

## Research Article

# Electrochemical Tailoring of Honeycomb-Structured ZnO Thin Films by Interfacial Surfactant Templating

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Zinc oxide thin films with honeycomb structures can be electrochemically produced by interfacial surfactant templating. Newly synthesized 4-amino-1-(2,3-dihydroxy propyl) pyridinium hydroxide ionic liquid exhibiting the hydroxyl functionalized ionic liquids (HFILs) was used in electrodeposition. This method utilizes amphiphile assemblies at the solid-liquid interface (i.e., the surface of a working electrode) as a template to gain the precisely tailor zinc oxide nanostructures. The results described here will provide a useful foundation to design and optimize greener protocol for the electrochemical construction of inorganic nanostructures thin films for possible application of films in nanotechnology field. Moreover, it is believed that this electrochemical tailoring approach can be extended to fabricate other porous metal oxide materials with a unique morphology or shape.

## 1. Introduction

Recently, ionic liquids (ILs) created a center of attention due to their unique materials and solvent properties and the growing interest in academia as well as applicative purposes. Salts with organic cations open a window for the liquid state at more moderate temperatures. Adopting such ideas, the past decade has seen the advent of a new class of solvents, referred to as “ionic liquids”. This term describes organic salts that are liquid at or near room temperature which have melting point below some arbitrary temperature, such as 100°C [1]. The unique properties of ILs such as high conductivity, nonvolatility, low toxicity, large electrochemical window, good electrochemical stability, and high ionic mobility favor its applications in diverse fields, such as synthesis, catalysis, separation technology, electrochemistry, analytical chemistry, and nanotechnology [2]. But the highly viscous nature of ILs has low ionic conductivity at room temperature, which inevitably affects their performance. Therefore, designing an IL with high conductivity and a large voltage window for practical applications is still challenging. The unique variability of the ions often allows the properties of interest to be imparted, so that ILs are denoted as “designer

solvents” or “task-specific ionic liquids (TSILs)”, which can solve the regarding problems.

Recently, much advancement of zinc oxide nano- and microstructure with various applications [3–8], is because zinc oxide (ZnO) is a versatile material of compound semiconductors with excellent properties and extensive applications in electronics, photoelectronics, sensors, and catalyses. The remarkable properties of ZnO are its wide direct-band gap of 3.37 eV and high-exciton-binding energy of 60 meV at room temperature. Nanomaterials of ZnO with one-dimensional structures such as nanowires, nanowhiskers, nanotubes, nanobelts, and nanorods have been intensively studied for applications of opto-electronic devices in nanoscale because the optical and electronic properties in these nanostructures are enhanced by the quantum confinement effect [9–13]. Different methods have been put forward to prepare ZnO including chemical vapour deposition (CVD), thermal oxidation, radiofrequency magnetron sputtering, pulsed laser deposition, electron beam evaporation, spray pyrolysis, and electrodeposition [14–19]. Among them, electrodeposition from aqueous solution is uncomplicated, environmentally friendly, and low-cost technique by which uniform film with controlled stoichiometry

can be produced due to this, many efforts on electrodeposition of ZnO films are reported [20–28]. However, only a few works are focused on interfacial surfactant templating. In 2002, nanostructured ZnO films were utilizing self-assembly of surfactant molecules at solid-liquid interfaces. This method utilizes cetyl trimethylammonium bromide (CTAB) or anionic surfactant, sodium dodecyl sulfate (SDS) [29]. In 2005, lamellar-structured ZnO films by interfacial surfactant templating, utilizes amphiphile assemblies at the solid-liquid interface surfactants with anionic headgroups (e.g., 1-hexadecanesulfonate sodium salt, dodecylbenzenesulfonate sodium salt, dioctyl sulfosuccinate sodium salt, mono-dodecyl phosphate, and sodium dodecyl sulfate), are critical because they incorporate  $\text{Zn}^{2+}$  ions into their bilayer assemblies as counterions and guide the lamellar growth of ZnO films [30].

