Electronic Supplementary Information

Morphological Evolution of ZnO Nanorod Arrays Induced by a pH-buffering Effect during Electrochemical Deposition

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Experimental

Electrodeposition of ZnO. All aqueous solutions were prepared using reagent-grade chemicals and deionized water purified by a Milli-RX12 Plus system. Prior to the electrodeposition, FTO (Asahi Glass, ~10 Ω/sq) substrates were treated with a UV-ozone cleaner, subsequently washed ultrasonically with ethanol and rinsed with deionized water. ZnO was galvanostatically electrodeposited from 0.5 mM $Zn(NO_3)_2 \cdot 6H_2O$–0.1 M $NaNO_3$ based aqueous solutions (150 mL) containing various concentrations of NH_4NO_3 by applying a cathodic current density of 0.2 mA cm^{-2} (total electric charge = 2.0 C cm^{-2}) at 75 °C with a potentio/galvanostat (Hokuto Denko HABF5001) using the FTO (deposition area = 1.0 × 1.5 cm^2) substrate as the working electrode and a Zn bar as the counter electrode.

Characterization of ZnO. Structural and morphological characterization of electrodeposited ZnO was performed with a field-emission scanning electron microscope (FESEM, JEOL JSM6700F) and an X-ray diffractometer using Cu Kα radiation (XRD, Rigaku RINT2500).

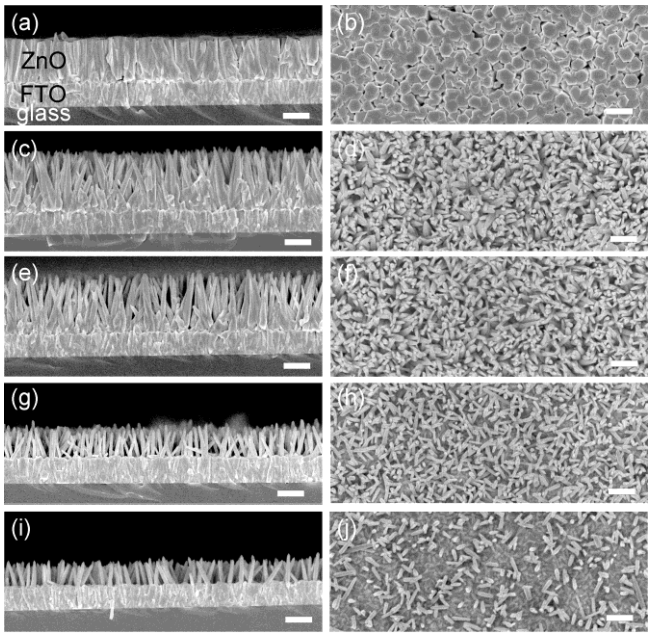

Figure S1. Cross-sectional (left) and top-view (right) FESEM images of ZnO electrodeposited on FTO substrates at a current density of 0.2 mA cm^{-2} with a total electric charge of 2.0 C cm^{-2} from $Zn(NO_3)_2$–0.1 M $NaNO_3$ aqueous solutions at 75 °C with various $Zn(NO_3)_2$ concentrations: (a, b) 50, (c, d) 5.0, (e, f) 1.0, (g, h) 0.5 and (i, j) 0.2 mM. All scale bars are 1 μm. The shape of the electrodeposited ZnO changed from (a, b) a form of film to (c–f) nanorod arrays with coalescence, (g, h) separated nanorod arrays and (i, h) sparse nanorod arrays. The diameters of ZnO nanorods obtained from 0.5 and 0.2 mM $Zn(NO_3)_2$ solutions were approximately the same (~0.14 μm). Furthermore, the amounts of ZnO deposited from these dilute solutions were much smaller than those deposited from solutions with higher [Zn^{2+}]; the volume of ZnO deposited per unit substrate area was estimated from the FESEM images to be 1.3 (50 mM Zn^{2+}), 0.25 (0.5 mM Zn^{2+}) and 0.03 (0.2 mM Zn^{2+}) $\mu m^3/\mu m^2$ sub. These results indicate a poor controllability of nanorod diameter and a poor deposition efficiency (i.e. current efficiency) in the case of the electrodeposition from the dilute Zn^{2+} solutions.

