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Wavelength Dependent Photochemical Charge Transfer at the Cu_2O – $BiVO_4$ Particle Interface – Evidence for Tandem Excitation

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EXPERIMENTAL DETAILS

Chemicals:

Copper(II) acetylacetonate (Acros Organics, 98%), Acetone (Fisher Scientific, >99.7%), Methanol (Sigma-Aldrich, >99.8%), Bismuth (III) oxide (99.9999% Acros Organics), vanadium(IV) oxide (99+% Strem Chemicals), were used as received. Acetic acid(glacial, Macron) were used after proper dilution. Water was purified to 18 MΩ·cm resistivity by a Nanopure II system.

Cu_2O nanoparticles:[1] Copper(II) acetylacetonate (0.25 g, 1.91 mmol) was suspended in acetone (20 mL). The suspension was sonicated for 30 min and then transferred to a 40 mL Teflon cup in a stainless-steel-lined autoclave. The autoclave was maintained at 140 °C for 24 h and was then allowed to cool to room temperature. The resulting brown product was retrieved by centrifugation, washed three times with 10 mL methanol to remove any starting material, and finally vacuum dried at room temperature overnight. The yield was 91%.

$BiVO_4$ Synthesis: $BiVO_4$ was synthesized via a revised solid-solution method at room temperature. [2] First, 1.15 g (2.5 mmol) of Bi_2O_3 and 0.42 g (5 mmol) of VO_2 were vigorously stirred in 25 mL of 1.0 M aqueous acetic acid solution at room temperature for 11 days. The obtained powder was isolated by filtration, and elaborately washed with water, then 0.5 M nitric acid and then water. After vacuum drying the $BiVO_4$ powder was calcined at 673 K for 5 hours in air to yield 0.76 g (94 %).

To prepare particle films, aqueous dispersions of 0.1 g/L to 0.8 g/L catalysts were drop-coated onto FTO substrates (Thermo Scientific Corporation), dried in air to form thin films, then annealed at 350 ^{0}C under Argon for 5h. For the

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Cu_2O-$BiVO_4$ bilayer, a suspension of Cu_2O particles in water was drop coated onto FTO substrate first, followed by annealing in argon at 350 ^{O}C. Then an aqueous $BiVO_4$ particle suspension was added on top using the same procedure. Virous concentration and number of layers were used to achieve different thickness for both materials.

Characterizations

Transmission electron microscopy (TEM) images were taken with a Philips CM-12 TEM with accelerating voltage of 120 kV. To prepare the samples, aqueous dispersions of the catalyst were dropped onto copper grids with carbon film, and dried in air. Scanning electron microscopy (SEM) images were taken using a Philips XL30 SFEG-SEM microscope operating at an accelerating voltage of 20 kV and using TLD and EBSD detectors. Energy-dispersive X-ray spectroscopy (EDS) were recorded using a FEI Scios Dualbeam FIB/SEM microscope with Oxford MaxN 50 EDS system, with an accelerating voltage of 10 kV. Powder X-ray diffraction patterns were recorded with a Scintag XRD at the wavelength of 0.154 nm, with 2 mm tube slit divergence, 4 mm scatter, 0.5 mm column scatter and 0.2 mm receiving widths. UV-Vis diffuse reflectance spectra were recorded on the thin films pasted on white filter paper using a Thermo Scientific Evolution 220 UV-Vis spectrometer. Film thickness was measured by a Veeco Dektak profilometer.

Surface photovoltage Spectroscopy (SPS) measurements were conducted using a vibrating gold Kelvin probe (Delta PHI Besocke) mounted inside a home-built vacuum chamber ($<1\times10^{-14}$ mbar). To prepare the samples, aqueous dispersions of 0.5 mg catalysts were drop-coated onto Au/FTO substrates (Thermo Scientific Corporation), dried in air to form thin films and annealed at 673 K for 5h. Samples were illuminated with monochromatic light from a 150 W Xe lamp filtered through an Oriel Cornerstone 130 monochromator (1-10 $mW\cdot cm^{-2}$). The CPD spectra were corrected for drift effects by subtracting dark scan background.

