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Electrochemical Synthesis of Nanostructured ZnO Films Utilizing Self-Assembly of Surfactant Molecules at Solid−Liquid Interfaces

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Solid−liquid interfaces provide a unique environment for surfactant assembly.[1] 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.[2] 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. Burgess et al. demonstrated potential-controlled transformation of hemimicellar aggregates of dodecyl sulfate (SDS) aggregates into a condensed monolayer at the gold electrode surface by inducing rearrangement of surfactant molecules that can match the surface charges on the electrode.[3]

We postulated that these potential-controlled surfactant assemblies at the interface can be utilized as templates for the production of thin semiconducting and metallic nanostructured films when they are combined with an electrodeposition process. In our strategy, the working electrode immersed in a plating solution containing surfactant and inorganic metal ions serves as a substrate for both surfactant aggregation and film deposition. When potentials required to reduce inorganic ions lie within the range of potentials required to induce a desired surface assembly of surfactant−inorganic aggregates (i.e., bilayers to template lamellar structure), the inorganic species will be deposited as organized by surfactants on the surface, resulting in the formation of nanostructured films.

Our approach is conceptually and strategically different from the previous approach of using liquid crystalline phases of surfactants as a direct physical cast to electrodeposit mesoporous films[4] in that we manipulate only a thin interfacial region to organize surfactant−inorganic aggregates by electrochemically controlling surface interactions. Therefore, our method efficiently utilizes dilute surfactant solutions for the production of various nanostructured films without forming corresponding liquid crystalline phases in the rest of the solution. We report here the electrochemical synthesis of high-quality nanostructured ZnO films templated from extremely dilute SDS solution (0.1 wt %).

ZnO films can be cathodically deposited from a nitrate bath by reduction of nitrate ions ($NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$).[5] The generation of OH^- at the working electrode increases the local pH and provides for the cathodic deposition of ZnO. To investigate the effects of surfactant types and concentrations on the microstructure and nanostructure of the deposits, ZnO films were deposited from 0.02 M aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ mixed with various weight percents (0.1−20 wt %) of cationic surfactant, cetyl trimethylammonium bromide (CTAB), or anionic surfactant, sodium dodecyl sulfate (SDS).[6]

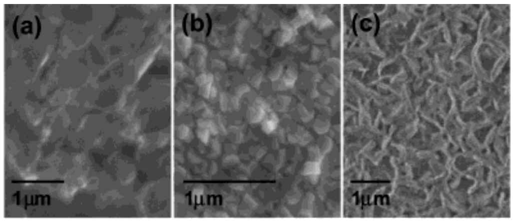

Figure 1. SEM images of the surface morphology of the ZnO films deposited (a) without surfactants, (b) with 5 wt % CTAB, and (c) with 5 wt % SDS.

The surface morphology of the ZnO films imaged by scanning electron microscopy (SEM) is shown in Figure 1. ZnO films deposited both without surfactant and with CTAB are composed of crystalline particles and show similar surface features, suggesting that the positively charged headgroups of CTAB cannot strongly coordinate zinc species (i.e., $[Zn(H_2O)_4]^{2+}$)[7] and fail to form organized nanostructured surfactant−inorganic aggregates on the electrode surface. The smaller size and the well-defined faces of the particles in Figure 1b is due to the adsorption of CTAB on the growing surface of the ZnO particulates, which affects crystal growth patterns.

The film deposited with SDS, however, shows dramatic changes in shapes and crystallinity of the ZnO deposits, which no longer show the X-ray diffraction pattern expected for crystalline ZnO. This and the following results indicate that the anionic headgroups of SDS cooperatively interact with the inorganic species under our deposition condition to form effective in situ templates on the electrode for the production of nanostructures films. Increasing or decreasing the content of either CTAB or SDS in the solution (0.1−20 wt %) does not influence the surface morphology of the resulting films, suggesting that the interfacial structure is not significantly affected by bulk surfactant concentration when the surfactant concentration is above surface micelle concentration.

The nanostructure of the ZnO film deposited with 0.1 wt % SDS was examined by small-angle X-ray diffraction (XRD) (Figure 2). The diffraction patterns are unambiguously indexed as two different lamellar phases, one with $d_{001} = 31.7$ Å and the other with $d_{001^*} = 27.5$ Å, implying two slightly different pathways to form stable surfactant bilayers under our deposition condition. Identical d spacings were obtained in multiple repeat experiments. The presence of high-order 00l peaks for both phases are indicative of well-defined nanostructures with long-range order.

