. In the past two decades, various methods have been reported, including sol–gel process [17], sonochemical method [18], spray pyrolysis [19], hydrothermal [20], chemical vapor deposition (CVD) [21], precipitation [22], and electrochemical deposition [23]. However, most of these routes are disadvantageous or complicated for the synthesis of high crystalline nanosized metal oxide. For examples, the sol–gel process is disadvantageous for synthesis of composite power due to different reaction properties of reagents. Precipitation and sonochemical methods are relatively simple in terms of experimental procedures and preparation conditions, but the shape of produced nanoparticles are irregular and the calcination process for crystallization is usually necessary. In the case of spray pyrolysis and chemical vapor deposition, high temperature conditions and expensive equipments are needed, which limits their extensive applications.

In order to overcome these disadvantages in synthesizing nanosized metal oxide nanocrystals, we introduce a new electrochemical etching method to prepare highly crystalline metal oxide nanoparticles from corresponding metals. Compared with those methods mentioned above, electrochemical etching method might have following advantages: first, preparation can be carried out at room temperature, without needing calcination or milling. Second, it is easy to control the size of nanoparticles by modulating electrochemical parameters, such as applied potential window, current density, and electrolysis time. Third, the electrochemical etching method is simple, low cost, easy in performance, and may become a universal method for synthesizing many kinds of metal oxide semiconductors. Herein, the electrochemical etching method for synthesizing nanosized metal oxide particles from metals was presented by taking ZnO crystals or quantum dots (QDs) as an example,

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since ZnO is one of the most typical and successful metal oxide semiconductors, with a wide band gap (3.37 eV) and large exciton binding energy (about 60 meV), and has been used as a versatile material in various fields [24–26,11]. Additionally, electrochemiluminescent (ECL) properties of the synthesized ZnO QDs were investigated since ZnO QDs may have promising applications as a new ECL reagent for immunoassays and DNA analysis in the future.

2. Experimental

2.1. Chemicals

Metallic zinc wire of 2.0 mm in diameter (99.95%), tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$, 98%) and N,N-dimethylformamide (DMF, 99.9%) were all purchased from Alfa Aesar and used as received from the suppliers. Molecular sieves with an average pore size of 0.4 nm (Ningbo, China) was activated and used for drying DMF, according to a previously reported method [27]. All experiments were performed under room temperature ($25 \pm 0.5\,^{\circ}C$) and 40% humidity.

2.2. Electrochemical synthesis of ZnO nanocrystals

The electrochemical synthesis of ZnO QDs were carried out in an electrochemical cell containing a Zn wire working electrode (1.0 cm in length, 2.0 mm in diameter), a Pt wire counter electrode, a Ag wire reference electrode, and 0.05 mol dm^{-3} $TBAPF_6$ DMF electrolyte. The applied potential at the Zn working electrode was cycled between −3 V and +3 V with a scan rate of 0.05 V s^{-1}, during which electrochemical (EC) and electroluminescence (ECL) signals were recorded simultaneously to monitor electrolytic process. The electrolysis was terminated after 120 min, then the resulting ZnO QDs was centrifuged and washed with DMF for three times to remove $TBAPF_6$, and finally the purified ZnO QDs was re-dispersed in DMF.

2.3. Apparatus

EC and ECL measurements were carried out on an EC and ECL detection system (MPI-E, Remex Electronic Instrument Ltd. Co., Xi'an, China) with a small ECL cell containing a Pt disc (2.0 mm in diameter) working electrode, a Pt wire counter electrode, and a Ag wire quasi-reference electrode and a Ag/AgCl (3 mol dm^{-3} KCl solution, 0.218 V vs. SHE at 298 K) reference electrode in organic phase and phosphate buffer solution (PBS), respectively. High-resolution transmission electron micrographs (HRTEM) of ZnO QDs were obtained by employing an electronic microscope (Technai G2 F20 S-TWIN, 200 kV). The sample for TEM measurement was prepared by dropping the ZnO QD solution on a carbon-coated copper grid and dried at 80 °C. To investigate the optical properties of ZnO QDs, UV–vis absorption and photoluminescent spectra were recorded on a UV/Vis/NIR spectrophotometer (Lambda 750, PE) and a fluorescence spectrophotometer (Cary Eclipse, Varian), respectively. The X-ray photoelectron spectra (XPS) were measured with a XPS system (ESCAlab 250) for determining the composition and chemical bonding configurations of ZnO QDs.

