Electrochemical Synthesis of Zinc Nanoparticles via a Metal-Ligand-Coordinated Vesicle Phase

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Two salt-free Zn^{2+} -ligand-coordinated vesicle phases were prepared from the mixtures of alkyldimethylamine oxide (C_nDMAO , n = 14 and 16, i.e., $C_{14}DMAO$ and $C_{16}DMAO$) and zinc laurate [($CH_3(CH_2)_{10}COO$)₂Zn] in aqueous solution. The two salt-free Zn^{2+} -ligand-coordinated vesicle phases were subsequently used as the templating media for fabricating zinc nanoparticles on an indium-doped tin oxide (ITO) electrode via electrodeposition. Influence of temperature, direct current density, and composition of the surfactant mixtures on the average diameter and size distribution of Zn nanoparticles was investigated in more detail. The structure of Zn@ITO was determined by scanning electron microscope and energy-dispersive X-ray spectroscopy analysis. Monodispersed Zn nanoparticles on ITO electrode (ZnNPs@ITO) with different average diameters were obtained, and the distribution can be controlled. Finally, ZnO nanostructures on the ITO substrate were prepared from the as-synthesized Zn@ITO nanoparticles through electrochemical surface oxidation. The preparation of nanostructured Zn and ZnO particles by our established method may pave the way for a new templating route from metal-ligand-coordinated vesicles.

Introduction

Nanoparticle synthesis has attracted much attention¹ as a result of its optical, electronic, magnetic, and chemical properties and its subsequent technological potential applications. Many strategies have been employed for synthesizing metal nanoparticles in aqueous media, including chemical reduction in the presence of a stabilizing agent such as polymers or surfactants,²⁻⁴ electrochemistry,⁵ sol-gel processes,⁶ and so forth. In general, if metal particles in nanometer-scale or patterned arrays are wanted, one resorts to various organic assembly templates such as lyotropic liquid crystals,7 reverse microemulsions,8 and vesicles.⁹ Among the examples we have quoted, there are not so many works reported concerning the preparation of metal nanoparticles through vesicle-templating media. Faure et al. prepared onion-type multilayer vesicles using single nonionic surfactant under shearing, serving as the template and reductant to prepare Ag nanoparticles.⁹ However, in most of the examples, inorganic salts such as silver nitrate, zinc acetate, ¹⁰ and so forth are used as the metallic source and mixed with the templating material (surfactant or polymer) before or after assembly template formation. It is believed that the metallic source combines to the assembly template through interaction such as electrostatic or dipole-dipole interactions.¹¹

Metal ion-ligand-coordinated vesicles, as novel salt-free surfactant vesicle phases, have attracted much interest in recent years. As early as 1999, Hoffmann's group reported the formation of vesicle phase from the mixture of tetradecyldimethylamine oxide (C_{14} DMAO) and calcium dodecyl sulfate [$Ca(DS)_2$] for the first time.^{12a} In our previous work,^{12b-e} the Zn²⁺, Ba²⁺, Ca²⁺, and Al³⁺ coordination complex vesicles were prepared from mixtures of C_{14} DMAO with zinc, 2,2-dihydroperfluorooctanote [Zn(OOCCH₂C₆F₁₃)₂], calcium oleate [Ca(OA)₂], barium oleate [Ba(OA)₂], and aluminum oleate

[Al(OA)₃], respectively. We have primarily deduced the schematic model of metal ion coordination complex vesicles, in which the metal ions were actually coordinated to form the complexes of four chains (either CH chains or CF chains), leading to a pronounced increase in the geometrical packing parameter and resulting in a vesicle phase with much better stability than those of the individual surfactants.^{12c} Electrochemistry has been employed as a means of preparing large numbers of metal nanoparticles,¹³ and some advantages of electrochemical methods over chemical ones for synthesizing small metal particles are the high purity of the particles and the possibility of a precise particle size control achieved by adjusting current density or applied potential.¹⁴ Electrodeposition has also been coupled with surfactant templating to produce films containing ordered structures on solid substrates.¹⁵

