Tailoring Copper Oxide Semiconductor Nanorod Arrays for Photoelectrochemical Reduction of Carbon Dioxide to Methanol

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Abstract

Solar photoelectrochemical reduction of carbon dioxide to methanol in aqueous media was driven on hybrid CuO/Cu2O semiconductor nanorod arrays for the first time. A two-step synthesis was designed and demonstrated for the preparation of these hybrid copper oxide one-dimensional nanostructures on copper substrates. The first step consisted in the growth of CuO nanorods by thermal oxidation of a copper foil at 400 °C. In the second step, controlled electrodeposition of p-type Cu2O crystallites on the CuO walls was performed. The resulting nanorod morphology with controllable wall thickness by adjusting the Cu2O electrodeposition time as well as their surface/bulk chemical composition were probed by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. Photoelectrosynthesis of methanol from carbon dioxide was demonstrated at −0.2 V vs SHE under simulated AM1.5 solar irradiation on optimized hybrid CuO/Cu2O nanorod electrodes and without assistance of any homogeneous catalyst (such as pyridine or imidazole) in the electrolyte. The hybrid composition, ensuring double pathway for photoelectron injection to CO2, along with high surface area were found to be crucial for efficient performance in methanol generation under solar illumination. Methanol formation, tracked by gas chromatography/mass spectrometry, indicated Faradaic efficiencies of ∼95 %.

Keywords: carbon remediation dioxide, electrodeposition, methanol, photoelectrochemistry; semiconductors