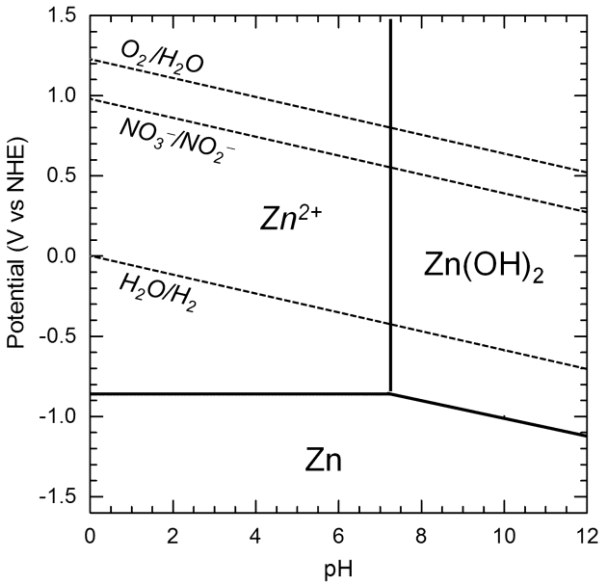

Figure S2. Potential-pH diagram of the Zn−H_2O system (solid line) at 25 °C: $a(Zn^{2+}) = 5 \times 10^{-4}$, $a(NO_3^-) = 0.1$, $a(NO_2^-) = 10^{-6}$, $p(O_2) = 1$ and $p(H_2) = 1$ atm.[1]

1. M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, NACE, Houston, TX, 1974.

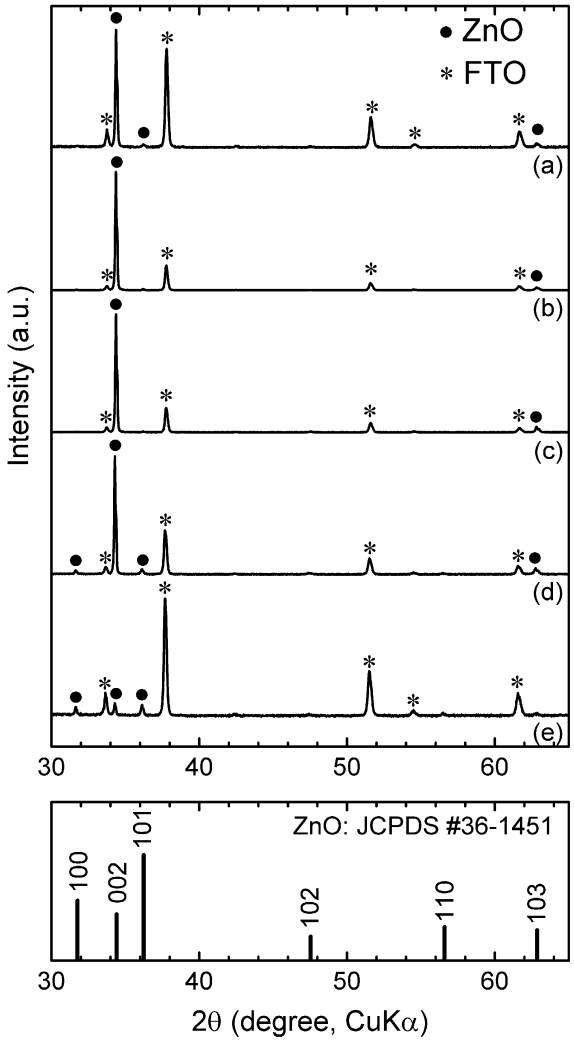

Figure S3. XRD patterns of ZnO electrodeposited on FTO substrates at a current density of 0.2 mA cm^{-2} with a total electric charge of 2.0 C cm^{-2} from 0.5 mM $Zn(NO_3)_2$–0.1 M $NaNO_3$ aqueous solutions at 75 °C with various NH_4NO_3 concentrations: (a) 0, (b) 1.0, (c) 5.0, (d) 10 and (e) 20 mM. JCPDS-ICDD data for ZnO are also shown for comparison.

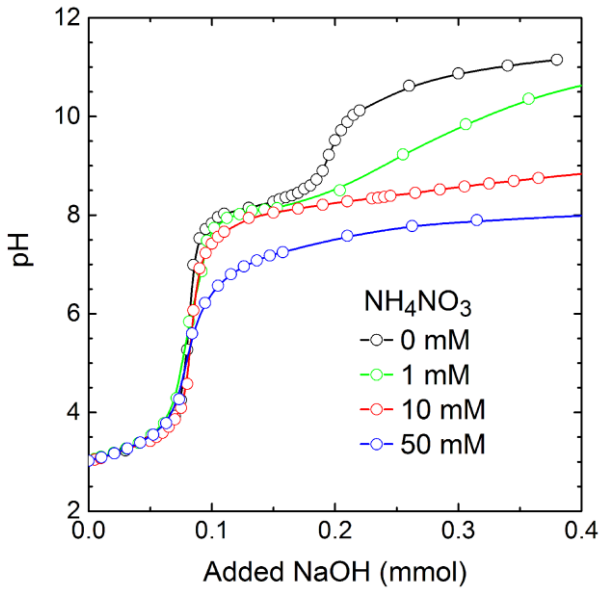

Figure S4. pH titration curves of 0.5 mM $Zn(NO_3)_2$–0.1 M $NaNO_3$ aqueous solutions with different NH_4NO_3 concentrations of 0, 1.0, 10 and 50 mM. All solutions were initially adjusted to pH = 3.0 with HNO_3 and subsequently titrated with 10 mM NaOH at room temperature.