In the system we applied in the current work, a Zn^{2+} surfactant, zinc laurate ([CH₃(CH₂)₁₀COO]₂Zn), serves as the source of Zn²⁺ ions which are fixedly combined into the membranes of the vesicles. It is quite different from the traditional source-template model. By electrodeposition in a simple two-electrode setup, well-dispersed Zn nanoparticles with selfpatterned array on the ITO substrate were obtained. We discovered, for the first time, that by varying the experiment conditions such as temperature, composition of the surfactant mixture, or the applied current density, the morphology of the Zn nanoparticles on the ITO substrate can be extremely changed. Thus, the new route reported here has provided a new way not only to prepare well-dispersed metal nanoparticles but also to control their size and shape. The metal reported here is of interest not only on its own but also for the extraordinary optical properties of its oxide. ZnO/Zn@ITO with novel morphology was synthesized from Zn@ITO, which we previously obtained by electrochemical surface oxidation in alkaline solutions of amine-alcohol mixtures,16 and the influences of various experiment conditions on the morphology of the oxide layer were investigated. This work may reveal a new route for the

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Figure 1. Setups for Zn@ITO nanoparticle perparation (A) and ZnO@ITO electrochemical surface oxidation (B).



Figure 2. Phase diagrams and conductivity data of 100 mmol L⁻¹ C₁₄DMAO (a) and 100 mmol L⁻¹ C₁₆DMAO (b) micelle solution with increasing amounts of $(CH_3(CH_2)_{10}COO)_2Zn$ at 70.0 ± 0.1 °C.

preparation and size control of metal nanoparticles and promise further application of the metal-ligand-coordinated vesicles.

Experimental Section

Chemicals. Alkyldimethylamine oxides (C₁₄DMAO and C₁₆DMAO) were gifts from Clariant AG Gendorf and delivered as a 25 wt % solution in water. They were crystallized twice from acetone and characterized by their cmc values and melting points (mp); C₁₄DMAO: mp = 130.2–130.5 °C and cmc = 1.4×10^{-4} mol L⁻¹ (25 °C), and C₁₆DMAO: cmc = \sim 7.0 × 10^{-5} mol L⁻¹ (62 °C).¹⁷ Zinc laurate was purchased from Wako Co. and was used without further purification. Poly(ethylene imine) was purchased from Alfa Aesar. All other chemicals used were analytical grade. The water was triple-distilled.

Preparation of Birefringent Lα Phase. A 100 mmol L⁻¹ C₁₄DMAO micellar solution was mixed with different amounts of zinc laurate, $[CH_3(CH_2)_{10}COO]_2Zn$. The sample solutions were prepared at around 70 °C under stirring and then thermostatted at 70.0 ± 0.1 °C to equilibrate for at least four weeks. The sample solutions were thermodynamically stable up to a mole fraction $x_{CH_3(CH_2)_{10}COO^-} = [CH_3(CH_2)_{10}COO^-]/[CH_3(CH_2)_{10}COO^- + C_{14}DMAO] = 0.5$. Between $x_{CH_3(CH_2)_{10}COO^-} = 0.35$ and 0.46, a single transparent birefringent Lα phase that was very stable, turbid, and slightly bluish was observed.

As to the comparison system, the mixture of C₁₆DMAO and zinc laurate, with the addition of zinc laurate into the 100 mmol L⁻¹ C₁₆DMAO micellar solution, a similar phase transition process could be observed at T = 70 °C. Between $x_{\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-} = 0.3$ and 0.39, there was a single transparent biregringent L α phase.

Conductivity Measurements. The conductivity data of 100 mmol L^{-1} C₁₄DMAO or C₁₆DMAO micelle solutions with increasing different amounts of [CH₃(CH₂)₁₀COO]₂Zn were

measured on a conductivity meter DDSJ-308A and a glass electrode DJS-1C at 70.0 \pm 0.1 °C.

Cryogenic Transmission Electron Microscopy (Cryo-TEM) Observations of Birefringent La Phase Sample Solution. Carbon film grids with a hole size between 1 and 12 mm were used for specimen preparation. A drop of the sample solution that was thermostatted at 70.0 \pm 0.1 °C to equilibrate for at least four weeks was put on the untreated coated TEM grid (copper grid, 3.02 mm, 200 mesh). Most of the liquid was removed with blotting paper, leaving a thin film stretched over the holes. The specimens were instantly shock frozen by plunging them into liquid ethane in a temperature-controlled freezing unit (Zeiss). After the specimens were frozen, the remaining ethane was removed using blotting paper. The specimens were inserted into a cryo-transfer holder (Zeiss) and transferred to a Zeiss CEM 902, equipped with a cryo-stage. Examinations were carried out at a constant temperature of 90 K. The TEM was operated at an accelerating voltage of 80 kV. Zero-loss filtered images ($\Delta E = 0$ eV) were taken under low dose conditions.

