Selective Preparation of Zinc Oxide Nanostructures by Electrodeposition on the Templates of Surface-functionalized Polymer Particles

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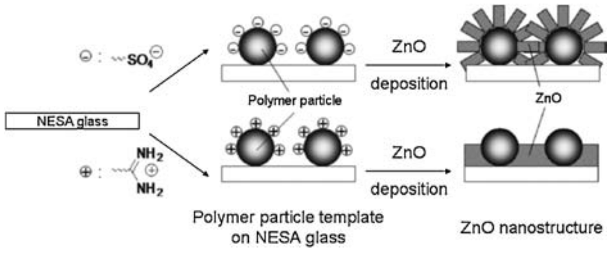
A novel method of controlling zinc oxide (ZnO) nanostructures was developed. The sphere-like ZnO nanostructure was obtained from the electrodeposition on the polymer particle template having anionic surface groups, and under the same electrodeposition condition, microporous ZnO layer was obtained on the polymer particle template having cationic surface groups. These contrasting structures were attributed to the ZnO nucleation site selectivity derived from the specific binding between the polymer particle template surface and Zn^{2+} ion.

An n-type semiconducting zinc oxide (ZnO) has attracted increasing attentions as components in an ultraviolet-light-emitting diode, electron-transporting layer in organic and dye-sensitized solar cells, and sensors. The pursuit of enhancing the device performances leads to acquire the high quality and to gain the wide range of nanostructures, such as continuous layer,[1] pillar,[2] flower,[3] tube,[4] and wound coil.[5] The ZnO nanopiller array has been employed as the anode in a dye-sensitized solar cell and demonstrated the advantages over the conventional anode of sintered TiO_2 nanoparticles.[6] And, the diode of ZnO nanopillar array with a polymer semiconductor exhibited high performance of emitting narrow ultraviolet light at room temperature.[7] Also, ZnO electrodeposition employing templates such as a polymer particle array[8] or anodic alumina membranes[9] has allowed the fabrication of the highly ordered three-dimensional and complicated ZnO nanostructures. The ZnO inverse opal structure constructed by a polymer particle array template demonstrated an isotropic photonic pseudo gap.[10]

Polymer particles have a variety of chemical and physical properties. Among those properties, functional groups expressed on the particle surface have been reported to play an important role in adhering inorganic components on the polymer particles.[11] Also in the construction of ZnO nanostructures employing templates, the surface functional groups may affect the interaction between ZnO and template surface. There is a possible strategy of controlling the interaction by tailoring the surface functionality and constructing new types of ZnO nanostructures (Scheme 1). Electrodeposition is the most suitable method to obtain high-quality ZnO on the template because of the perfect infiltration and low preparation temperature under mild reaction conditions.[12]



Scheme 1. Representative image of ZnO electrodeposition onto polymer particle templates with tailored surface functional groups.

Monodispersed polymer particles (diameter = ca. 400 nm) having anionic and cationic surface groups were prepared by an emulsifier-free emulsion polymerization of styrene monomer with potassium persulfate (KPS) and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA) as a radical initiator, respectively. The monolayer of randomly adsorbed particles was formed without any aggregation and accumulation by electrophoretic deposition (EPD).[13] The anionic particles were adsorbed on the NESA ($F:SnO_2$) glass anode (Figure 1a). Also, the cationic particle could be adsorbed on the NESA cathode in a similar manner (Figure 2a). Number of particles adsorbed on a unit surface area of the electrode was about 3.2 particles/μm^2. The NESA glasses adsorbed with anionic and cationic polymer particles were used as the templates and employed to subsequent ZnO electrodeposition by potentiostatic condition at the potential of -1.0 V referenced to Ag/AgCl standard electrode for electric charge of 0.3 C/cm^2.

Characterizations of the resultant structures were carried out by X-ray diffraction (XRD) and optical transmittance spectrum measurements (Figure S1 in Supporting Information).[15] The absorption edge was observed at about 375 nm for the both structures prepared with anionic and cationic particle templates, and the bandgap energy was estimated to be the characteristic value of 3.4 eV with the assumption of direct transition. Both the XRD spectra of structures on the anionic and cationic template demonstrated the direct formation of wurtzite-type ZnO

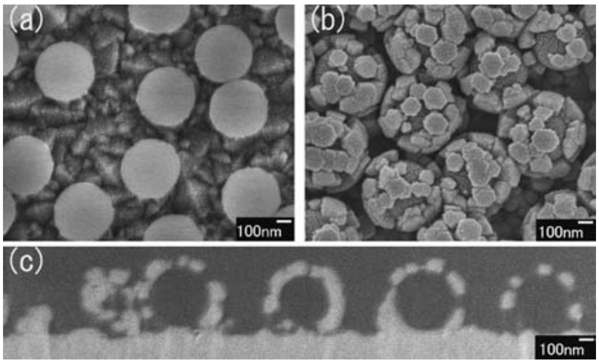


Figure 1. FE-SEM images of (a) anionic polymer particles adsorbed on a NESA glass, (b) after ZnO electrodeposition, and (c) the cross sectional image of (b).

