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A copper borate as photocathode in p-type dye-sensitized solar cell

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Experimental Details

Sol-gel synthesis of "$CuBO_2$"

"$CuBO_2$" nanoparticles were synthesized by the sol-gel method of Santra et al.[1] Typically, 0.484 g $Cu(NO_3)_2$•$3H_2O$ was dissolved in 5 mL H_2O, and 0.124 g H_3BO_3 was dissolved in 5 mL H_2O with 4 mL 4 M HNO_3. Then the two solutions were mixed together, and 0.7685 g citric acid was added as a chelating agent. The pH value of the above solution was adjusted by using ethylenediamine to 0.5. After refluxing the solution at 75 °C for 8 hours, the solution was heated at 110 °C for 20 h to remove water. Dark green $CuBO_2$ particles were obtained after sintering the gel under air at 550 °C.

Characterization

The X-ray diffraction (XRD) patterns were characterized by an X-ray diffractometer (Bruker, D8) with Cu-Kα radiation (λ = 0.15418 nm). The thermogravimetric analysis-differential thermal analysis (TGA-DTA) was carried out on a thermogravimetry apparatus (SETARAM TG-ATG 92). BET specific surface area was measured on a Micromeritics 3Flex Surface Characterization Analyzer. The Raman spectrum was recorded on a Raman spectrometer (CARTO, Renishaw). The UV-vis transmission spectra of $CuBO_2$ film was recorded on a UV-vis spectrophotometer (Perkin Elmer, Lambda 1050). Transmission electron microscopy (TEM) observations were carried out on a transmission electron microscope (Hitachi, H9000NAR, working at 300 kV and room temperature, Hitachi, HF2000-FEG, working at 100 kV and liquid nitrogen temperature).

Electrochemical impedance spectroscopy (EIS) measurements.

"$CuBO_2$" powder was pressed under 100 bars to generate a hard pellet. Carbon paste was painted on one side to make the back contact between "$CuBO_2$" pellet and copper wire. Then the pellet was sealed by resistant epoxy. Before EIS measurement, the surface of "$CuBO_2$" 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 $LiClO_4$ aqueous solution (pH ~ 9.4), and a platinum electrode and a saturated calomel electrode (SCE) was served as counter electrode and reference electrode, respectively.
We have calculated the carrier density by using the Mott-Schottky equation:

$1/C^2 = (2/e\varepsilon_0\varepsilon N_a)[(V - V_{FB}) - kT/e]$

where C represents the capacitance of the space charge region, ε_0 is the vacuum permittivity, ε is the dielectric constant, e is the electron charge, V is the electrode applied potential, V_{FB} is the flat band potential, k is the Boltzmann constant, T is the absolute temperature, and N_a is the carrier density. The temperature term is generally small and can be neglected.

N_a is 3.07 x 10^{13} cm^{-3} for $CuBO_2$ and 5.00 x 10^{16} cm^{-3} for NiO. The dielectric constant of NiO is 9.7.[2] Since there is no report on the dielectric constant for $CuBO_2$, we used the dielectric constant of $CuAlO_2$ (ε = 10)[3] instead. The area of the electrode is 0.5 cm^2.

Preparation of the $CuBO_2$ photocathode and fabrication of p-DSSCs.

The "$CuBO_2$" films were prepared by the screen printing method.. First 100 mg $CuBO_2$ powder were ball milled with 3 mL ethanol. Then the mixture was dropped into a solution of 3mL ethanol, 1 mL terpineol, and 1 mL 5% ethyl cellulose solution in ethanol under stiring. After stiring for 15 min, the ethanol was removed by using rotary evaporator to get the paste for screen printing. The as prepared films were sintered at 350 °C for 1 h to remove all the organic materials. Then they were dipped into 0.2 mM DPP-NDI dye solution in dichloromethane/tetrahydrofuran (2:1) for 24 h at room temperature.

Counterelectrodes were prepared by chemical deposition of platinum from 2 mg/mL hexachloroplatinic acid solution in isopropanol and subsequent fired at 375°C for 30 mn. A thin transparent film of Surlyn polymer (DuPont, 25 µm) 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 electrolyte is 0.1 M tris(4,4'-bis-tert-butyl-2,2'-bipyridine) cobalt (III/II) and 0.1 M $LiClO_4$ in propylene carbonate. The electrolyte was injected into the cell by the vacuum backfilling method. The active area of the cell is 0.25 cm^2.