Electrochemical Deposition of Zinc Nanoparticles on ITO Substrate. Electrochemical deposition was performed in a twoelectrode cell. A 1 cm × 1 cm Pt plate was used as the anode, and a 1 cm × 0.5 cm ITO glass slice was used as the cathode. ITO glass was pretreated in H₂O/NH₃/H₂O₂ (17:3:1) for 20 min for surface hydrophilization and then immersed in 2 mg mL⁻¹ poly(ethylene imine) for another 20 min, and afterward, in distilled water for 15 min. The electrolytic solution was basic C₁₄DMAO/[CH₃(CH₂)₁₀COO]₂Zn aqueous solution mixed in different molar ratios without adding any inorganic salt as conducting agent. The cell was properly deaerated by N₂ for 10 min before each experiment. The electrolysis was carried out in the galvanostatic manner at 70 °C. The current density



Figure 3. Typical birefringent textures of the L α phase for the two systems of C₁₄DMAO/[CH₃(CH₂)₁₀COO]₂Zn/H₂O with *x*_{CH₃(CH₂)₁₀COO⁻ = 0.39 (a), *x*_{CH₃(CH₂)₁₀COO⁻ = 0.45 (c), and C₁₆DMAO/[CH₃(CH₂)₁₀COO]₂Zn/H₂O with *x*_{CH₃(CH₂)₁₀COO⁻ = 0.35 (d), and *x*_{CH₃(CH₂)₁₀COO⁻ = 0.39 (e). *T* = 70.0 ± 0.1 °C.}}}}



Figure 4. Typical cryo-TEM image of birefringent L α phases for 100 mmol L⁻¹ C₁₆DMAO and [CH₃(CH₂)₁₀COO]₂Zn ($x_{CH_3(CH_2)_{10}COO^-} = 0.35$) at 25.0 \pm 0.1 °C.

and electrolysis time were chosen depending on the experimental requirements. The setup for electrochemical preparation of Zn@ITO is shown in Figure 1A.

Electrochemical Surface Oxidation of Zn@ITO into ZnO@ITO. Following the literature,¹⁶ a mixture of 11.5 mL of H₂O, 7.5 mL of 2-propanol, 3 mL of diethylamine, 0.5 mL of H₂O₂, and 0.17 g of NaCl was used as the electrolyte. The electrolytes were deoxygenated before each experiment. The electrochemical surface oxidation was carried out in a 50-mL cell at a temperature of 22 °C with the potential fixed at 1.2 V. A 1 cm \times 1 cm Pt plate served as the anode, and the as-synthesized Zn@ITO was used as the cathode. The elec

trolysis time was chosen depending on the experimental requirements. The setup for electrochemical surface oxidation for Zn@ITO to ZnO@ITO is shown in Figure 1B.

Characterization. Polarized microscopy observations of birefringent L α phase samples were carried out on an AX-IOSKOP 40/40 FL (Zeiss) microscope. The nanostructures of Zn@ITO and ZnO@ITO were characterized by a JEOL JSM6700F field emission scanning electron microscopy.

Results and Discussion

Phase Behavior of C₁₄DMAO/[CH₃(CH₂)₁₀COO]₂Zn/H₂O and C₁₆DMAO/[CH₃(CH₂)₁₀COO]₂Zn/H₂O Systems. We mixed 100 mmol L⁻¹ C₁₄DMAO micellar solution with increasing amounts of [CH₃(CH₂)₁₀COO]₂Zn. The solubility of [CH₃-(CH₂)₁₀COO]₂Zn is low in water at room temperature. When [CH₃(CH₂)₁₀COO]₂Zn was mixed with 100 mmol L⁻¹ C₁₄DMAO micellar solution, the Krafft point of the Zn surfactant became lower and the phase behavior was much more interesting. The samples were prepared at 70 °C and then thermostatted at 70.0 ± 0.1 °C. The phase diagram of 100 mmol L⁻¹ C₁₄DMAO micellar solution mixed with amounts of 100 mmol L⁻¹ is shown in Figure 2a, which includes the conductivity data of the mixed aqueous solutions. The different phase boundaries could be determined by the conductivity data. The samples are thermodynamically stable up to a mole ratio,



Figure 5. SEM images of the deposition layer of Zn particles on ITO glass surface without (A) and with (B) poly(ethylene imine) pretreatment from L α phase solution at $x_{CH_3(CH_2)_{10}COO^-} = 0.39$.

