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Microwave-electrochemical formation of colloidal zinc oxide at fluorine doped tin oxide electrodes

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ABSTRACT

Colloidal ZnO is obtained during microwave-enhanced electrochemical deposition experiments from an aqueous solution containing 0.1 M $Zn(NO_3)_2$ and 0.02 M H_2O_2 via repetitive negative going potential cycles from 0.3 to −0.8 V *vs.* SCE. The effects of temperature and temperature gradients on ZnO electro-formation at fluorine doped tin oxide (FTO) electrodes are investigated with both a conventional thermostated bath system (isothermal) and an in situ microwave electrochemistry system (non-isothermal). Mainly electrodeposition of ZnO is observed in uniformly heated stagnant solution and predominantly the electro-formation of ZnO colloid is observed in the presence of microwave-induced temperature gradients in a flowing solution. For the ZnO colloid prepared via microwave activation, SAXS data suggests an average particle radius of ca. 18 nm. The increase of ZnO nanoparticle concentration during repetitive potential scans is followed by photoluminescence spectroscopy. A possible mechanism for ZnO colloid formation during electrochemical reduction of H_2O_2 is suggested.

1. Introduction

Thermal activation can be applied beneficially in order to enhance electrochemical processes [1]. Non-isothermal methods such as heating of micro-wires via alternating currents [2] or of microelectrodes via radio frequency radiation [3] have been introduced as new tools in thermo-electrochemistry [4]. The use of in situ microwave activation in electrochemical processes was proposed in 1998 [5] and has been shown to provide both high temperature reaction conditions generated locally at the electrode–solution interface and fast transient changes in temperature when microwave pulses are applied. Considerable superheating effects also can be achieved which is useful for high temperature non-isothermal electrochemical processes [6]. Therefore microwave radiation adds an interesting tool for the control of electrochemical processes [7–9]. Effects introduced by microwave radiation have been shown to be beneficial in electroanalysis [10] and more recently also for electrodeposition [11]. Studies on the effect of microwave radiation on processes at metal microelectrodes have revealed an “antenna effect” which causes field and energy focusing locally at the electrode surface [12,13]. For sub-micrometer sized electrodes, this effect was shown to result in discharge cavitation [14], but for larger electrodes, the effects of microwave fields are based on the preferential heating of the electrode materials (e.g. thin conducting films) compared to the solution phase dielectric. Thermal gradient effects were explored recently for 1 cm^2 tin-doped indium oxide (ITO) electrodes during electrodeposition of titanium dioxide and of gold [10].

Zinc oxide is of special interest as a material for a wide range of applications. Thin films of doped zinc oxide have shown good conductivity and high transparency in the visible region and have been used as transparent electrodes in solar cells [15]. Zinc oxide nanoparticles have been used in photovoltaic cells [16], sensor devices [17], piezoelectric devices [18], and in catalysis [19]. ZnO exhibits a wide band gap (between 3.2 and 3.4 eV) and shows good environmental acceptability and biocompatibility at the same time as being inexpensive. Zinc oxide nanoparticles have been prepared by various techniques including colloidal synthesis [20], pulse laser ablation [21], high temperature hydrothermal synthesis [22,23], and chemical vapour deposition [24]. Electrochemical formation of ZnO nanostructures on transparent fluorine doped tin oxide electrodes (FTOs) surface has been reported for electrodeposition of zinc oxide for application in solar cells [25]. The electrochemical formation of ZnO colloids in solution has not been previously

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reported and is demonstrated here in the presence of microwave activation.

Potential benefits of electrosynthesis of nanoparticles at an electrode surface are to control reaction conditions and the use of controlled current to introduce defined amounts of material (in this study hydroxide) to control particle size and distribution.

For the electro-formation of solid oxide films or products at electrode surfaces there are usually two main approaches: (i) redox species can change the local pH at the electrode surface when it is reduced (e.g. during nitrate reduction [26] or during H_2O_2 reduction [27]) so that metal hydroxide precipitates are formed on the electrode surface or (ii) the metal species in solution undergo an oxidation or reduction at the electrode surface to form highly insoluble hydroxides or oxides. In this study, we investigate the first approach based on H_2O_2 reduction to prepare thin films of zinc oxide on FTO electrode surfaces and a colloid of ZnO in solution. The ZnO films are investigated by SEM methods and the ZnO colloids are characterized by SAXS and photoluminescence spectroscopy.

2. Experimental

2.1. Chemical reagents

Chemical reagents such as $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, and H_2O_2 (aqueous 35%) (all from Aldrich) were obtained commercially and used without further purification. Solutions were prepared using deionized and filtered water taken from a Thermo Scientific water purification system (Barnstead Nanopure) with a resistivity of not less than 18.2 MΩ cm. Argon (Pure shield, BOC) was employed for de-aeration of electrolyte solutions.

