



## Photoelectrocatalytic behavior of electrodeposited zinc ferrite films with varying Zn:Fe ratio

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### ABSTRACT

We report on stoichiometrically varied zinc ferrite films prepared by electrochemical deposition which can potentially be used as photoanodes in solar water splitting cells. The ferrite films are prepared from an electrodeposition bath containing iron and zinc ions in the presence of triethanolamine as a complexing agent. The ratio of Zn to Fe is controlled by fine tuning of the deposition potentials and the concentrations of the two metal ions. The film thickness is monitored by the time of deposition or the charge passing during the deposition process. The deposited films are amorphous and converted to highly crystalline oxides by post thermal treatment at 600 °C. Structural and morphological characterization was performed by transmission electron microscopy and X-ray diffraction. Raman spectroscopy was used to locally identify the phase compositions. The surface composition and the chemical state of the species were investigated by X-ray photoelectron spectroscopy which shows that the surface composition of some films is different from the bulk. Photoelectrochemical measurements show that the ferrites are n-type semiconductors and the onset and the magnitude of the photocurrent is strongly dependent on the ratio Zn:Fe at the surface. Photoelectrodes containing understoichiometric amount of zinc at the surface (Zn:Fe ratio = 0.25–0.40) exhibit higher photocurrents than those being stoichiometric or slightly excessive in zinc.

### 1. Introduction

Photoelectrochemical cells (PECs) are analogs to commercial electrolyzers but the voltage required to electrolyze water partly comes from the photovoltage generated from absorbed solar photons by the constitute semiconductor electrodes [1]. For sustainable and efficient operation of the PECs, the electrodes should meet several prime criteria; high stability under solar irradiation, being cheap and abundant, possessing enough catalytic activity and selectivity, and having suitable band positions for water reduction or oxidation reactions [2]. Transition metal containing oxide semiconductors are attractive as electrode materials for PECs due to their good catalytic properties, narrow band gap for visible light absorption and stability [2–4]. Particularly, iron oxide and iron containing mixed metal oxides are widely investigated as electrode materials for PECs [4–7]. The class of spinel-type iron containing oxides ( $MFe_2O_4$ ,  $M = Zn, Ca, Mg, Co, Cu$ ) are recently investigated for solar energy conversion attributed to their chemical and thermal stability and the rich chemistry of spinel structure enabling the modulation of the optical band gap (1.6–2.2 eV) [8,9] with the selection of  $M^{2+}$  or fine adjustment of the M:Fe ratios [10]. In this regard several recent reports investigated spinel ferrites, particularly  $ZnFe_2O_4$ , as

photoanode for the oxygen evolution reaction (OER) [11–14] or coupled with other well-known n-type oxide semiconductors to improve their PEC performance [15,16]. Furthermore, ferrites are also widely used as gas sensors (e.g. CO, VOCs,  $NH_3$ ) [17], for photocatalytic degradation of organic pollutants [18] and as catalysts (e.g. for the oxidation of primary alcohols and selective reduction of nitroarenes) [19,20].

Solution-based approaches for the preparation of spinel ferrite electrodes are attractive as they are easy to implement and use metal salts as less toxic precursor materials. Electrodeposition (ED) is one of such methods which is widely used for the synthesis of many transition metal oxide semiconductors [21,22] including different spinel ferrites [23,24]. Simple instrumentation, high flexibility in terms of composition and experimental parameters, and direct growth of the films on conductive substrates renders ED attractive. Most importantly, the fine controlling of the deposition potential leads to several compositional variations and M:Fe ratios. Switzer et al. reported electrodeposited ferrite films with varying Fe(II)/Fe(III) and Zn:Fe ratios exhibiting interesting resistance switching and magnetic properties [25,26]. Recently, Rivero et al. reported the electrosynthesis of zinc ferrite nanoparticles of well controlled size and chemical composition with varied