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.

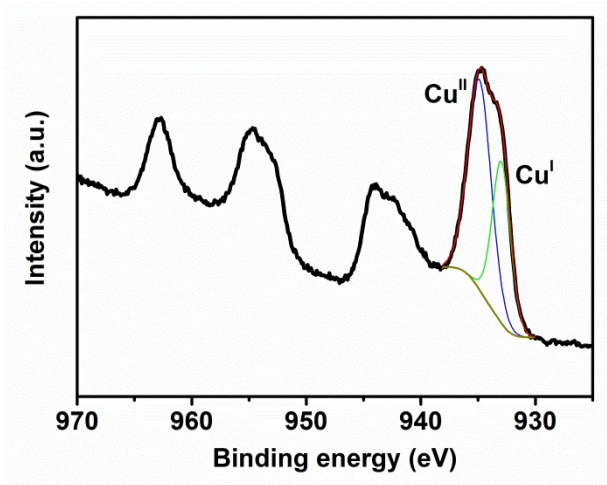

Fig. S1. Cu 2p XPS spectrum of $CuBO_2$.

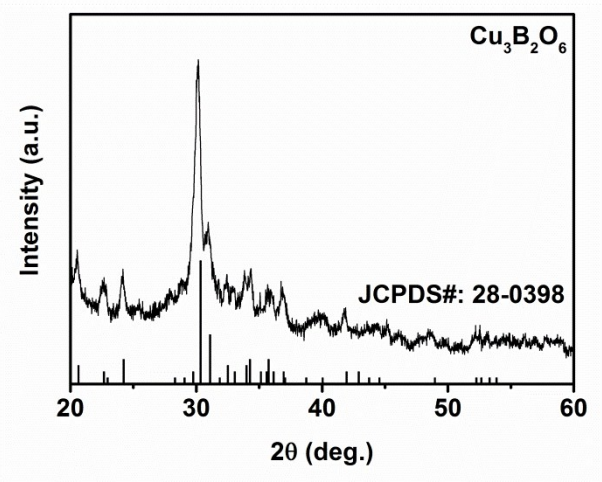

Fig. S2. XRD pattern of $Cu_3B_2O_6$ obtained by sintering as-prepared $CuBO_2$ at 800 °C for 5 min with a heating rate of 5 °C/min.

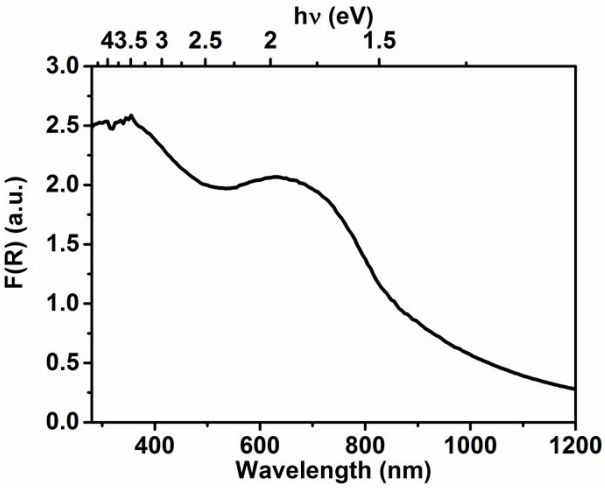

Fig. S3. The transformed Kubelka-Munk reflectance spectrum of $CuBO_2$.