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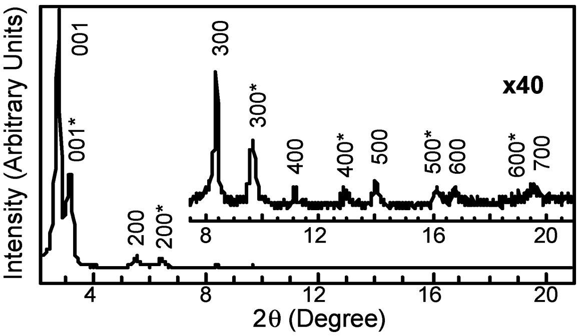

Figure 2. XRD pattern of the ZnO film deposited with 0.1 wt % SDS.

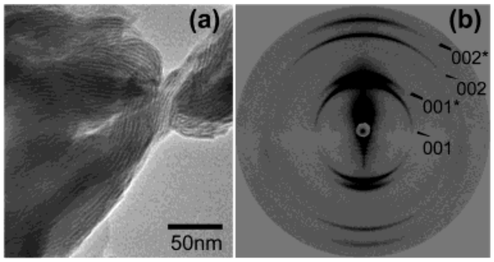

Figure 3. (a) TEM image and (b) 2D-giSAXS pattern of the ZnO film deposited with 0.1 wt % SDS.

Transmission electron microscopy (TEM) images of the same ZnO film confirmed that each ZnO particle is composed of a lamellar nanostructure (Figure 3a). The interlayer spacing and the inorganic wall thickness are estimated to be $\sim$15 and $\sim$15 Å, respectively, which corroborates well with small-angle XRD results. Comparing the particle orientations on the surface (Figure 1c) and the stacking directions of the layers in each particle shown in Figure 3a suggests significant regions of the film with the layers stacked not parallel to the substrate. This arrangement, which will allow facile access of guest molecules or analytes to the interlayers but has never been assembled through other approaches, was confirmed by two-dimensional grazing-incidence small-angle X-ray scatterring (giSAXS) of the ZnO film. The broad arcs in Figure 3b gave definitive proof of a wide distribution of the stacking directions. A lamellar structured film prepared by sol−gel dip coating methods with the layers strictly parallel to the substrate would have resulted in discrete spots in the vertical direction.

This result suggests that the formation mechanism of nanostructures in electrochemical synthesis is fundamentally different from other routes to nanoporous films. In sol−gel dip coating, for example, the orientation of the mesostructures (i.e., 2D hexagonal and lamellar phases) is solely determined by the thermodynamically stable packing of surfactant−inorganic aggregates when the substrate is exposed to air and the solvents are evaporated.[8] This results in one homogeneous orientation of layers or one-dimensional pores parallel to the substrate. In an electrodeposition process, nanostructured films are formed while the substrate remains in solution. When the electric field is applied, surfactant−inorganic assembly and deposition of the inorganic species occur simultaneously. In this situation, the arrangement of surfactant−inorganic aggregates is kinetically determined by the dynamics of charged species near the electrode and by the mechanism of the deposition processes (i.e., growth pattern of particles, deposition rate, redox mechanism). This results in orientations and forms of nanostructures not accessible by other means.

The ZnO films deposited from more concentrated SDS solutions (5, 10, and 20 wt %) show no observable difference in TEM images and XRD patterns. This indicates that 0.1% of SDS, which is below the cmc of pure SDS solution,[9] can fully cover the electrode surface under the deposition condition and effectively templates nanostructures in the ZnO films.

Analysis for carbon−hydrogen−nitrogen in the as-deposited films shows 2.4% carbon content, indicating that the majority of surfactants can be removed by thoroughly washing the films with water and ethanol. This implies another unique feature of electrochemical methods. When the charged zinc species is deposited as neutral ZnO particles by the redox reaction, the electrostatic interactions between the inorganic ions and the surfactant headgroups disappear. Therefore, the surfactant molecules that are only physically adsorbed on the nanostructured walls can be washed away without disrupting the structures. The lamellar structure, however, is not thermally stable and collapses upon heating at 500 °C for 2 h.

In summary, we electrodeposited nanostructured ZnO films utilizing cooperative surface assembly of surfactants and inorganic species under the influence of an electrostatic potential. This approach effectively manipulates surfactant−inorganic aggregates at low concentration in solution to generate high-quality nanostructured films. The unique synthetic mechanism of this approach is expected to generate other metallic and semiconducting nanostructured films of technological importance with architectures, which cannot be assembled by other means.

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