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stoichiometry and studied their magnetic properties [27]. The influence of the M:Fe ratio is not limited to the magnetic properties but also affects the optoelectronic properties. Sutka et al. reported the electronic conductivity and gas sensing properties of zinc ferrite is highly dependent on the Zn:Fe metal ratios [28]. Kimmich et al. very recently prepared a compositional library of Fe and Zn with inkjet printing and shows there exist an optimum Zn:Fe ratio for enhanced photoanode performance [29]. Following these findings, we investigated the photoelectrochemical properties of electrodeposited zinc ferrite ( $Zn_xFe_{3-x}O_4$ ,  $x = 0.2-1.1$ ) films and show that indeed the Zn:Fe ratio plays a crucial role on the photoanode performance. Interestingly, the ED parameters affect more the surface composition than the bulk. To our knowledge, this is the first report studying the photoelectrochemical properties ferrite films of varied stoichiometry synthesized by electrodeposition.

## 2. Experimental

### 2.1. Chemicals

All chemicals in this work were used without further purification. Iron (III) nitrate nonahydrate ( $Fe(NO_3)_3 \cdot 9 H_2O$ , > 99%), sodium hydroxide (> 99%), acetone (> 99.9%) and hydrochloric acid (37 wt %) were purchased from VWR Germany. Zinc (II) nitrate tetrahydrate ( $Zn(NO_3)_2 \cdot 4 H_2O$ , > 98%) was purchased from Merck KGaA. Triethanolamine (TEA) (> 99%) was purchased from Sigma-Aldrich, Germany. Ethanol (> 97%) was purchased from Berkel AHK. Hydrochloric acid (HCl) and nitric acid ( $HNO_3$ ) with trace analysis quality (ROTIPURAN<sup>®</sup> Supra) were purchased from Carl Roth GmbH + Co.KG, Germany. Deionized water (DI water) (> 18M $\Omega$ ) was produced in-house by a Satorius arium<sup>®</sup> pro water purification system. Zinc ferrite powder (> 99%), hematite powder (> 99%) and zinc oxide powder (> 99%) were purchased from Sigma-Aldrich, Germany and used as reference materials.

### 2.2. Electrodeposition of zinc ferrite films

Electrodeposition of the zinc ferrite thin films was conducted following a modified given procedure [25,26] using a potentiostat/galvanostat AMEL MODEL 7050 controlled by the enclosed JuniorAssist software. The electrodeposition was conducted in a double-walled glass deposition cell attached to a thermostat at 80 °C and magnetic stirrer with Pt wire as counter electrode and Ag/AgCl/sat. KCl (+0.197 V vs. NHE, XR300 Radiometer Analytical) as reference electrode. Fluorine-doped tin oxide (FTO) glass (NSG TEC C15D 14  $\Omega$ /sq., Pilkington Germany) was used as substrate for the working electrodes. Prior to usage the FTO substrates were cleaned by ultrasonication subsequently with 0.1 M sodium hydroxide, 0.1 M hydrochloric acid, DI water, ethanol and acetone for 10 min each and dried with compressed air afterwards. A circular deposition area of diameter 2.0 cm was defined by a scotch tape. The composition of the electrodeposition bath was adapted from literature [24]. 3.23 g  $Fe(NO_3)_3 \cdot 9 H_2O$  was added to 20 ml aqueous solution containing 1.99 g triethanolamine (TEA) and thoroughly mixed to form a scarlet solution. This solution was added dropwise to a stirred solution of 60 ml DI water containing 8.00 g NaOH pellets, and subsequently diluted to a total volume of 100 ml. Afterwards the desired amount of  $Zn(NO_3)_2 \cdot 4 H_2O$  was added to get the final composition of 80 mM  $Fe^{3+}$ , 0.1 M TEA, and 20, 30 or 50 mM  $Zn^{2+}$  in 2 M NaOH solution. The electrodeposition was conducted at potentials between  $-0.91$  V and  $1.07$  V vs. Ag/AgCl/sat. KCl at a bath temperature of 80 °C. Post-thermal heat treatment of the films were performed at 400 °C, 500 °C and 600 °C for 3 h each with a heating ramp of 2 °C/min leading to crystalline films.

