Supplementary information

Photoelectrochemically Homogeneous Nickel Oxide Photocathode Composed of Nanocrystals Prepared by Supercritical Hydrothermal Synthesis

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1. FT-IR spectrum after annealing and UV/O_3 treatment

We removed organic molecules from the NiO-NC films by annealing and UV/O_3 ashing treatment because the insulation molecules prevent charge transfer and the reactive molecules work as sacrificial reagents. We annealed and ashed the NiO NCs synthesized in the presence of OA as a sample for the validation of eliminating OA. Figure S1 shows the FTIR spectrum of NiO-NCs after annealing and UV/O_3 treatment. Vibrational signals at 2800-3000 cm^{-1}, and 1400–1600 cm-1 of OA were not observed, indicating the elimination of OA.

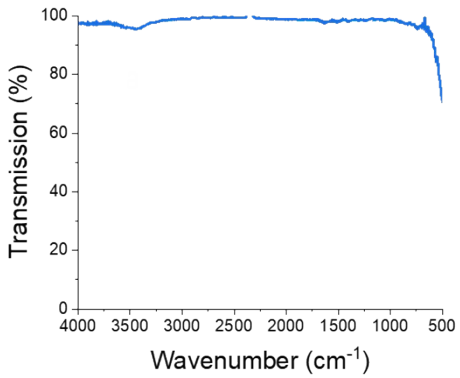

Figure S1. FTIR spectrum of NiO NCs after annealing at 600°C and UV/O_3 treatment.

2. Surface profiles of NiO-NC films

Figure S2 shows the height profiles of the NiO-NC films prepared using the LS and PC methods. Some parts of the NiO-NC films were manually peeled off to reveal the bare substrate. The thicknesses of the NiO-NC films were estimated as the difference between the film height (red lines in Figure S2) and the height of the bare substrate (black lines in Figure S2).

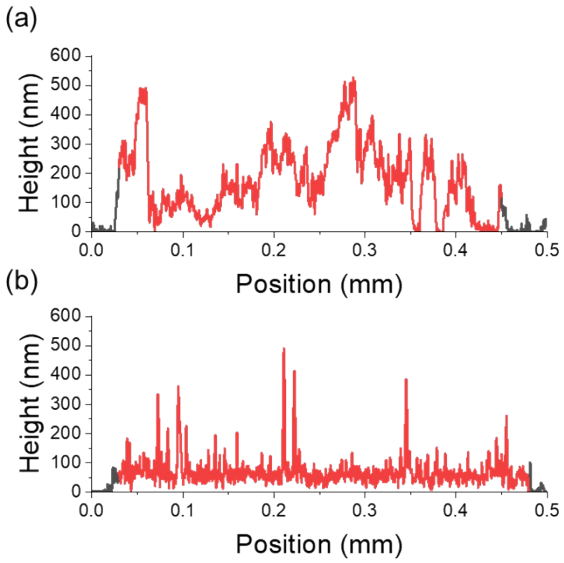

Figure S2. Typical height profiles of the NiO-NC film prepared by (a) LS and (b) PC methods from a 3 wt% NiO-NC dispersion in *n*-octane. The thickness and roughness of the NiO-NC films were calculated based on red lines. The black line parts were ignored because they corresponded to the nude substrates.

3. Energy band gap of the NiO-NC film

The direct energy bandgap was calculated using the Tauc plot depicted in Figure S3 for the NiO-NC film prepared using the PC method. The Tauc plot was obtained using Equation S1:

$$(\alpha h\nu)^2 = (A \cdot (h\nu - E_g)) \quad \text{(S1)}$$

where, α is the absorption coefficient, $h\nu$ represents incident photon energy, A is a constant, E_g is the energy band gap.[1]

In this study, the extinction of the NiO-NC film was employed instead of α because α is proportional to extinction.

Figure S3 shows the Tauc plot of the NiO-NC film prepared using the PC method. The extinction values were obtained from Figure 3a. The energy band gap of the NiO-NC film was 3.5 eV.

