CuO nanomaterials for p-type dye-sensitized solar cells

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Experimental Details

Electrochemical impedance spectroscopy (EIS) measurements.

CuO powders were pressed under 100 bars to generate hard pellets. Carbon paste was painted on one side to make the back contact between CuO pellet and copper wire. Then the pellet was sealed by resistant epoxy. Before EIS measurement, the surface of CuO pellet was polished by SiC paper to get a mirror-like smooth surface. EIS measurements were carried out with an electrochemical workstation (SP-300, Biologic Sciences Instruments). The electrolyte is 1 M LiClO₄ aqueous solution (pH = 9.4), and a platinum electrode and a saturated calomel electrode (SCE) was served as counter and reference electrode, respectively.

Prepration of the CuO photocathode and fabrication of p-DSSC.

The CuO films were prepared by screen printing method. First 100 mg CuO powder was ball milled with 3 mL ethanol. Second the mixture was dropped into a mixed solution with 3mL ethanol, 1 mL terpineol, and 1 mL 5% ethyl cellulose solution in ethanol under stirring. After stirring for 15 min, the ethanol was removed by using rotary evaporator to get the paste for screen printing. A layer of CuO paste was coated on the FTO glass plates by screen printing. Then the as-prepared films was sintered at 350°C under air atmosphere for 1 h to eliminate the organic components of the used paste and favor a good adhesion of the mineral on the substrate. Then they were dipped into 0.2 mM DPP-NDI dye solution in dichloromethane/terahydrofuran (2:1) for 24 h at room temperature.

Counter electrodes were prepared by chemical deposition of platinum from 2 mg/mL hexachloroplatinic acid solution in isopropanol. A thin transparent film of Surlyn polymer (DuPont, 25 μ m) was placed between the photocathode and Pt electrode as a spacer to form the electrolyte space and both electrodes were sealed by heating the edges at 200 °C. The cobalt electrolyte is 0.1 M tris(4,4'-bis-tert-butyl-2,2'-bipyridine) cobalt (III/II) and 0.1 M LiClO₄ in propylene carbonate. The electrolyte used for P1 is 0.1 M I₂ and 1 M LiI in acetonitrile. The electrolyte was injected into the cell by vacuum backfilling method. The active area of the cell is 0.25 cm².

Characterization of the CuO based p-DSSCs

The photocurrent-photovoltage characteristics were measured using a Keithley model 2400 digital source meter. The solar simulator is an Oriel Lamp calibrated to 100 mW/cm². The overall conversion efficiency (η) of the photovoltaic cell is calculated from the integral photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light.

The intensity modulated photocurrent spectroscopy (IMPS) was measured on a ZAHNER CIMPS workstation. The transport time can be calculated from the IMPS response by $\tau = 1/(2\pi f_{min})$, where f_{min} is the characteristic frequency minimum of the IMPS imaginary component.¹



Fig. S1. TEM, HRTEM, and SAED images of CuO nanowires, (a)-(c), CuO nanorods 1, (d)-(f), and CuO nanorods 2, (g)-(i).

All the diffraction rings can be ascribed to the CuO phase (space group: C2/c). The 0.23 nm and 0.25 nm observed d-spacings correspond to the (111) and (-111) CuO lattice planes respectively.



Fig. S2. Low magnification SEM images of CuO nanowires (a), CuO nanorods 1 (b), and CuO nanorods 2 (c).



Fig. S3. The molecular structure of tris(4,4'-di-tert-butyl-2,2'-bipyridine)cobalt(III/II) electrolyte.



Fig. S4. Overlay of the absorption spectra recorded in solution of the dyes P1 (red) in CH_3CN and DPP-NDI (black) and YF1 (blue) in CH_2Cl_2 .



Fig. S5. Relative positioning of the energy levels of CuO, the dye, and the redox mediator.

We have provided Mott-Schottky plots because they allow to accurately measure the valence bands of the various CuO materials (Fig. 4.). Besides, flat band potentials measured by the Mott-Schottky are determined relative to a reference electrode (herein saturated calomel electrode) and in presence of the solvent, which is far from the UPS measurement that are conducted in vacuum and that give energy relative to vacuum. Since the UPS is only surface sensitive, UPS data would be redundant and less accurate than Mott-Schottky measurements. So we use the electrochemistry method to determine the energy level of CuO. If we take the CuO nanowire as example, the flat band potential is 0.27 V vs. SCE at pH 9.4 (1.07 V vs. NHE). (Ref: J. Mater. Chem., 2012, 22, 14353) The maximum achievable V_{oc} is equal to the difference between the quasi-Fermi level close to the VB and redox potential of electrolyte. When using I₃-/I⁻ as the redox mediator, (E = 0.35 V vs. NHE, Ref: Nat. Commun. 3, 631) the above determined valence band matches that of the electrolyte. Besides, we wish to underline that in a proper case-study p-DSSC, there is no reaction between CuO and the electrolyte, apart from deleterious concomitant shunt reactions. The purpose of the electrolyte is to regenerate the reduced dye (following hole injection).

Reference:

1 Y.-F. Wang, K.-N. Li, W.-Q. Wu, Y.-F. Xu, H.-Y. Chen, C.-Y. Su and D.-B. Kuang, RSC Adv., 2013, 3, 13804.