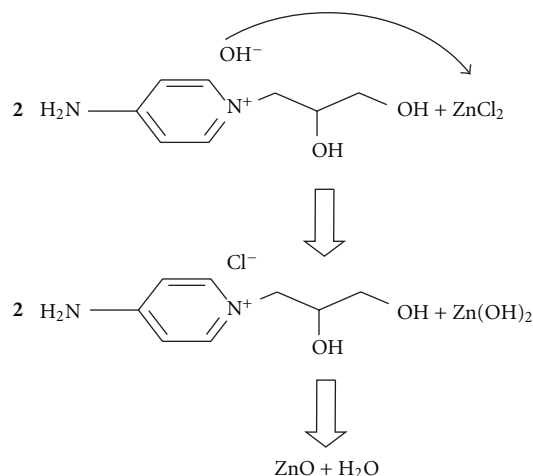
Therefore, to increase the control of electrochemical interfacial surfactant templating, we investigated potential usefulness of newly synthesized 4-amino-1-(2,3-dihydroxy propyl) pyridinium, hydroxide [ADPPY][OH] ionic liquid. This is the first report on interfacial surfactant templating by [ADPPY][OH] ionic liquid producing honey comb structured zinc oxide. Consequently, these results will provide a useful foundation to design/optimize synthetic conditions for broader types of inorganic nanostructures with different morphology for technological application.

## 2. Experimental

**2.1. Synthesis of Ionic liquid.** The TSIL, 4-amino-1-(2,3-dihydroxy propyl) pyridinium, hydroxide was synthesized by our reported procedure [31] (See Figure 5).

**Electrochemical tailoring of zinc oxide:** the zinc oxide thin films were prepared potentiostatically. The electrolyte used for deposition of zinc oxide consists of a 0.1 M TSILs and 0.1 M zinc chloride. The electrodeposition was performed potentiostatically at a potential difference of 1.9 V with respect to SCE (saturated calomel electrode) at room temperature. The electrochemical tailoring of zinc oxide was made in the compartment; is consists of three electrode system with electrolyte; the graphite was the counter electrode; the indium doped tin-oxide-(ITO-) coated glass substrates were working electrode, and SCE (saturated calomel electrode) was the reference electrode. All the voltages were measured with respect to SCE. Deposition was made at room temperature with varying the deposition time from 30 sec to 600 sec.

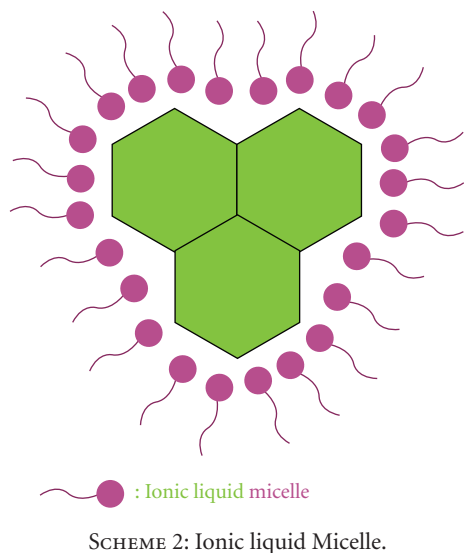
**2.2. Material Characterization.** The thickness of ZnO thin film was measured by surface profiler AMBIOS (XP-1) unit. The structural analysis was carried out using Bruker axS D-8 advanced X-ray diffractometer (XRD) within the range 20–60°C on computer controlled Cu-K $\alpha$  radiations source. The microstructure of the film was observed using Scanning Electron Microscopy (SEM). The wettability of the films was evaluated by measuring the contact angle ( $\theta$ ) of a water droplet of 10  $\mu\text{L}$  placed on the film surface using the contact angle meter equipped with a CCD camera (Ramehart



Instrument Co., USA) at an ambient temperature. The photo luminescence study was carried out on spectrofluorimeter 2000 model.

## 3. Results and Discussion

Solid-liquid interfaces provide a unique environment for surfactant assembly [32]. Micelles can form at the interface even when the surfactant concentration is lower than the critical micelle concentration (cmc) due to surface forces. The assembly patterns of the surface aggregates are mainly determined by the substrate properties (i.e., hydrophobicity, surface charge density) and are frequently different from those in free solution [33]. This makes it possible to separately control the surfactant assembly at the interface by applying a bias voltage to the substrate and tuning the surface charge densities. TSIL [ADPPY][OH] constructed by [ADPPY] that is, 4-aminopyridinium dihydroxy butane functionalized cation and [OH] anion. In the formation of ZnO, anion that is,  $\text{OH}^-$  plays crucial role, in the formation of zinc hydroxide [34].  $\text{Zn}^{2+}$  combines with two molecules of [OH] anion of the ionic liquid and forms hydroxide, as shown in Scheme 1. An important point is to understand the deposition solution chemistry and especially the zinc species involved in the deposition process. In aqueous solution, Zn(II) soluble species are  $\text{Zn}^{2+}$  and hydroxide or chloride complexes. Considering the structural aspects of the ionic liquids is usually helpful for the rationalization of physical and chemical processes occurring in the RTILs. In RTILs, there is a complex interplay of forces (Coulombic, van der Waals (dipole-dipole, dipole-induced dipole, dispersion), hydrogen bond, and possible  $\pi$ - $\pi$  or  $n$ - $\pi$  stacking), which controls the solvation and is the dominant stabilizing force, but the charge transfer and orbital interaction can contribute significantly [35]. The possible ZnO-IL-coordination is shown in Scheme 3. We expect that the unique mechanisms of electrochemical interfacial surfactant templating for building organic assemblies and inorganic frameworks will broaden the type of inorganic materials that can be produced



