CHAPTER VI
Surfactant Mediated Growth of Nanostructured Zinc Oxide Thin Films and their Photoelectrochemical Performance
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CHAPTER VI

Surfactant Mediated Growth of Nanostructured Zinc Oxide Thin Films and their Photoelectrochemical Performance

6.1. Outline

In this chapter zinc oxide (ZnO) thin films were electrodeposited from an aqueous zinc acetate solution on to fluorine doped thin oxide (FTO) coated conducting glass substrates. The effect of organic surfactants like polyvinyl pyrrolidone (PVP), sodium dodecyl sulphate (SDS), poly ethylene glycol (PEG), ethylene glycol (EG) and polyvinyl alcohol (PVA) on their structural, morphological, optical and photoelectrochemical properties was studied. The films deposited using organic surfactants exhibit different surface morphologies. It was observed that the organic surfactants play important roles in modifying the surface morphology and size of the crystallites. FTIR study was used to confirm the removal of adsorbed stray surfactant molecules from the samples. Moreover the samples are photoelectrochemically (PEC) active and exhibit highest photocurrent of 231 µA, photo voltage of 492 mV and 0.42 fill factor for the ZnO:SDS films.
6.2. Introduction

The addition of surfactants (additives) in the precursor solution is extremely important due to their influence on morphological and structural properties of electrodeposits. Organic surfactants are commonly used in zinc electrodeposition to control the crystal shape and size, in order to produce high quality deposits [1]. The role of the organic surfactants is to change the morphology of the deposit owing to their concentration dependent specific activity during electrodeposition. They are known to possess the unique ability to self assemble into aggregates, such as micelles, which serve as templates during electrodeposition process [2, 3]. When the concentration approaches the critical micelle concentration (Cmc) the bilayers or multilayers at the electrode interface are formed [4]. In case of electrodeposition, the solid-liquid interface in the plating bath provides a unique environment for surfactant assembly i.e. template formation [3]. In aqueous medium, micelles can form due to electrostatic force at the electrode surface even if the surfactant concentration is lower [5, 6]. D. Schlettwein et al. reported that one-step synthesis, achieved by dissolving an organic dye in the bath and found that it enables simultaneous self-assembly of ZnO and the adsorbed dye, yielding a homogeneously colored particulate ZnO film with porous morphology [7]. Recently an electrochemically synthesized nanostructured ZnO by utilizing the self assembly of sodium dodecyl sulphate surfactant has been reported [8].

Dye-sensitized solar cells (DSSCs) based on porous thin films of wide band gap oxide semiconductors modified by dye molecules have received considerable attention as a cost effective alternative to conventional solar cells [9-11]. ZnO is one of the potential semiconductor materials in DSSCs due to its stability against photo corrosion and photochemical properties similar to TiO₂. However, the energy conversion efficiencies of ZnO film-based DSSCs are relatively low. The reason for low efficiency is that ZnO has inherent defects that cause decrement in efficient effective surface area. It is well known that nanoporous film like TiO₂, reported by Gratzel and co-workers [10, 11], can lead to very high solar-to-electric energy conversion efficiency (above 10%). Therefore, the preparation of nanoporous ZnO film with less or no defects is a key to improve the performance of ZnO-based DSSCs.
The aim of the present work is to examine the role of organic surfactant molecules in modifying surface morphology and crystallinity of the deposits, by virtue of their ability to act as template. Also, to pin-point the organic surfactant that gives rise to the most suitable morphology. We have demonstrated a soft electrochemical route that enabled the formation of the compact, large effective (photoactive) surface area and defect-free ZnO electrodeposits, suitable for PEC solar cells.

6.3. Experimental procedure

The zinc oxide films have been synthesized using two different electrochemical routes (i) without organic surfactant and (ii) with organic surfactants. In the first route 50 mM zinc acetate (Thomas Baker, 99.5%) aqueous solution has been used. 0.1M KCl solution was added to it as a supporting electrolyte. This solution is denoted as precursor solution. The fluorine doped thin oxide (FTO) coated conducting glass substrates (10-15 Ω/cm²) of 3 cm² area were used as working electrodes. The thin films of zinc oxide were obtained by potentiostatic electrodeposition at -0.750 mV (vs SCE) for 60 minutes. Oxygen gas was bubbled through the bath during the electrodeposition. Further, to study the effect of organic surfactants on ZnO growth and their properties, various polymers like poly vinylpyrrolidone (PVP; MW=1,40,000 g/mol), poly ethylene glycol (PEG; MW=646.87 g/mol) sodium dodecyl sulphate (SDS; MW=569 g/mol) ethylene glycol and polyvinyl alcohol were added in definite proportion to the aqueous precursor solution, separately. The concentration of organic surfactants (polymers) was kept constant at 1 wt % in the final solution. All the experiments were performed in quiescent solution at room temperature.