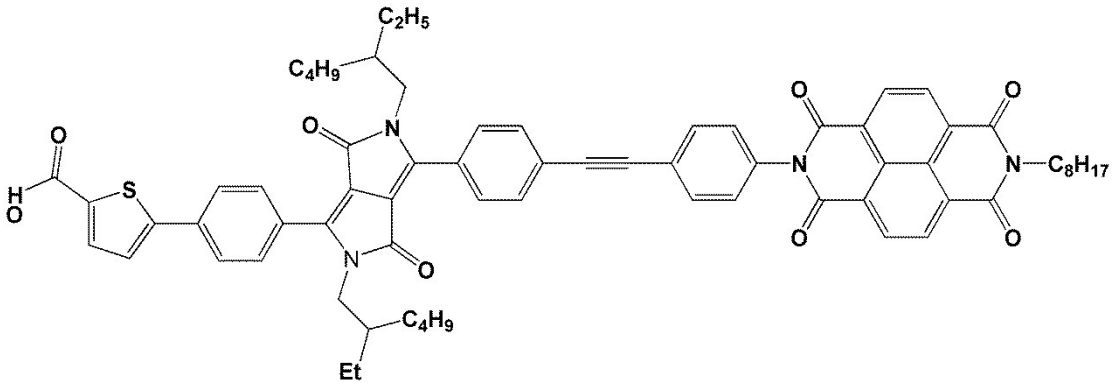

Fig. S4. The molecular structure of DPP-NDI sensitizer.

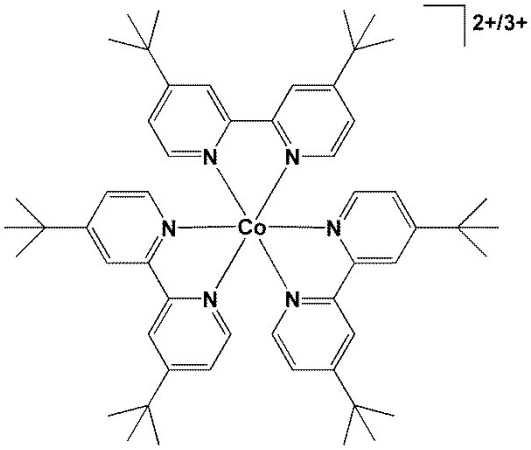

Fig. S5. The molecular structure of tris(4,4'-di-tert-butyl-2,2'-bipyridine)cobalt(III/II) electrolyte.

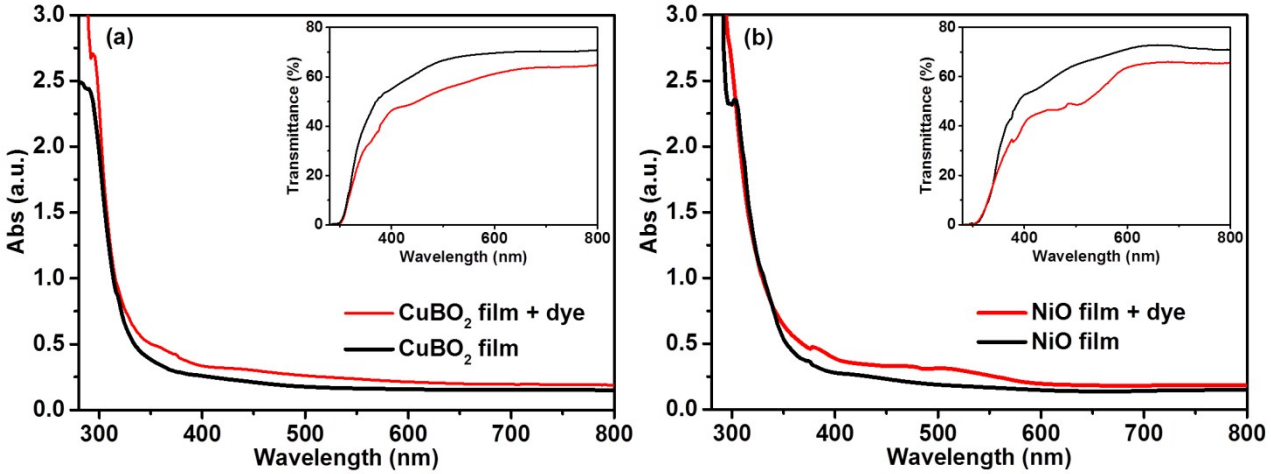

Fig. S6. UV-vis absorption spectra of "$CuBO_2$" (a) and NiO (b) films on FTO substrate before and after sensitized prepared by screen printing and sintered at 350°C for 60 min under air. The thickness of the film is ~1 μm. Insert: The transmittance spectra of the films.

References:

1. S. Santra, N. S. Das and K. K. Chattopadhyay, Mater. Lett., 2013, 92, 198–201.

2. F. Odobel and Y. Pellegrin, J. Phys. Chem. Lett., 2013, 4, 2551-2564.

3. B. J. Ingram, T. O. Mason, R. Asahi, K. T. Park and A. J. Freeman, Phys. Rev. B, 2001, 64, 155114.