2.2. Instrumentation

Voltammetric studies were carried out with a microAutolab III potentiostat system (EcoChemie, Netherlands) in staircase voltammetry mode. The working electrode was FTO (Tec 8, coated glass, 10 mm × 5 mm, resistivity 6–9 Ω square^{-1}, Pilkington Ltd.). An Elite tube furnace system was employed for cleaning FTO electrode surfaces (at 500 °C in air). Prior to conducting electrochemical experiments, all solutions were purged with argon (BOC, UK). Scanning electron microscopy (SEM) images were obtained with a JEOL JSM6310 system. Prior to imaging samples were gold sputter coated in order to improve conductivity. Fluorescence data were obtained with a fluoroSENS – fluorimeter system (Gilden photonics) with an excitation at 312 nm and a bandpass of 5 nm. The emission data were recorded from 360 to 600 nm wavelength. SAXS (small-angle X-ray scattering) data were obtained on an Anton Paar SAXSess system using a PANalytical PW3830 X-ray generator. The small-angle patterns were recorded with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 50 mA in the region of 2θ from 0° to 10° with an exposure time of 30 min while simultaneously recording small-angle patterns in the region of 0.08–5 nm^{-1}. The X-ray image plates were observed using a Perkin-Elmer Cyclone Storage Phosphor System. The sample was a solution of ZnO nanoparticles in zinc nitrate in a sealed 1 mm X-ray glass capillary and data for 0.1 M zinc nitrate solution as background in a similar capillary was collected for the same exposure time and subtracted from the scattering data from the sample. The "Lake" program supplied by Anton Paar was used to correct the scattering for the slit-like X-ray beam shape using the Lake desmearing method [28]. A small-angle scattering analysis package written by "The SANS Group" at NIST for the Igor Pro platform [29] was used to determine the dimensions of the ZnO colloid particles in the $Zn(NO_3)_2$ solution. A Panasonic multi-mode microwave oven (NN-3456, 2.45 GHz) with modified power supply, a water energy sink, and a port for the electrochemical cell was used. For electrochemical measurements in presence of microwaves, an electrochemical flow cell was employed (see Fig. 1A) and placed through a port into a multi-mode microwave cavity [21]. The electrochemical cell consists of a three-electrode arrangement with a saturated calomel (SCE, REF401, Radiometer) reference electrode (up stream) and platinum gauze counter (down stream). The working electrode was a FTO slide with 0.5 cm^2 exposed surface area connected to 200 μm diameter insulated copper wire with a silver epoxy contact. During experiments, a flow of electrolyte solution (ca. 28 cm^3 min^{-1}) through the electrochemical cell was maintained to minimize bulk solution heating within the cell and to avoid overheating of the solution in inlet and outlet. *Special care is required when inserting metal objects into microwave systems and experiments should always be conducted at low power. Before and during operation, the system was monitored for leaking microwave radiation with an Apollo radiation meter.*

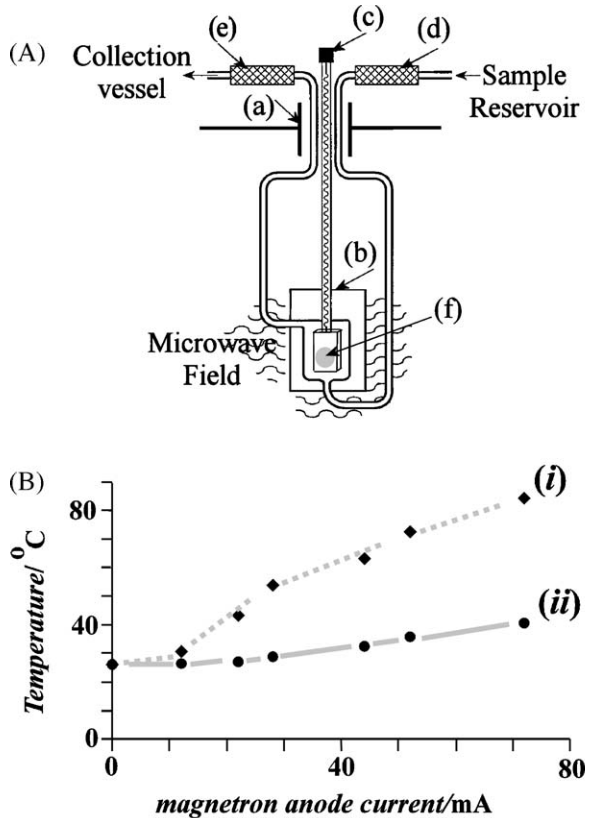

Fig. 1. (A) Schematic drawing of the custom-made 10 cm^3 electrochemical glass cell (b) placed through a port (a) into the multi-mode microwave system. A flow system driven with a peristaltic pump (28 cm^3 min^{-1}) was employed to pump electrolyte solution from a reservoir through the reference connection (d), through the cell, and out through the counter electrode (e) into the collection vessel. The working electrode (c) with a FTO slide attached (f) was placed from the top into the cell. (B) Plot of (i) the average electrode temperature, $T_{\text{electrode}}$ (estimated from the shift in equilibrium potential of 1 mM $Fe(CN)_6{}^{3-}$ and 1 mM $Fe(CN)_6{}^{4-}$ in aqueous solution of 0.1 M $Mg(NO_3)_2$) and (ii) the solution outlet temperature *vs.* the magnetron anode current (applied microwave intensity).

2.3. Procedure for electrode temperature calibration during microwave operation

In order to determine and calibrate the temperature at the FTO electrode surface, the shift in equilibrium potential for an aqueous solution of 1 mM $Fe(CN)_6{}^{3-}$ and 1 mM $Fe(CN)_6{}^{4-}$ in 0.1 M $Mg(NO_3)_2$ (this electrolyte was chosen to closely mimic the effect of aqueous 0.1 M $Zn(NO_3)_2$ due to precipitation of