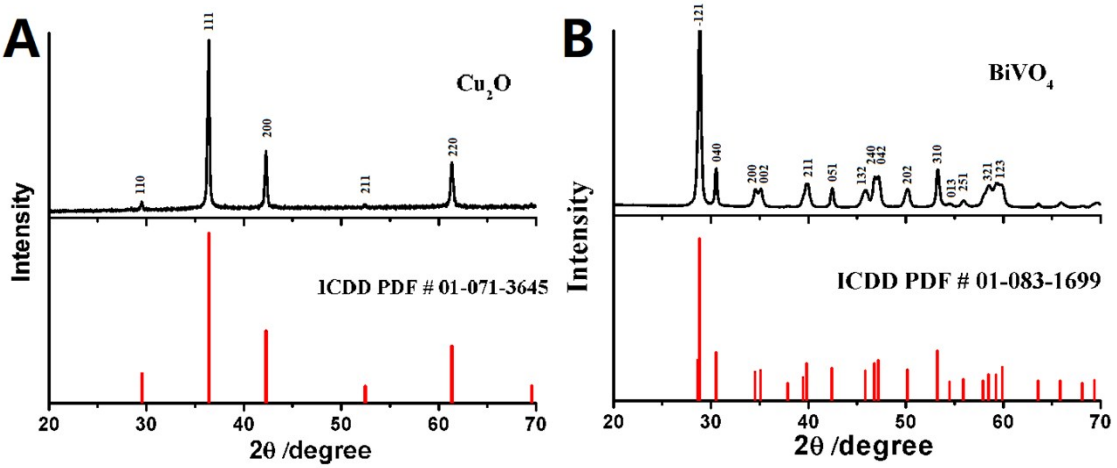

Figure S1. XRD result for (A) Cu_2O nanoparticles and (B) $BiVO_4$ nanoparticles

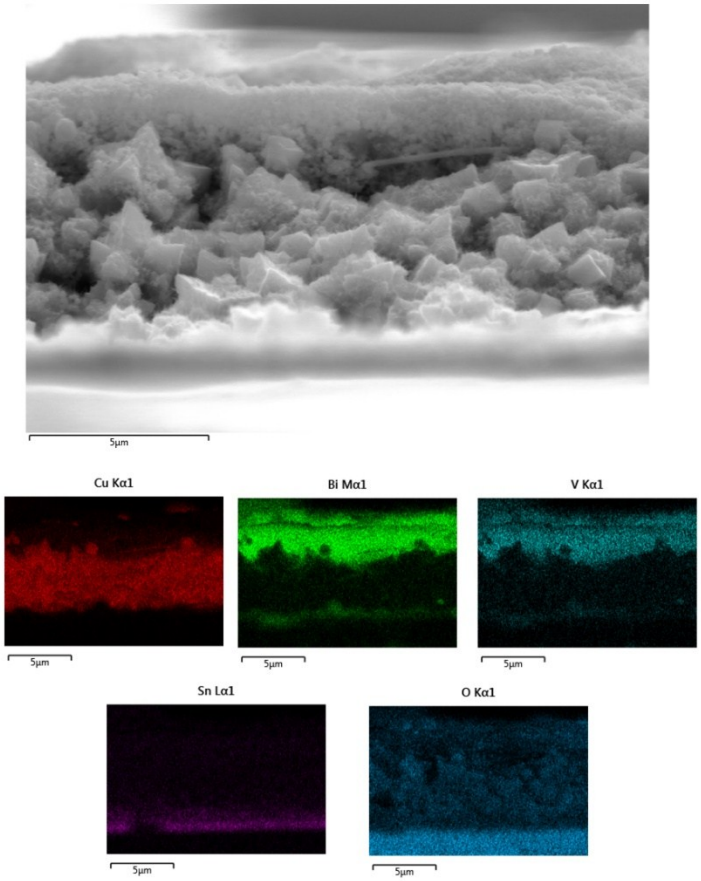

Figure S2. SEM images and EDS elemental mapping for cross section

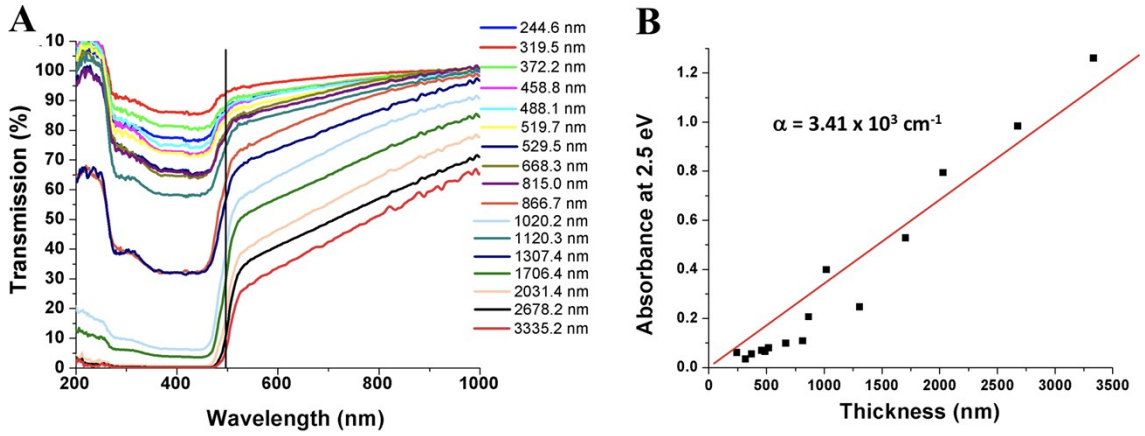

Figure S3. A) transmission spectra of $BiVO_4$ particle layers on glass. B) plot of 2.5 eV absorbance versus particle film thickness as measured by profilometry.

References

1. Singhal, A.; Pai, M. R.; Rao, R.; Pillai, K. T.; Lieberwirth, I.; Tyagi, A. K., Copper(I) Oxide Nanocrystals - One Step Synthesis, Characterization, Formation Mechanism, and Photocatalytic Properties. *Eur J Inorg Chem* **2013,** (14), 2640-2651.

2. Wang, J. R.; Osterloh, F. E., Limiting factors for photochemical charge separation in BiVO4/Co3O4, a highly active photocatalyst for water oxidation in sunlight. *J Mater Chem A* **2014,** *2* (24), 9405-9411.