*x*_{CH₃(CH₂)₁₀COO⁻ = 0.50. From *x*_{CH₃(CH₂)₁₀COO⁻ = 0-0.175, one can note a single transparent solution, which is the L₁ phase. Between *x*_{CH₃(CH₂)₁₀COO⁻ = 0.175 and 0.35, we observe that macroscopic phases separate into a birefringent Lα phase at the top of the isotropic L₁ phase. After the L₁/Lα region, from *x*_{CH₃(CH₂)₁₀COO⁻ = 0.35 to 0.46, we observe a single transparent birefringent, slightly turbid, and bluish Lα phase that is very stable for more than 1 year at 70.0 ± 0.1 °C. The polarizer images of a single transparent birefringent, slightly turbid, and bluish Lα phase of a C₁₄DMAO/[CH₃(CH₂)₁₀COO]₂Zn/H₂O system with different amounts of [CH₃(CH₂)₁₀COO]₂Zn are shown in Figure 3a-c.}}}}

We also studied the phase behavior of the system 100 mmol $L^{-1} C_{16}DMAO$ micellar solution with increasing amounts of $[CH_3(CH_2)_{10}COO]_2Zn$. Phase behavior similar to that of the $C_{16}DMAO/[CH_3(CH_2)_{10}COO]_2Zn/H_2O$ system was obtained, as shown in Figure 2b. The polarizer images of the single transparent birefringent, slightly turbid, and bluish L α phase of the $C_{16}DMAO/[CH_3(CH_2)_{10}COO]_2Zn/H_2O$ system with different amounts of $[CH_3(CH_2)_{10}COO]_2Zn/H_2O$ system with different amounts of $[CH_3(CH_2)_{10}COO]_2Zn/H_2O$ system with different amounts of $[CH_3(CH_2)_{10}COO]_2Zn$ are shown in Figure 3d,e.

Vesicle Structures of Birefringent La Phase Sample **Solution.** The L α phase samples for the two systems of C₁₄DMAO/[CH₃(CH₂)₁₀COO]₂Zn/H₂O and C₁₆DMAO/[CH₃-(CH₂)₁₀COO]₂Zn/H₂O are birefringent, which can be demonstrated by the maltese cross texture of the samples, as shown in Figure 3. The maltese cross texture demonstrates the existence of lamellar phase.¹⁸ The vesicle structures of birefringent La phases of a typical sample solution for the system C₁₆DMAO/ [CH₃(CH₂)₁₀COO]₂Zn/H₂O were determined by the cryo-TEM micrographs in Figure 4. The vesicular phase should be triggered through Zn²⁺-ligand complexation between C₁₄DMAO (or $C_{16}DMAO$) and $[CH_3(CH_2)_{10}COO]_2Zn$.^{12b-e} The vesicles are not shielded by excess salts in solution because of an absence of counterions and there are no additives such as cosurfactant in the aqueous solutions. Such a vesicle phase has many latent applications, one of which is to be used to synthesize inorganic nano- or microparticles.¹⁹ We attempted, for the first time to our knowledge, to synthesize zinc nanoparticles by using electrochemical deposition from the studied Zn²⁺-ligandcoordinated vesicles as templating media.

Surface Pretreatment of ITO by Poly(ethylene imine). Because the deposition process was performed in aqueous environment, the ITO glass that serves as the conducting substrate for deposition has to be pretreated to achieve firm adhesion to the metal nanoparticles. Following the literature,^{20,21} we pretreated the ITO glass by simply immersing it into the diluted aqueous solution of poly(ethylene imine), a highly branched water-soluble polymer with a distribution of primary, secondary, and tertiary amino groups in the ratio 1:2:1. It is demonstrated that the metal particles bond to the layer of polyelectrolyte through amine functionalities, resulting in a much better nanoparticle coverage on the solid substrate than that on a bald ITO glass without poly(ethylene imine) modification, as shown in Figure 5, which was determined by scanning electron microscope (SEM) observations.