as nanoporous films with new phases and orientations. Synthesized ionic liquid [ADPPY][OH] plays dual role in entire system as micelle as shown in Scheme 2 which acts as interfacial surfactant. The basic nature of IL (pH 10.7) successively replaces the external basic buffers. Synthesized IL exhibits intrinsic properties due to its green nature. Primary and secondary hydroxyl group of IL enhance the basicity and structural property. The reusability of IL successively replaces the conventional buffers. IL also plays the role as amphiphile of template for ZnO nanostructure tailoring.

The hydrogen group of aminopyridine moiety hence is constructing partial O–H bonding with oxygen atom of ZnO. Due to this bonding, the growth rate slightly decreases but enough to grow along (101) plane, which leads to form nanoflex, but the arrangement of nanoflex is exhibiting honeycomb-like construction.

**3.1. XRD.** XRD pattern of electrodeposited ZnO at 5 and 10 minutes deposition time exhibited that crystals are oriented along the (101) diffraction plane (Figure 1), which confirms the formation of pure ZnO with the hexagonal crystal structure, correspondance with JCPDS (card number 75–1533).

**3.2. SEM.** SEM image of scanning electron microscopy images of 10 minutes deposition time of ZnO thin film deposited on ITO substrate at different magnification are shown in Figure 2(a). The film is porous and well covered with overgrown particles on substrate. This overgrowth can be attributed to a nucleation and coalescence process. The surface morphology at 10,000 magnification (Figure 2(b)) is seen to be well covered, interconnected, microporous, and honeycomb like structure. The flake nanoparticle- and nanorods-like morphologies lead to high specific surface area and porous volume. An enlarged image (Figure 2(c)) clearly

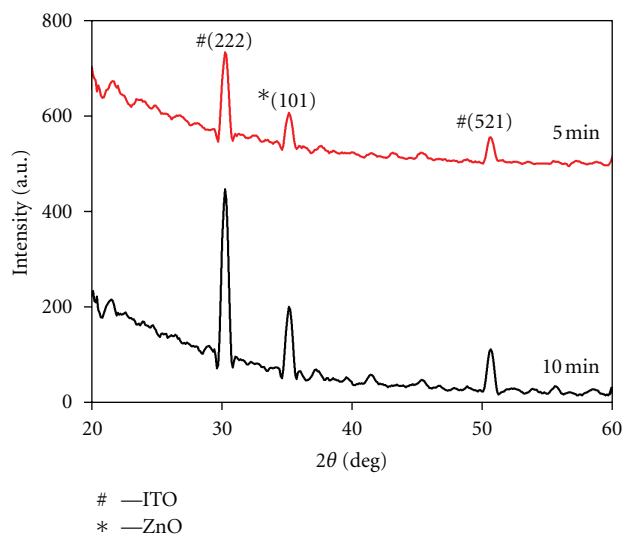
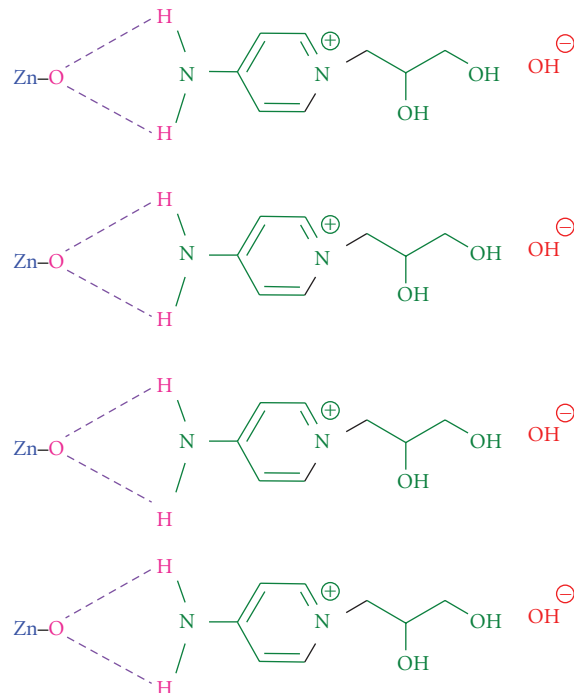


