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Supplementary Information

Hydrothermal synthesis of ultrasmall $CuCrO_2$ nanocrystals alternative to NiO nanoparticles in efficient p-type dye-sensitized solar cells†

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In order to accurately test the flatband potential of NiO and $CuCrO_2$, Mott-Schottky plots ($1/C^2$ vs. E) were done at a wide frequency range from 1000 Hz to 10000 Hz. The test results of $CuCrO_2$ films and NiO reference are shown in Fig. S1. It can be found in Fig. S1(a) that the flat band potential of $CuCrO_2$ obtained by fitting from the results tested at 1000 Hz, 5000 Hz and 10000 Hz were constant with the value of 0.60 V. From Fig. S2(b), it can be found that the flat band potential of NiO was fixed at 0.32 V when the test frequencies were varied from 1000 Hz, 2000 Hz to 3000 Hz. These results reflect that at the test frequency range, the flat band potential was not influenced by the surface charge at the semiconductor/electrolyte interface and should be accurate to some extent to predict the conduction band position of the semiconductor.

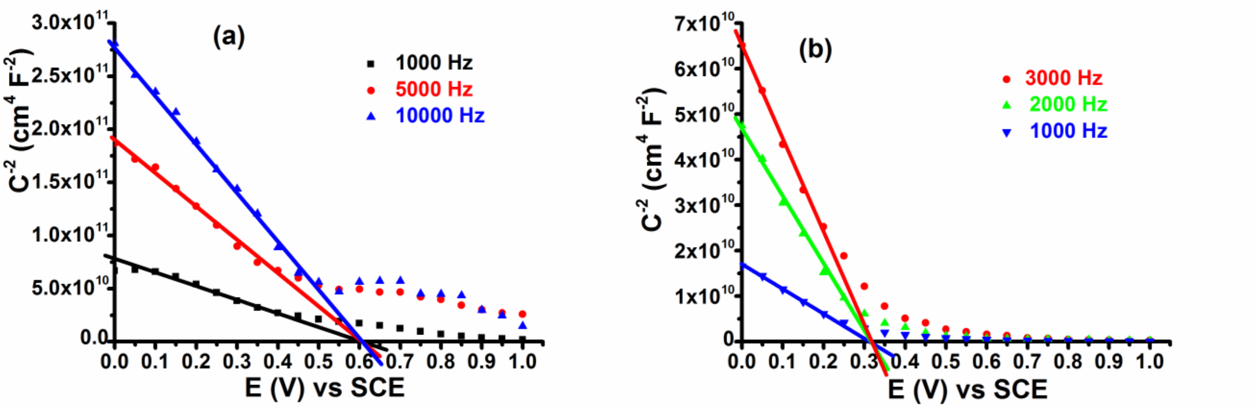

Fig. S1. Mott-Schottky plots of: (a) $CuCrO_2$ films (sintered in air at 400 °C for 1 h, the test frequencies were 1000 Hz, 5000 Hz and 10000 Hz) and (b) NiO references (sintered in air at 500 °C for 0.5 h, the test frequencies were 1000Hz, 2000 Hz and 3000 Hz).

For transient photovoltage decay measurement, DSSC was exposed to the white bias light from an array of light emitting diodes (LEDs) to generate a photovoltage. A blue light pulse (with the pulse width of 80 ms and the rise and fall time of 100ns) from a LED controlled by a fast solid-state switch led to a small increase of the photovoltage. After the blue light pulse was shut down, the increased photovoltage began to decay. The decay of such a photovoltage dynamics was recorded on a PC-interfaced Keithley 2400 source meter. By fitting the voltage decay signal, one could get the electron recombination lifetime (τ_r). In order to measure the transient photocurrent decay, V_{oc} of the DSSC under the white bias light was offset by a constant voltage that was exactly the same as V_{oc} while the polarity was opposite. A pulse of blue LED resulted in a current flow through the external load, and the current decay dynamics on a 50 K resistor was recorded with the Keithley 2400 source meter. The perturbation signal was small enough that the photocurrent decay could be fitted as a single exponential decay. The decay rate of current signal is corresponding to the electron

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transport time (τ), which could be gotten by exponential fitting of the decay signal. By varying the white light bias intensity, the recombination rate constant and hole diffusion rate constant could be estimated over a range of open circuit voltage, which is equal to the electron quasi Fermi level of $CuCrO_2$ offset with respect to the electrolyte redox Fermi level ($_nE_F$-$E_{F,redox}$).[1-3]

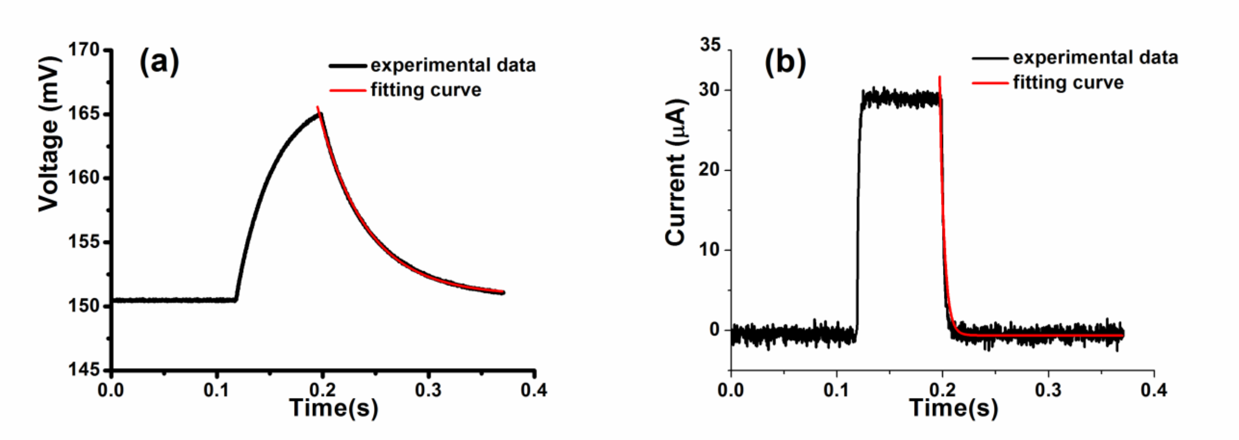

Fig. S2. An exemplary show of: (a) photovoltage decay and (b) photocurrent decay curves of the DSSC based on 1.1 μm $CuCrO_2$ films under the blue bias light of 50 mW cm^{-2}. The red curves represent the exponential decay fitting of the experimental data. Fitting both transient curves with single exponential decay gave the value of hole recombination time (τ_r) = 45.07 ms and the hole transport time (τ) = 2.21 ms.

In view of the difficulty for the direct measurement on the conductivity of the nanoporous semiconductive film, we have tried the Hall effect measurement on the $CuCrO_2$ sample prepared by the powder pellet method, using Ag coating at four contact points on the as-prepared $CuCrO_2$ tablet to decrease the contact resistance. The carrier concentration of $CuCrO_2$ tablet is 2.42×10^{19} cm^{-3}. The confirmed p-type conductivity is as high as 1.88 S cm^{-1}. Such a high value is consistent with reported data of the dense $CuCrO_2$ films in many previous literatures.[4-6]

Table S1. The test results of Hall effect measurement on $CuCrO_2$.

	Resistivity (Ω cm)	Conductivity (S cm^{-1})	Hall Coefficient [cm/C]	Type	Carrier Density (cm^{-3})	Hall Mobility [cm/(VS)]
$CuCrO_2$	5.32E-01	1.88	2.58E-01	p	2.42E+19	3.11E-01

Reference

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