A three electrode electrochemical cell was used for the electrodeposition. The FTO coated conducting glass substrate is used as a working electrode, a helical platinum wire is used as a counter electrode and saturated calomel electrode (SCE) as a reference electrode (SCE, E₀ = 0.244 V (vs SHE), the saturated hydrogen electrode). The electrodes were placed parallel to each other with a distance of 2 cm between them. Prior to the film deposition, the substrates were cleaned with detergent in distilled water and under ultrasonic cleaner, with acetone, alcohol and finally with distilled water.
The films prepared by using different surfactants such as PVP, PVA, PEG, EG and SDS are denoted as ZnO:PVP, ZnO:PVA, ZnO:PEG, ZnO:PEG and ZnO:SDS respectively, and those without surfactant are denoted as ZnO. After the electrodeposition, the films were soaked in ethanol for 24 hours to remove stray organic surfactant molecules from the final deposits.

The deposition potential to yield phase-pure ZnO electrodeposits at room temperature was estimated from linear sweep voltammetry using a scanning potentiostat EG & G versastat-II model PAR-362. The photoelectrochemical study was performed in a conventional three electrode arrangement with the deposited thin film as working electrode, a graphite counter electrode and a SCE reference electrode. A 0.5 M Na₂SO₄ aqueous solution is used as an electrolyte. The photoelectrochemical (PEC) characteristics were measured under constant illumination of 5 mW/cm² from 18W UV lamp with excitation wavelength of 365 nm.
6.4. Results and Discussion

6.4.1. X-ray diffraction (XRD) study

Figure 6.1 shows the X-ray diffraction patterns of the films deposited with and without surfactants. The samples exhibit phase pure ZnO phase with hexagonal wurtzite structure (JCPDS card No. 36-1533). All the films are polycrystalline with reflections along (002), (103), (200) (104) and (203) planes corresponds to hexagonal wurtzite zinc oxide. The substrate peaks are indicated by star. The XRD patterns for the films deposited with and without surfactants showed absolutely no difference. This reveals that the organic surfactant does not affect the orientation of the samples, over studied preparative parameters.

![XRD patterns](image_url)

**Figure 6.1.** The XRD patterns for the films deposited using various organic Surfactants in the Zinc acetate bath onto FTO coated conducting glass substrates.
6.4.2. Surface morphology

Figure 6.2 (a) shows the SEM image of zinc oxide thin film onto the FTO coated conducting glass substrate prepared in absence of any surfactant. It shows compact, well defined grains of about 250 nm. Figure 6.2 (b) shows the SEM image of zinc oxide thin films with PVP as a organic surfactant. The PVP has a structure of polyvinyl skeleton with polar groups as reported by Y. Tang [12]. The lone pairs of nitrogen and oxygen in polar group of one PVP unit may occupy the orbital of metal ion. The Zn$^{2+}$ can coordinate with PVP, which can take part in controlling the grain size and morphology of ZnO by reducing the reaction rate [13]. The PVP can adsorb on different crystal faces due to formation of granular shape. From the figure it is observed that the nanocrystalline grains of about 150 nm are obtained. It is supported that in presence of PVP smaller grains are formed due to lower crystal growth and aggregation rate [14]. The image in the inset depicts uniform coverage of such features over the substrate.

Figure 6.2 (c) shows the SEM image of ZnO thin film deposited using SDS. The image in the inset depicts uniform coverage of such features over the substrate. The vertically aligned thin and compact hexagonal crystallites stem from the SDS mediated growth. SDS is a peculiar surfactant, which acts like template and catalyze the self-assembled growth of lamellar nanostructures [14]. It has been recently explored to modify the morphology of ZnO [8].

The SEM images of the films deposited using PEG and EG surfactants are shown in figure 6.2 (d) and figure 6.2 (e) respectively. The image in the inset depicts uniform coverage of such features over the substrate. The morphology and grain size are both dependent on the presence of organic surfactant. Microporous corrugated morphology is observed for PEG mediated growth. In the presence of EG the nanocrystalline grains of about 100 nm are obtained (figure 6.2 (e)). In the presence of PEG the morphology is completely different than that obtained in the presence of EG. Compact structure is obtained for the films deposited using PVA as organic surfactant. The SEM image is shown in figure 6.2 (f). The image in the inset displays uniform coverage of such features over the substrate. The surface adsorption of surfactant molecules on the growing ZnO surface significantly modifies the
crystal growth of ZnO. This observation leads to a clear conclusion that the polymers PVP, PVA, PEG, EG and SDS act like template during electrodeposition of ZnO that alters the way ZnO grows onto the substrate, upon cathodic polarization.