Electrochemical Deposition of Zn Nanoparticles and Size Control. Self-assembled structures of surfactants have been extensively studied as templating media for preparing nanoparticles in recent years. Although a general approach to their fabrication in a precisely controlled manner is not yet available in the case of synthesizing nanomaterials in surfactant systems, it is widely accepted that synthesized surfactants have a key role in determining not only the size but also the shape of the products. A typical synthesis system consisting of synthesized surfactants (e.g., Cd(AOT)₂ or Zn(AOT)₂) at the same time as precursors has been already used to prepare colloidal nanocrystals.^{22,23} It is probable to control nanoparticle size and shape by simply varying phase behavior of the surfactant system.

(i) Electrochemical Deposition under Different Surfactant Compositions. We fixed the temperature at 60 °C and selected surfactant mixtures with different molar ratios, $x_{CH_3(CH_2)_{10}COO^-}$, as the electrolyte to prepare Zn nanoparticles under otherwise identical condition. The applied current density is 20 μ A/cm², and the charge time is fixed to be 5 min. The volume of surfactant-mixed solution for each experiment is 2 mL. After electrolysis, a golden metal layer on the ITO surface could be obviously observed. The as-synthesized Zn@ITO was rinsed in ethanol and distilled water right afterward under the protection of nitrogen to clean the surface from attached surfactants. The microscopic structure of the deposit has been investigated by SEM (Figure 6) observations subsequently, and the elements of the deposition layer were determined by EDS (Figure 7).

At $x_{CH_3(CH_2)_{10}COO^-} = 0.1$, the surfactant solution is a transparent single L₁ phase and the deposited Zn nanoparticles show large fragments without regular shape. We notice that some of the large pieces seem to be the assemblies of small particles in irregular spherical shape. At $x_{CH_3(CH_2)_{10}COO^-} = 0.35$, the surfactant solution starts to separate into a birefringent L α phase at the top of the isotropic L₁ phase. The deposition layer shows a mixture of particles with a wide size distribution. As could be deduced from the histograms in Figure 6, the average diameter of the particles is 42.0 nm and the standard deviation (SD) is ± 20.7 nm. At $x_{CH_3(CH_2)_{10}COO^-} = 0.39$, the surfactant solution is a single L α phase that is birefringent. One can notice that Zn nanoparticles have a narrow average size distribution with an average diameter of 52.6 nm and SD of ± 12.2 nm. The Zn



Figure 6. SEM images of Zn nanoparticles prepared by electrochemical deposition at different molar ratios of the surfactants from the C₁₆DMAO and [CH₃(CH₂)₁₀COO]₂Zn/H₂O systems. L₁ phase solution at $x_{CH_3(CH_2)_{10}COO^-} = 0.1$ (A), L₁/L α phase solution at $x_{CH_3(CH_2)_{10}COO^-} = 0.35$ and corresponding particle size distribution (B), L α phase solution at $x_{CH_3(CH_2)_{10}COO^-} = 0.39$ and corresponding particle size distribution (C), and L₁/precipitates solution at $x_{CH_3(CH_2)_{10}COO^-} = 0.5$ (D). The ITO surface was pretreated by poly(ethylene imine).

distribution and better coverage. By increasing $x_{CH_3(CH_2)_{10}COO^-}$ to 0.5, at which ratio the surfactant solution shows a two-phase $L_1/L_{crystal}$ region, it seems that transformed nanospheres larger than 100 nm fuse into continuous bulks. From the above, it can be primarily deduced that only the single L α phase consisting of vesicles is the best media as the electrolyte template to the

electrochemically synthesis of comparatively smaller and monodispersed Zn nanoparticles.

