Experimental Supplementary Information

Ruthenium Based Nanostructures Driven by Morphological Controls as an Efficient Counter Electrode for Dye-Sensitized Solar Cells

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Experimental Methods

**Synthesis of RuO\textsubscript{2} Nanoparticle precursors.** 20.7 mg of RuCl\textsubscript{3}·xH\textsubscript{2}O powder was dissolved in 20 mL of deionized water (5 mM) to synthesize RuO\textsubscript{2}·xH\textsubscript{2}O amorphous nanoparticles precursor. Then, 0.4 M of sodium hydroxide solution was injected with a speed of 3 \( \mu \)L/min for 8 h. Vacuum filtration is performed to collect RuO\textsubscript{2}·xH\textsubscript{2}O nanoparticles. Separated nanoparticles were dispersed in 1 mL of H\textsubscript{2}O with the concentration of 200 mM. 10 wt\% of PEO was dissolved in ethanol and filtered with 1.0 \( \mu \)m of glass-fiber syringe filter. RuO\textsubscript{2}·xH\textsubscript{2}O solution and PEO solution were mixed with a ratio of 1:1 (v/v). The total RuO\textsubscript{2}·xH\textsubscript{2}O concentration of is 100 mM.

**Preparation of Counter Electrodes.** The Pt counter electrode was prepared by spin coating of 7 mM of H\textsubscript{2}PtCl\textsubscript{6} in 2-propanol at 1000 rpm through the thermal reduction at 400
°C for 20 min. The RuO₂ counter electrode was prepared by sintering the prepared RuO₂·xH₂O nanoparticle film formed by spin-coating on the FTO glass substrate with a speed of 1000 rpm. The RuO₂·xH₂O nanoparticle film was sintered at 250 °C for 4 h in air. Sintering process led to the conversion of RuO₂·xH₂O into RuO₂. The reduction of RuO₂ nanostructure was directly carried out in a single zone quartz tube furnace, 2.5 cm in diameter and 60 cm long under H₂ atmosphere. The RuO₂ thin film sample on the quartz boat was first transferred to the center of the furnace. Before the beginning of ramping temperature, the quartz furnace was flushed with Ar (99.999%) carrier gas flowing for 2 hours. at a gas flow rate of 300 sccm in order to get rid of any contaminants. The temperature was gradually increased up to 150°C for 10 min and then maintained at the same temperature under H₂ (99.999%) carrier gas flowing for ~15 min. at a gas flow rate of 10 sccm. The furnace was finally allowed to cool to room temperature in the same H₂ gas flow.

Fabrication of DSSCs. FTO-coated glass substrates (8 Ω/cm) were cleaned in ethanol through ultrasonication for 20 min. Blocking layer was prepared by spin-coating of 0.38 M of titanium(IV)bis(ethyl acetoacetato)diisopropoxide in 1-butanol on a FTO glass, followed by annealing at 500 °C in the air for 15 min. The TiO₂ paste (ENB KOREA, Korea) was coated on the blocking layer using a doctor-blade and sintered at 500 °C for 30 min. The resulting thickness of the TiO₂ film was about 9.5 ± 1 μm. For the dye adsorption process, the sintered TiO₂ electrode was immersed in a 0.5 mM of N719 ethanol solution at 25 °C for 24 h. The dye-adsorbed TiO₂ electrode and the Pt or RuO₂ counter electrode were assembled using 60 μm-thick Surlyn (DuPont 1702) as the sealing agent. A liquid electrolyte was introduced through a pre-punctured hole in the counter electrode. The electrolyte solution was composed of 0.7 M of 3-propyl-1-methyl-imidazolium iodide, 0.03 M of I₂, 0.1 M of guanidinium thiocyanate and 0.5 M of 4-t-butylpyridine in a 85:15 (v/v) mixture of acetonitrile/valeronitrile.

Characterization. Current density-voltage characteristics were measured by a Keithley 2400 source meter under 1 sun illumination condition (100 mW/cm²) from a 150 W Xenon lamp based solar simulator (McScience, Korea). Electrochemical impedance spectroscopy (EIS) was measured at 1 sun illumination condition with a potentiostat (Solartron 1287) equipped with a frequency response analyzer (Solartron 1260). An Alpha-step IQ surface profiler (KLA Tencor) was used to determine the thickness of the TiO₂ film. Field emission
scanning electron microscope (FE-SEM) images were obtained using JSM-6700F (JEOL, Japan) to characterize nanostructure and morphology of counter electrodes. X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were performed to identify synthesized RuO$_2$ and Ru. Cyclic voltammetry was performed by using a three-electrode configuration (reference electrodes: Ag/AgCl, counter electrode: Pt wire) in an acetonitrile solution containing 10 mM LiI, 1 mM I$_2$ and 0.1 M LiClO$_4$ at a scan rate of 50 mV s$^{-1}$. Tafel polarization curves were obtained using a symmetric cell configuration with electrolyte same as that used for DSSC.