FIGURE 1: X-ray diffraction patterns of ZnO thin film at 5 and 10 minutes deposition time.

shows that the hallow nature of porous structure with wall thickness of 75–150 nm and pore diameter of 90–200 nm. The porous structure can be explained by interpenetrating network formation, similar to electrodeposited tungsten oxide thin films [36]. Zinc deposition is companied by hydrogen evolution at such negative potential in aqueous solution. Therefore, tiny hydrogen bubbles evolved during zinc deposition pores leads to porosity.

Wettability is a very important property governed by both the chemical composition and the geometrical structure

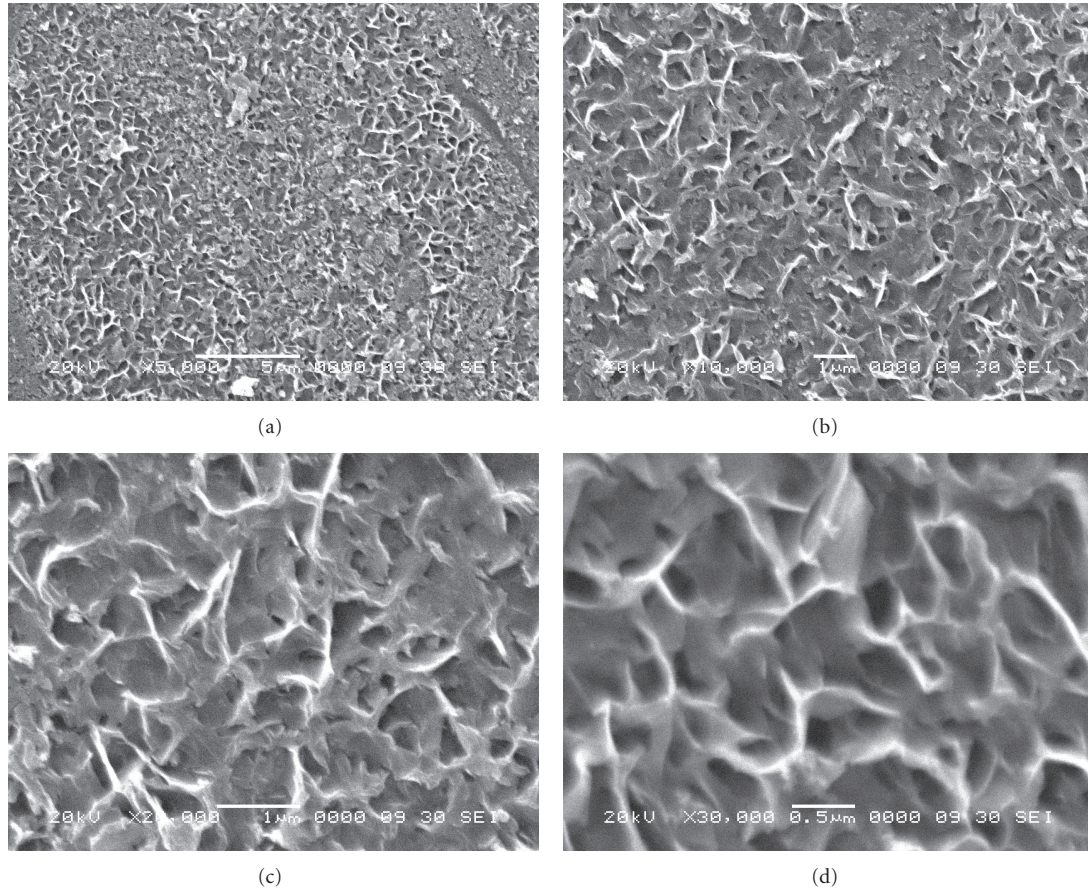


FIGURE 2: Scanning electron microscopy images at 10 minutes deposition time of ZnO thin film (a) 5000 magnification, (b) 10000 magnification, (c) 20000 magnification, and (d) 30000 magnification.