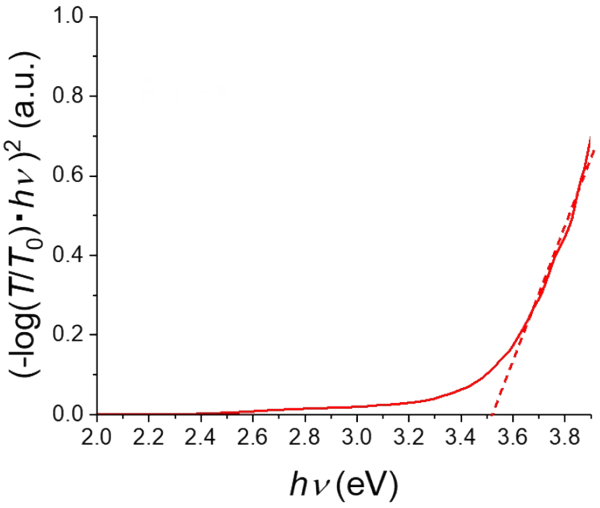

Figure S3. The Tauc plot of the NiO-NC film prepared using the PC method was constructed from Figure 3a.

4. Effect of OA on PC method

Figure S4 shows optical photographs of NiO-NCs on the TEC-glass substrate and PDMS mold after film fabrication using the PC method. Figures S4a and S4b indicate that NiO-NCs adhered to and remained on the PDMS mold after the PC method in the presence of 0 and 10 wt% of OA. This reduced the amount of NiO-NCs on the substrate and CR. In contrast, a small amount of NiO-NCs adhered to the PDMS mold after the PC method in the presence of 30 wt% of OA (Figure S4c). This suggests that OA acts as a release reagent. The quantitative analyses of CR at varying OA concentrations are shown in Table 2.

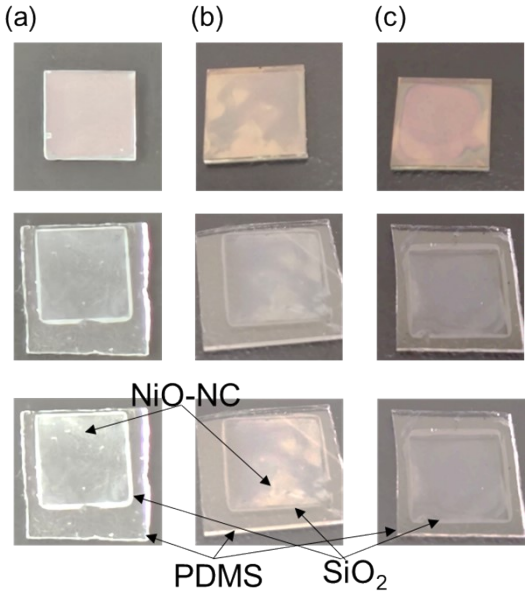

Figure S4. Photographs of (upper) NiO-NCs on TEC-glass, (middle) PDMS mold after PC-method, and (lower) same photographs as in the middle panel with adjusted contrast to emphasize the NiO-NCs on the surface. (a) 3 wt% NiO-NC and 0 wt% OA, (b) 3wt% NiO-NC and 10 wt% OA, and (c) 3 wt% NiO-NC and 30wt% OA.

5. EIS measurements

Figure S5a shows the electrochemical impedance spectra in the form of Nyquist plots of the NiO-NC films prepared using the PC and PC/ALD methods. The equivalent circuits used for fitting are shown in Figures S5b and S5c. In the case of the PC method, we assumed two impedance layers in addition to the solution resistance according to the reported model for the semiconductor film: one is the interfacial charge transfer layer (R_{int} and CPE_{int}), and the other is the bulk charge transport layer (R_{NC} and CPE_{NC}, Figure S5b).[2] The Nyquist plot of the NiO-NC film prepared by the PC/ALD method was fitted using an equivalent circuit including the interfacial charge transfer layer, bulk charge transport layer, and an additional large impedance component derived from the ALD-NiO layer (R_{ALD} and CPE_{ALD}, Figure S5c). Figure S5d shows the cross-sectional SEM image of the NiO-NC films using a 3 wt% NiO-NC dispersion after additional deposition of NiO by PE-ALD with a reaction cycle of 870. The diameters of interparticle voids were tens of nanometers and smaller than those of before ALD treatment (Figure 2e).

