

Supporting Information Available

Solution-processed All-oxide Nanostructures for Heterojunction Solar Cells

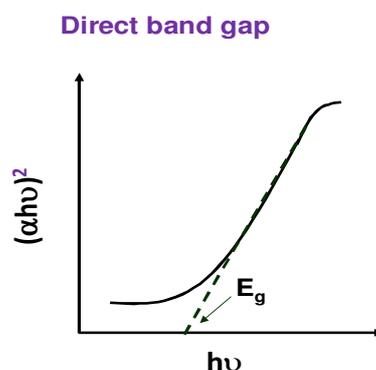
Hui-Ying Shiu, Chung-Min Tsai, Szu-Ying Chen, and Tri-Rung Yew*

National Tsing-Hua University, Department of Materials Science and Engineering, 101, Sec. 2, Kuang-Fu Road,

Hsinchu, Taiwan 30013.

E-mail: tryew@mx.nthu.edu.tw

The $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ and Cu_2O were direct band gap materials, which have been reported on previously report.^[1] According to the equation $\alpha h\nu = K(h\nu - E_g)^{1/2}$ (where α is the absorption coefficient, K is a constant, $h\nu$ is the discrete photo energy, and E_g is the band gap energy), a classical Tauc approach is further employed to estimate the E_g value of $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ and Cu_2O nanostructures. The plot of $(\alpha h\nu)^2$ versus $h\nu$ based on the direct transition is shown in Figure 2(d).



For direct band gap

$$\alpha \approx A^* \sqrt{h\nu - E_g} \quad A^* = \frac{q^2 x_{vc}^2 (2m_r)^{3/2}}{\lambda_0 \epsilon_0 \hbar^3 n}$$

- α is the absorption coefficient, a function of light frequency
- ν is light frequency
- h is Planck's constant ($h\nu$ is the energy of a photon with frequency ν)
- \hbar is reduced Planck's constant ($\hbar = h/2\pi$)
- E_g is the band gap energy
- A^* is a certain frequency-independent constant, with formula above

$$\alpha = -1/d \ln \left(\frac{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2}{2TR^2} \right), \quad h\nu \text{ (eV)} = 1240/\lambda$$

- α : absorption (cm^{-1}), d : thickness (cm), T : Transmittance , R : Reflectance

Experimental

ITO substrate preparation: Commercial ITO glass substrates with a 250 nm thick ITO film (sheet resistance $\sim 5 \Omega/\square$) deposited on soda line glass were used. All ITO substrates were cleaned sequentially in an ultrasonic bath with acetone, isopropanol, and deionized water for 20 min prior to use.

$\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ powder preparation: The $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles were synthesized by chemical reduction process. The 8.56×10^{-2} M $\text{SnCl}_2 \cdot \text{H}_2\text{O}$, 1.67 M $(\text{NH}_2)_2\text{CO}$, as well as 0 wt%, 0.025 wt%, and 0.075 wt% of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 100 mL of 1M NaOH aqueous, individually. The obtained solution was sonicated in an ultrasonic water bath for 30 min. The powders were precipitated at 90 °C and kept at the same temperature for several hours. After completely precipitating, the precipitates were collected through centrifuge and washed with alcohol for several times, and then dried at 60 °C. Annealing processes for 1 hr in air were performed at 400 °C to obtain $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles powders.

Cu_2O powder preparation: The Cu_2O network structures were synthesized as follows. The 2 mmol of hydrated $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in 70 mL N,N-Dimethyl Formamide (DMF)- H_2O solvent at a volume ratio of 70%/30%, followed by the addition of 8 mmole of Hexadecyltrimethyl Ammonium Bromide (CTAB). The obtained solution was sonicated in an ultrasonic water bath for 20 min. Following that, 1 mmol of NaBH_4 was added into the Cu(II)-CTAB solution. The reaction was carried out with magnetic stirring in a three-neck flask at 60 °C for 5 min. After this, 10 mmol of NaOH was further added to the mixture. The solution was then kept at 60 °C for 10 min, followed by the removal from the heater to the others for keep stirring and cool down to room temperature. When the reaction was finished, the precipitates were separated from the solution by centrifugation and washed with alcohol for several times.¹

Device fabrication: A Ti (20 nm) and a Pt (180 nm) layers were evaporated on glass sequentially as the bottom contact. Following that, the Cu_2O network nanostructures and $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles powders were dissolved in 0.1 M isopropanol, individually. After sonication in an ultrasonic water bath for several hours, the Cu_2O network nanostructures and $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles were sprayed onto Pt (180 nm)/Ti (20 nm)/glass at 90°C, in sequence. After spraying, the $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles/ Cu_2O network structures/Pt (180 nm)/Ti (20 nm)/glass were covered by the face-down glass with ITO film (250 nm) as the top contact. The device was then hot-pressed at 200 °C, 100 kg (device size: 0.4 cm^2) for 1 hr, followed by the cool down to room temperature.

Device performance measurements: J–V measurements were performed using a Keithley 2400 Source Meter with a custom-made LabView program. A solar simulator equipped with AM 1.5 was

used at 100 mW/cm² intensity. The device was measured in the dark, and under AM 1.5, one-sun illumination

Morphology characterization: The phase of the products was characterized by transmission electron microscopy (TEM, both JEOL JEM-2010 and JEM-3000F models) for the bright-field and dark-field imaging, and the EDS line-scan for elemental mapping. Scanning electron microscopy (SEM) images were obtained from a JEOL-6500 microscope operated at 15 kV. UV-Vis absorption spectra were measured at room temperature using a Jasco, ARSN-733 spectrophotometer in the wavelength range of 200-2500 nm.

Reference

- [1] Y. Luo, S. Li, Q. Ren, J. Liu, L. Xing, Y. Wang, Y. Yu, Z. Jia, J. Li, *Crystal Growth & Design*. **2007**, 7, 87