6.4.3. FTIR spectroscopy

FTIR study was used to confirm the removal of adsorbed surfactant molecules from the samples. The FTIR spectra of the samples, palletized with KBr, were recorded over 400 to 4000 cm\(^{-1}\) (figure 6.3). The spectra consist of seven vibrational bands. The band (\(v_1\)) at 468 cm\(^{-1}\) is due to zinc oxide and assigned to the stretching of Zn-O-Zn [15]. The vibrations due to carboxyl group (\(v_2\) and \(v_3\)) are obtained in the range of 1382 to 1393 cm\(^{-1}\). The stretching mode of vibration (\(v_4\)) corresponds to C=C is obtained at 1509, cm\(^{-1}\) [16], and due to alkyl group (\(v_5\) and \(v_6\)) are obtained in the range 2847-2923 cm\(^{-1}\) for all the samples. The bands (\(v_7\)) at 3200-3600 cm\(^{-1}\) correspond to O–H mode of vibration i.e. due to hydroxyl group. From the FTIR study it is concluded that electrodeposited ZnO thin films are free from the stray organic surfactants molecules.

6.4.4. Room temperature photoluminescence (PL)

Figure 6.4 shows the PL curves for all the samples. There are two emission bands. The weak emission band in the ultraviolet region is observed with a peak at 395 nm. It is well-known that the UV peak arises from band-edge emission of ZnO [17]. Other peak is located in the visible region, peaking at 478 nm, which is associated with defect levels in ZnO. The green emission is attributed to the transition between donor–acceptor and shallow donor-deep levels [18]. The mechanism of green emission has been suggested to be mainly due to the existence of various point defects that can easily form recombination centers [19]. In the present situation, the strong green emission suggests that ZnO has point defects, such as oxygen vacancies [20, 21]. Oxygen vacancies are the main luminescent centers of green light emission in ZnO thin film. The substantial decrement of this peak in figure 6.4, for ZnO-SDS, indicates reduction or passivation of defects. The similar mechanism is proposed for the ZnO in presence of polymers [22].
Figure 6.2(a-f). SEM image for the film deposited without and with organic surfactants a) pure ZnO, b) ZnO:PVP, c) ZnO:SDS, d) ZnO:PEG, e) ZnO:EG, and f) ZnO:PVA.
Figure 6.3. FTIR spectra for all the samples deposited with and without organic surfactants recorded in the range 400 to 4000 cm\(^{-1}\).

Figure 6.4. Room temperature photoluminescence for all the ZnO thin films deposited with and without organic surfactants.
6.4.5. Photoelectrochemical Measurements

To improve the PEC performance, generally the following photoelectrode properties are desirable: (i) a photoelectrode that has high surface area to increase the interfacial reaction sites, (ii) an optically thicker and efficient photoelectrode to enable total absorption of solar light [23], (iii) morphological features (size, shape, grain boundary, interconnection of particles that define energetics and kinetics at the electrode interface) that influence the PEC efficiency of the solar cell [24], and (iv) an electrode comprising densely packed array of grains, which can enhance PEC performance by virtue of the improvement in carrier transport mechanism and minimizing surface trap states [25]. Recently, an improvement in PEC properties of ZnO electrodes with different morphologies e.g., wire, belt, fiber, tube, has been demonstrated [24,26]. The unique structure combining high crystallinity and high surface area leads to a higher PEC efficiencies.