### 2.3. Characterization

Raman spectra were collected using a Bruker Senterra Raman microscope with a 633 nm He-Ne laser of 5 mW power in the range from 150–1500  $cm^{-1}$  at ambient conditions. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Thermo Fischer ESCALAB 250 Xi photoelectron spectrometer with a monochromic Al  $K_{\alpha}$  X-ray source (1486.6 eV). The measured binding energies were referenced to the C1s line at 284.8 eV. XPS depth profile measurement were conducted by etching with argon ions of an energy of 2000 eV for a total time of 60 s, and recording of XPS spectra in 10 s intervals. Cross-sectional scanning electron microscopy (SEM) images were taken with a JEOL JSM-7100f FEG. Grazing incidence X-ray diffraction (GIXRD) measurements were performed over a range of 15–80° (2 $\theta$ ) on a PANalytical Empyrean X-ray diffractometer using Cu- $K_{\alpha}$  X-ray source. Transmission electron microscopy (TEM) measurements were performed with a JEOL 2100FS-TEM operating at 200 kV. The zinc ferrite samples were scratched from the films, dispersed by ultrasonication in ethanol and mounted on copper grids by drop casting. Diffuse reflectance UV–VIS measurements were carried out using a Varian Cary 4000 in the range of 200–800 nm. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was measured with a Thermo Scientific XSeries II. 1000 mg/l. ICP-MS standard stock solutions of Fe and Zn (Carl Roth, Germany) were used for calibration without further purification. 100–1500  $\mu g/L$  calibration solutions were prepared in 2%  $HNO_3$  solution and the detection limit was calculated as 3 times the standard deviation measured from 30 repeated ion counts of the blank sample. The films were dissolved in 10 ml 30% HCl for 24 h and diluted with 4%  $HNO_3$  for a dilution factor of 1:80. For the investigation of photo-corrosion, the 1 M NaOH electrolyte was collected and neutralized with concentrated  $HNO_3$ . To avoid interference by the  $Na^+$  ions the neutralized electrolyte was diluted with 4%  $HNO_3$  to a factor of 1:100.

Photoelectrochemical measurements were performed using a ZAHNER ZENNIUM E potentiostat (ZAHNER-Elektrik GmbH) controlled by THALES Z (v3.04) software. The photoelectrochemical cell PECC-1 (ZAHNER-Elektrik GmbH) in three-electrode configuration with Pt wire as counter electrode and Ag/AgCl (sat. KCl) as reference electrode was used. Ferrite coated FTO electrodes were used as working electrodes. All measurements were performed in 1 M NaOH (pH 13.6) under back-side illumination. For chopped light voltammetry (CLV) measurements a white LED light source WLC01 (ZAHNER-Elektrik GmbH) controlled by PP211 potentiostat (ZAHNER-Elektrik GmbH) with an output intensity of 100 mW/cm<sup>2</sup> was used. The spectral output of the LED lamp is presented in the supporting information (Fig. SI 1). The potential was scanned at a rate of 10 mV/s between  $-0.4$  V and  $+1.0$  V vs. Ag/AgCl with light on and off cycles each lasting for 5 s. The wavelength dependent photocurrent response (or photon to current conversion efficiency, IPCE) was measured with a tunable LED light source TLS01 (ZAHNER-Elektrik GmbH) between 430 nm and 750 nm with 10 nm steps. Mott-Schottky measurements were conducted in the dark with a 10 kHz frequency and 10 mV AC amplitude between  $-0.6$  V and  $+0.4$  V vs. Ag/AgCl with a step size of 50 mV and a delay time of 30 s.

## 3. Results and discussion

The electrodeposition of zinc ferrite and magnetite is described in detail by Switzer and co-workers [25,26]. The role of TEA is to form a stable complex with the  $Fe^{3+}$  as  $Fe(III)$ -TEA complex. Thus,  $Fe^{3+}$  ions are stabilized in a wider potential window. The electroreduction of the  $Fe(III)$ -TEA complex will form  $Fe(II)$ -TEA ions on the surface of the electrode. The diffusion of  $Fe(III)$ -TEA together with other bivalent metal ions (e.g.  $Zn^{2+}$ ) from the solution to the surface will form magnetite structures in which some  $Fe^{2+}$  ions are replaced by the added metal ions (1). The deposition potential and the concentration of the

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