(ii) Electrochemical Deposition under Different Temperatures. Temperature plays an important role in the phase transition of mixed surfactant systems.²⁴ It has been demonstrated that temperature variation can effectively change the



Figure 7. Typical EDS analysis of Zn nanoparticles prepared by electrochemical deposition on ITO electrode surface from L α phase solution at $x_{CH_4(CH_3)_mCOO^-} = 0.39$.

interaction between surfactant molecules in the organized assemblies and thus affect the microscopic structure of the assembly. The single L α phase solution ($x_{CH_3(CH_2)_{10}COO^-} = 0.4$) was selected as the electrolyte to investigate temperature effect on the micromorphology of the deposition Zn nanoparticle layer. The C₁₄DMAO/(CH₃(CH₂)₁₀COO)₂Zn system is rather temperature-sensitive. When the single $L\alpha$ phase sample solution is kept at room temperature, the solution will turn into a twophase solution with white precipitates floating on top of the transparent L₁ phase. When the temperature fluctuates within a narrow span around 70 °C (i.e., 50-80 °C), the solution can remain a single L α phase. A series of electrolysis were done at 50, 70, and 80 °C under otherwise identical conditions. The Zn nanoparticles were determined by SEM observations, which are shown in Figure 8. It is distinctly shown that when temperature rises from 50 to 70 °C, the size of deposited particles is reduced.



Figure 8. Zn nanoparticles synthesized by electrochemical deposition from L α phase solution ($x_{CH_3(CH_2)_{10}COO^-} = 0.40$) of a C₁₄DMAO/(CH₃(CH₂)₁₀COO)₂Zn/H₂O system at different temperatures and corresponding particle size distribution. At T = 50 (A), 70 (B), and 80 °C (C).



Figure 9. Deposited Zn nanoparticle morphologies from the single L α phase solution ($x_{CH_3(CH_2)_{10}COO^-} = 0.35$) of the C₁₆DMAO/(CH₃(CH₂)₁₀COO)₂Zn system at different temperatures, corresponding birefringent texture, and corresponding particle size distribution. T = 70 °C (A, B, and C) and T = 25 °C (D, E, and F).

From the histograms shown in Figure 8, it is determined that the average diameters of the particles prepared at 50 and 70 °C are 57.8 nm with SD of ± 14.6 and 44.0 nm with SD of ± 11.6 nm, whereas at 80 °C there are no recognizable spherical particles yet, leaving only deposited pieces that may result from surfactant assemblies' destruction by overheating.

Similar to the studies above, the single $L\alpha$ phase solution of the C₁₆DMAO/(CH₃(CH₂)₁₀COO)₂Zn/H₂O system was used to obtain Zn nanoparticles by electrochemical deposition. It is different from the single L α phase solution of the C₁₄DMAO/ $(CH_3(CH_2)_{10}COO)_2Zn/H_2O$ system; the single L α phase solution of the C₁₆DMAO/(CH₃(CH₂)₁₀COO)₂Zn/H₂O system remains stable at much lower temperature (i.e., room temperature, ~ 25 °C). Zn nanoparticles can be synthesized from the single $L\alpha$ phase solution ($x_{CH_3(CH_2)_{10}COO^-} = 0.35$) of the C₁₆DMAO/ (CH₃(CH₂)₁₀COO)₂Zn/H₂O system within a wider temperature region, such as at 25 and 70 °C, and the temperature effect on nanoparticle size is more obvious. Figure 9 shows the SEM observations of the Zn nanoparticles synthesized by electrochemical deposition using the single $L\alpha$ phase solution $(x_{CH_3(CH_2)_{10}COO^-} = 0.35)$ and the corresponding birefringent texture of the single L α phase solution ($x_{CH_3(CH_2)_{10}COO^-} = 0.35$). When varying the temperature from 25 to 70 °C, one can clearly see that the average particle diameter reduces distinctly. From the histograms, as shown in Figure 9, we can determine that the average diameters of particles obtained at 25 and 70 °C are 31.0 nm with SD of \pm 9.7 nm and 60.4 nm with SD of \pm 11.3 nm.

(iii) Influence of Surfactant Chain Length. The C₁₆DMAO/ (CH₃(CH₂)₁₀COO)₂Zn/H₂O system is selected as the parallel to the C14DMAO/(CH3(CH2)10COO)2Zn/H2O system. According to the phase diagram, as shown in Figure 2, both solutions with the same composition, $x_{CH_3(CH_2)_{10}COO^-} = 0.35$, were used as the electrolyte to synthesize Zn nanoparticles on ITO electrode surface by electrochemical deposition. The results, as shown in Figure 10, clearly show that the CH chain length of the coordinated surfactants extremely influences the particle size no matter how much the applied current is. Under the same $x_{CH_3(CH_2)_{10}COO^-}$ value, Zn nanoparticles obtained from the $C_{16}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$ system are much smaller than those from the C14DMAO/(CH3(CH2)10COO)2Zn/ H₂O system at two different current densities of 200 and 300 μ A/cm². It is determined from the histograms in Figure 10 that the average diameters of the particles in Figure 10A-D are 59.4 nm with SD of ± 13.7 nm, 33.2 nm with SD of ± 9.4 nm, 70.0