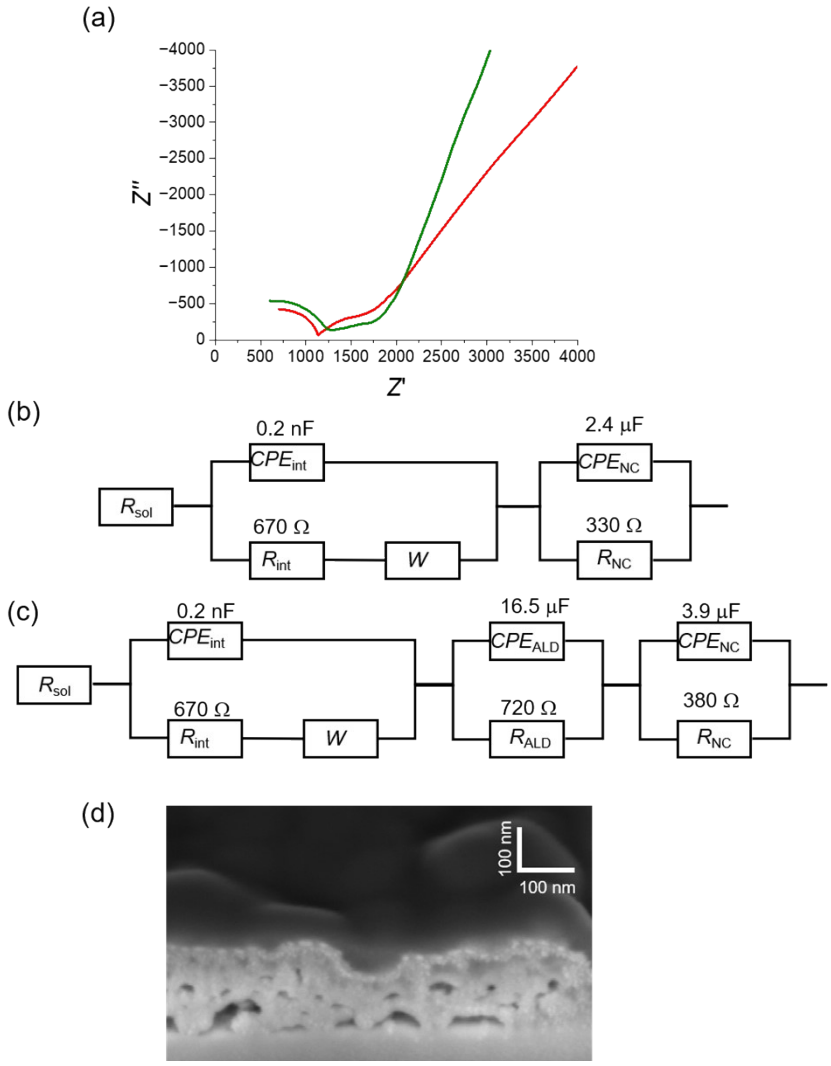

Figure S5. (a) EIS spectra of NiO-NC films (red) without and (green) with additional deposition of NiO by PE-ALD. (b,c) Equivalent circuits of NiO-NC films (a) with and (b) without additional deposition of NiO by PC/ALD. R_{sol}, R_{int}, R_{NC}, and R_{ALD} are the resistances in the solution, the interface between the solution and the substrate, the bulk NiO-NC film, and the ALD-NiO, respectively. CPE_{int}, CPE_{NC}, and CPE_{ALD} are the constant phase elements for the interface between the solution and substrate, bulk NiO-NC film, and ALD-NiO, respectively. W is the Warburg diffusion impedance. (d) Cross-sectional SEM image of the NiO-NC films using a 3 wt% NiO-NC dispersion after additional deposition of NiO by PE-ALD.

1. M. Hashem, E. Saion, N. M. Al-Hada, H. M. Kamari, A. H. Shaari, Z. A. Talib, S. B. Paiman and M. A. Kamarudeen, *Results Phys.*, 2016, **6**, 1024-1030.
2. T. Lopes, L. Andrade, F. Le Formal, M. Gratzel, K. Sivula and A. Mendes, *Phys. Chem. Chem. Phys.*, 2014, **16**, 16515.