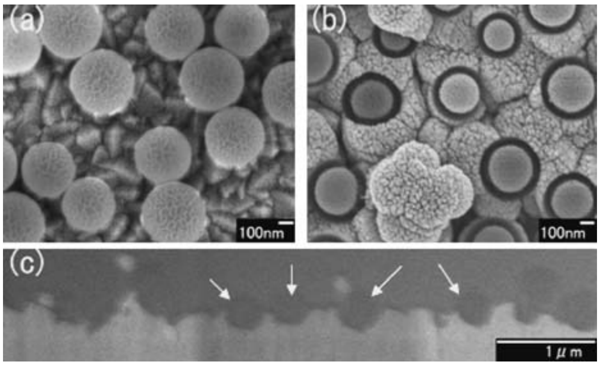


Figure 2. FE-SEM images of (a) cationic polymer particles adsorbed on a NESA glass, (b) after ZnO electrodeposition, and (c) the cross sectional image of (b).

with random orientation on the SnO_2.

Field emission scanning electron microscope (FE-SEM) images of the ZnO nanostructure deposited on the anionic particle template were shown in Figure 1. It could be clearly seen that hexagonal columnar ZnO graines of 100 nm in width grew radially from the polymer particles to form the sphere-like nanostructures (Figure 1b). The hexagonal facets corresponding to the (0001) plane in the wurtzite ZnO can be observed on the image. Its cross sectional image also showed that the ZnO selectively grew on the surface of the particles and formed a shell layer on each particle core (Figure 1c). Contrasting nanostructure was obtained on the cationic particle template (Figure 2). As shown in Figure 2b, the ZnO granular grains grew directly from NESA substrate surface, dodging the polymer particles. Its cross sectional image showed micropores of the ZnO layer (Figure 2c, pores are indicated by arrows), which corresponded to the site that particles exist.

These contrasting results will be attributed to the ZnO nucleation site selectivity derived from the functional groups of the particle surface. To confirm the expectation, bare NESA substrate, anionic particle template, and cationic particle template were only immersed into aq $Zn(NO_3)_2$ solution and rinsed with deionized water, and then they were analyzed by X-ray photoelectron spectroscopy (XPS, Figure 3). All samples showed a signal at 1022 eV, corresponding to Zn $2p_{3/2}$. The signals from the bare NESA and the cationic particle template showed almost the same intensity, whereas that of the anionic particle template was much intense. This result indicates that the sulfate groups on the anionic particle surface will interact with Zn^{2+} ion strongly, giving rise to high concentration of Zn^{2+} ion near the particles even before applying potential. This caused the selective ZnO nucleation on the particles when electrolysis was started. However, the amidine groups on the cationic particle surface would not have such the attractive interaction with Zn^{2+} ion, because the amidine groups were protonated under the reaction condition. The protonated amidinium ion on the particle surface repulsed Zn^{2+} ion, giving rise to low concentration of Zn^{2+} ion near the particles. Selective ZnO nucleation did not occur on the cationic particle surface but on the bare NESA surface.

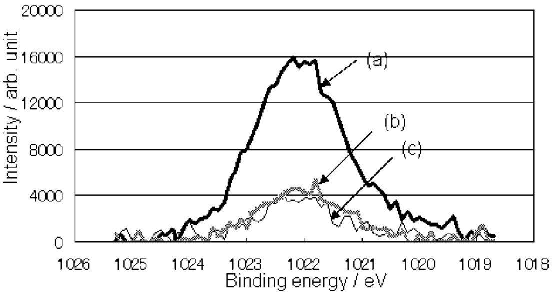


Figure 3. XPS (Mg Kα) of (a) anionic particle template, (b) cationic particle template, and (c) bare NESA after immersion into $Zn(NO_3)_2$ solution.

On the cathode, generation of OH^- by the reduction of nitrate ion led to raise the pH value in the vicinity of the cathode surface, resulting in the precipitation of ZnO. When the first ZnO nucleation occurred at the NESA surface, ZnO granular grains continued to precipitate because ZnO nucleation was preferred to ZnO crystal growth. This phenomenon is commonly seen also on the bare NESA substrate under the same electrolysis condition employed here.[12] As a result, ZnO granular grains filled the space between the cationic particles (Figure 2b). However, relatively large hexagonal columnar ZnO grains were obtained on the anionic particle template (Figure 1b). This indicated that ZnO was precipitated near the equilibrium condition during the electrolysis, resulting in only a small amount of nucleation and preferable crystal growth in the direction of $\langle 0001 \rangle$.[14] Incomplete coverage of the anionic particle surface by ZnO also can be explained by the small amount of nucleation. The ZnO crystal would grow slowly because it was apart from the OH^- source, i.e., NESA glass surface.

Two types of ZnO nanostructures, ZnO shell/polystyrene particle core structure and porous ZnO layer, have been fabricated using templates of polystyrene particles with controlled functional groups and ZnO electrodeposition. The type of functional group on the surface of the polymer particle resulted in the differences of resultant ZnO nanostructures.

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15 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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