3. Results and discussion

3.1. Synthesis and characterization of ZnO QDs

Fig. 1 shows that strong ECL with maximum emission wavelength of 575 nm were observed during electrolysis of Zn wire, which might be an indication of nanocrystal formation according

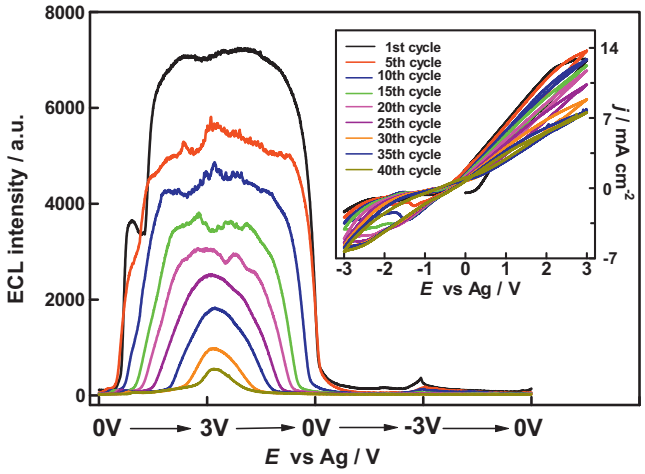

Fig. 1. ECL and EC (inset) responses obtained on a Zn electrode in DMF containing 0.05 mol dm^{-3} $TBAPF_6$. The applied potential was cycled between −3.0 V and +3.0 V (vs. a Ag wire quasi-reference electrode) at a scan rate of 0.05 V s^{-1}.

to a previous report [28]. In terms of CV (inset of Fig. 1), anodic currents (i.e. oxidation of metallic Zn) were larger than the cathodic currents (i.e. reduction of Zn(II)) at the same time scale, suggesting that metallic Zn were overall oxidized during the electrolysis. This was verified by the fact that the initially smooth surface of zinc wire electrode became porous and slimmer after the electrolysis. After 2 h electrolysis, a light brown solution was obtained and some flaky deposit was found near and on the surface of the Zn working electrode. Both the resulting electrolyte and deposit emit yellow light when exposed to 365 nm UV light.

The resulting electrolyte together with the deposit was ultrasonicated, centrifuged (13,000 rev min^{-1}) and washed with DMF in turn for three times, giving rise to a light brown DMF solution. The TEM (Fig. 2) showed that the purified electrolytic solution contained ZnO nanocrystals with the average size of 5 nm. The characteristic lattice spacings of wurtzite ZnO are readily identified in the high-resolution TEM images of those ZnO QDs. The presence of ZnO QDs in the electrolytic solution was further confirmed by X-ray photoelectron spectrometry (XPS), since the binding energy of Zn $2p_{3/2}$, Zn $2p_{1/2}$ and O 1s were found at 1022, 1045 and 530.5 eV, respectively (Fig. 3) [29].

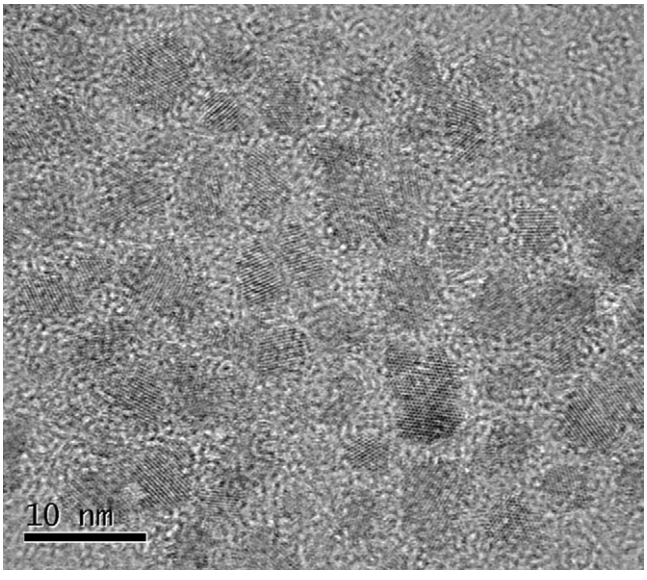

Fig. 2. HRTEM image of ZnO QDs synthesized by electrochemical etching method.