Figure 10. Deposited Zn nanoparticles from the two systems of $C_{14}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$ and $C_{16}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$ at $x_{CH_3(CH_2)_{10}COO^-} = 0.35$ under different current densities and corresponding particle size distribution (*i*). $C_{14}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$, $i = 200 \ \mu A/cm^2$ (A and C). $C_{16}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$, $i = 300 \ \mu A/cm^2$ (B and D).

nm with SD of ± 13.9 nm, and 29.0 nm with SD of ± 8.3 nm, respectively.

(iv) Influence of the Applied Current Density. To see the effect of the applied current density upon particle size, we



Figure 11. Deposited Zn nanoparticles under different applied current densities in the $C_{16}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$ system at $x_{CH_3(CH_2)_{10}COO^-} = 0.39$ and corresponding particle size distribution. The applied currents (*i*): 20 (A), 100 (B), 200 (C), and 300 μ A/cm² (D).

repeated the electrolysis process of the C₁₆DMAO/(CH₃-(CH₂)₁₀COO)₂Zn/H₂O system with $x_{CH_3(CH_2)_{10}COO^-} = 0.39$ using current densities of 20, 100, 200, and 300 μ A/cm² under otherwise identical conditions. We found that, when the applied current density is lower than 100 μ A/cm², there are hardly any

deposited Zn particles (Figure 11A). Significantly, from the histograms and the SEM images in Figure 11B–D, we determined that the average diameters of the particles prepared at 100, 200, and 300 μ A/cm² are 28.6 nm with SD of ±8.0 nm, 47 nm with SD of ±9.9 nm, and 60.8 nm with SD of ±12.6



Figure 12. ZnO nanoparticle morphology evolution by galvanization time. Zn nanoparticles (A), after 3 h (B), after 10 h (C), and a larger region of the ZnO@ITO at lower magnification (D). ZnNPs@ITO was produced from the $C_{16}DMAO/(CH_3(CH_2)_{10}COO)_2Zn/H_2O$ system at $x_{CH_3(CH_2)_{10}COO^-}$ = 0.39. $i = 150 \ \mu \text{A/cm}^2$, E = 1.2 V, and $T = 22 \ ^\circ\text{C}$.

nm, respectively. Thus, it could be concluded that in electrochemical deposition experiment there is a critical current density to obtain obvious deposition layers, and this value will change in accord with temperature and surfactant CH chain length given other conditions.

Electrochemical Surface Oxidation of ZnNPs@ITO. Although the electrochemical surface oxidation on a Zn cathode has been reported before,¹⁶ there is little work about the surface oxidation on a ZnNPs@ITO surface which may result in novel nanostructures. As the ITO glass is used as the conducting substrate, transparent ZnO@ITO nanostructures with novel optical characters could be expected. The experiment setup was a simple two-electrode cell according to the literature,¹⁶ and the as-synthesized ZnNPs@ITO served as the cathode.

It is worth noting that the surface morphology of the oxide seems to have close relation to the galvanization time. After 3 h, there was no evident change of the morphology compared with the source. However, after 10 hours of electrolysis, a considerable proportion of the nanospheres on the surface transformed into nanorods parallel to the substrate with a mean length around 200 nm and width around 30 nm (Figure 12). Further observation shows that among the rods some nanospheres still remain, and they may be the survivors of the oxidation due to not enough galvanization time or to the protection of the oxide layer formed regionally during ZnNPs@ITO preparation.

Conclusions

In summary, we used Zn²⁺-ligand-coordinated vesicles as a template for electrochemical fabrication of zinc nanoparticles on the ITO substrate, which was rarely reported before. It was discovered that by adjusting the temperature, surfactant molar ratio, applied current density, and the CH chain length of the applied amine oxide surfactant, we could effectively control the average diameter and size distribution of the particles. Moreover, ZnO nanorods on the ITO glass were made from the assynthesized ZnNPs@ITO by electrochemical surface oxidation.

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