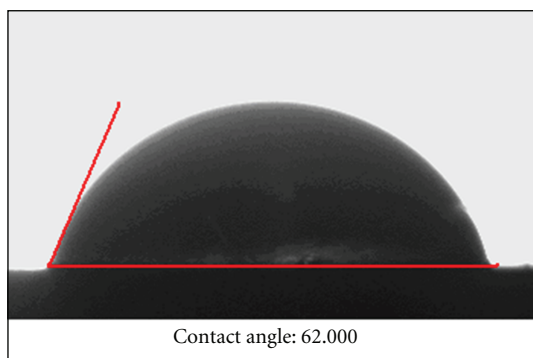


FIGURE 3: Static water contact angle of ZnO thin film.

of solid surfaces [37]. With the development of smart devices, such as intelligent microfluidic switch, reversibly controlling the surface wettability has aroused great interest and been realized by modifying the surface with stimuli-responsive organic compounds [38]. The wetting behavior of surfaces is governed by both their chemical composition and geometric microstructure. Latthe et al. investigated the effect of morphology and porous nature on the static water contact angle of the thin films [39]. The influence of the surface microstructure on the wetting property of air-dried

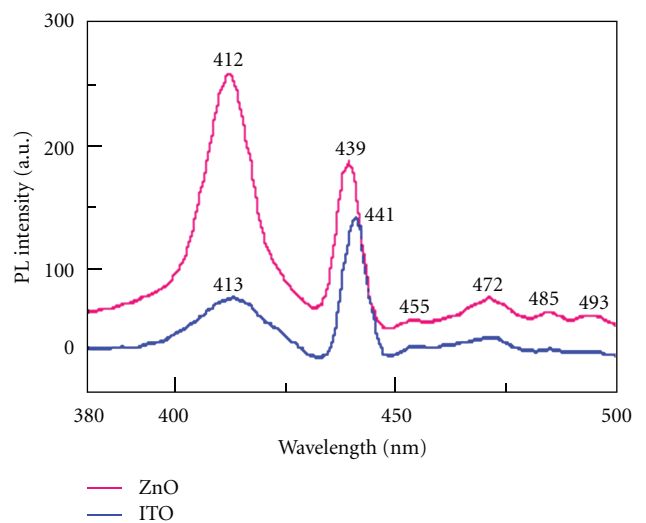


FIGURE 4: Room temperatures photoluminescence spectrum of ZnO thin film.

ZnO thin film was observed by measuring the static water contact angle. The static water contact angle of ZnO thin film was observed to be 62°, which indicates the hydrophilic nature of thin film (Figure 3). The wettability of any solid

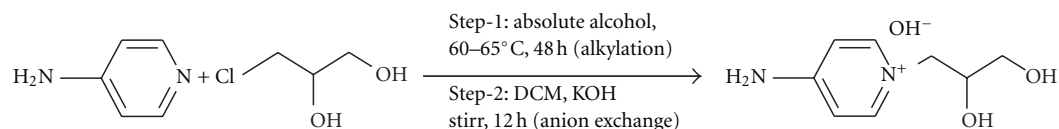


FIGURE 5

surface by a liquid increases with its porosity and it decreases the contact angle.

Zinc Oxide (ZnO) can emit three luminescence bands in the ultraviolet (UV), green, and yellow regions. The strong emission is due the direct recombination of photogenerated charge carriers. The relatively weak UV emission is due to the defects that may trap the photogenerated holes or electrons [12, 40]. The presence of defects in crystal is important for application in optoelectronics devices [41]. In the present case, visible light range 412 and 439 nm strong emission occurs, and with weak peak centered at about 455, 472, 485, 493 nm. The PL peak from the ITO layer is situated at 413, 441 nm with wider full width of half maximum as shown in Figure 4. Strong peak is observed at 412, 439 nm due to blue emission of the ZnO thin film Which is similar to the earlier reported by chemical vapour deposition method [42]. Because there is no any evidence for the existence of cubic ZnO from XRD analysis of the thin film, this result indicates that the PL peak position of ZnO thin film on ITO glass substrate depends on the excitation intensity and could be adjusted by the PL from ITO buffer layer. The shifting of the peak towards lower wavelength increasing the peak intensity from ITO substrate is due to thin layer of ZnO nanostructure on ITO substrate.

#### 4. Conclusion

In conclusion, ZnO thin films with porous morphology were electrosynthesized at room temperatures on ITO-coated glass substrate. Newly synthesized dihydroxylated ionic liquid based on 4-aminopyridinium cation and hydroxyl anion simultaneously acts as an electrolyte and surfactant. XRD pattern confirms crystal orientation along the (101) diffraction plane of pure ZnO with the hexagonal structure. The water contact angle measurements and PL result indicate that film is suitable for the device application, and ionic liquid is a suitable electrolyte and interfacial surfactant templating to develop greener protocol for electrochemical tailoring of thin film for technological application.

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