Figure 6.5 (a-f) shows the photocurrent-voltage (I-V) curves for the films deposited without and with surfactants in dark and under illumination with UV light. For the ZnO films deposited using various surfactants the parameters under UV illumination in terms of open circuit voltage (Voc), short circuit current density (Isc), and fill factor (ff) are presented in Table 6.1. The obtained values are in good agreement with the reported values [12]. In dark and under illumination current–voltage (I–V) characteristics of "Glass/FTO/Surfactant mediated ZnO/SCE" cells were measured. These (I-V) curves in dark indicate good junction rectification property. From the I-V measurements it is observed that the higher magnitudes of Isc, Voc, and fill factor (231 μA, 492 mV and 0.42 respectively) are obtained for the films deposited using SDS organic surfactant. This is significant improvement as compared with the pure ZnO thin films (fill factor = 0.13) deposited without surfactant. The densely-packed vertically aligned ZnO hexagonal crystallites (ZnO:SDS) and compact layered (ZnO:PVA) films can absorb enough light. Furthermore, the photogenerated electrons can transport directly through the hexagonal crystallites and compact layers to the conducting substrates with minimum loss. This greatly reduces the recombination losses of the photogenerated charge-carriers due decrement in grain boundary resistance in charge transportation process. The fill factor values obtained in our
experiments are quite close to that of the solar cells based on ZnO nanoparticulate films with a thickness of 7-9 μm under the same conditions [12, 26]. In conclusion, the improvement in the PEC properties of the surfactant mediated ZnO thin films is due to (i) morphological modifications that enhance active surface area and (ii) quenching of the defect levels responsible for recombination losses; as compared to the ZnO films grown without surfactant [24, 27]. This approach may pave the way to synthesize better ZnO electrodes for DSSCs.

6.4.6. Atomic Force Microscopic Study

The AFM images were recorded in order to confirm the morphologies of films deposited using various surfactants. A quantitative method to examine the surface morphology and structure is obtained by analyzing the surface roughness using AFM. Figure 6.6 (a-f) shows 3D (a) and 2D (b) AFM images of pure ZnO films and for the samples deposited using PVP, SDS, PEG, EG and PVA respectively. The AFM images are in well agreement with the SEM images recorded for the ZnO thin films deposited using various surfactants.

Table 6.1. Photoelectrochemical parameters of the cell with “Glass/FTO/Surfactant mediated ZnO/SCE” configuration.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample</th>
<th>Isc (μA/cm²)</th>
<th>Voc (mV)</th>
<th>Fill factor</th>
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<tr>
<td>1</td>
<td>Pure ZnO</td>
<td>52</td>
<td>280</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>ZnO:PVP</td>
<td>45</td>
<td>416</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>ZnO:PEG</td>
<td>202</td>
<td>450</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>ZnO:SDS</td>
<td>231</td>
<td>492</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>ZnO:EG</td>
<td>193</td>
<td>480</td>
<td>0.31</td>
</tr>
<tr>
<td>6</td>
<td>ZnO:PVA</td>
<td>245</td>
<td>456</td>
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Figure 6.5 (a-f). Photocurrent-voltage curves for the ZnO thin films in dark and under illumination a) pure ZnO, b) ZnO:PEG, c) ZnO:PVA, d) ZnO:PVP, e) ZnO:SDS, and f) ZnO:EG
Figure 6.6 (a)

Figure 6.6 (b)
Figure 6.6 (c)

Figure 6.6 (d)
Figure 6.6 (e)

Figure 6.6 (f)

Figure 6 (A-E). 3D (a) and 2D (b) AFM images of ZnO films for the samples deposited using PVP, SDS, PEG, EG and PVA
6.5. Conclusions
Nanostructured ZnO thin films with different morphologies were deposited by cathodic electrodeposition in the presence of organic surfactants such as PVP, SDS, PEG, EG and PVA in the zinc acetate bath onto FTO coated conducting glass substrates. The organic surfactants profoundly modify the surface morphological features, suitable for an intended application, without affecting crystallographic orientations. The SDS and PEG surfactants were found to be dominant in altering the morphologies of ZnO films and effectively catalyze the growth of the ZnO films. Vertically aligned thin and compact hexagonal crystallites stem from the SDS, where as microporous corrugated morphology is observed for PEG mediated growth. However granular films were obtained for the films deposited using PVP EG and PVA. It is concluded that the surfactants-mediated route is a promising approach to achieve ZnO films with controlled morphologies. All the samples exhibit room temperature photoluminescence (PL). Oxygen vacancies contribute to the active luminescent centers for the emission of green light in ZnO thin films. PL gets quenched for the SDS surfactant due to screening effect. The samples are photoelectrochemically active and exhibit highest photocurrent of 231 μA, photo voltage of 492 mV and 0.42 fill factor for the ZnO:SDS films.

After carefully investigating the nucleation and growth behavior and influence of process parameters namely complexing agents, bath temperature, organic surfactants on the nucleation and growth behavior of ZnO thin films, we purport that it is necessary and feasible to augment the process for the synthesis of nanocrystalline ZnO thin films.
Surfactant Mediated Growth of Nanostructured Zircon Oxide

References


