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Photo-generated carrier behavior at gas-solid interface for CO_2 adsorption on $Cs_2AgBiBr_6$ nanocrystals

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Experimental Section

Materials

CsBr (99.9%), $BiBr_3$ (≥ 98%) and AgBr (98%) were received from Aladdin. Dimethyl sulfoxide (DMSO 99.5%) was purchased from DAMAO Chemical Reagent Factory and isopropanol (99.7%) was from Tiantai.

Synthesis of $Cs_2AgBiBr_6$ NCs

The precursor solution with CsBr, $BiBr_3$ and AgBr was prepared by following previous work.[1] That is, CsBr (0.04 M), $BiBr_3$ (0.02 M) and AgBr (0.02 M) were dissolved in 1 mL DMSO at room temperature while stirring for a while. Then, 20 mL isopropanol was slowly added to 1 mL of the above solution, until light green clear solution gradually turned orange suspension. After centrifuging and washing with isopropanol, the orange product was dried in vacuum drying chamber at 60°C for 2 h. This orange powder was $Cs_2AgBiBr_6$.

Characterization

X-ray diffraction (XRD) patterns was obtained on powder X-ray diffractometer (Rigaku/Ultima IV diffraction instrument with Cu Kα radiation). The morphology information was obtained from SEM (Gemini 550 field emission scanning microscope) and TEM (JEM2200FS) images. X-ray photoelectron spectroscopy (XPS) was carried out on Thermo VG Scientific Escalab 250xi spectrometer with a monochromated Al

Ka excitation source. UV-vis diffuse reflectance spectrum was recorded on Shimadzu UV-3600 spectrophotometer. Fourier Transform Infra-Red (FT-IR) spectra was tested on Bruker VERTEXV 80V. Surface photovoltage (SPV) and Transit photovoltage (TPV) spectra were performed on our lab-made device.[2, 3] For SPV testing, the testing equipment fixed with 24Hz testing frequency, was composed of a 500 W Xe lamp (CHF-XM-500 W), a monochromator (ZLolix SBP500), a lock-in amplifier (SB830-DSP) with a light chopper (SR540) and a computer. Testing transient photovoltage (TPV) spectra was on testing apparatus assembled with a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix) and a laser pulse (Polaris II, New Wave Research, Inc). For routine SPV and TPV testing, "ITO-sample-ITO/Brass" structure was applied, however, for *in-situ* SPV and TPV (g-SPV, g-TPV) testing, a sealed device was adopted with "ITO-sample-Brass" structure in which gas can be injected.[4] SPV and TPV spectra of each sample were measured at least 3 times to give the right tendency.

Theoretical methods

Density functional theory (DFT) calculation has been performed by using the Vienna Ab initio Simulation Package (VASP 5.4.4). We chose PBE functional based on the generalized gradient approximation to account for the exchange-correlation energy.[5] The kinetic energy cut-off of the plane wave basis set was set as 450 eV. A Gaussian smearing of the population of partial occupancies with a width of 0.05 eV was used during iterative diagonalization of the Kohn-Sham Hamiltonian. The threshold for energy convergence for each iteration was set to 10^{-5} eV. Geometries were assumed to be converged when Hellmann-Feynman forces on each atom were less than 0.01 eV/Å. The 3×3×1 gamma-centered k-points meshes have been applied to sample the Brillouin zones of $Cs_2AgBiBr_6$. Optimized lattice parameters for $Cs_2AgBiBr_6$ were a= 11.46 Å. ΔE_{ads} (adsorption energy) was calculated as $E_{ads} = E_{total} - E_{Cs2AgBiBr6} - E_{CO2}$.

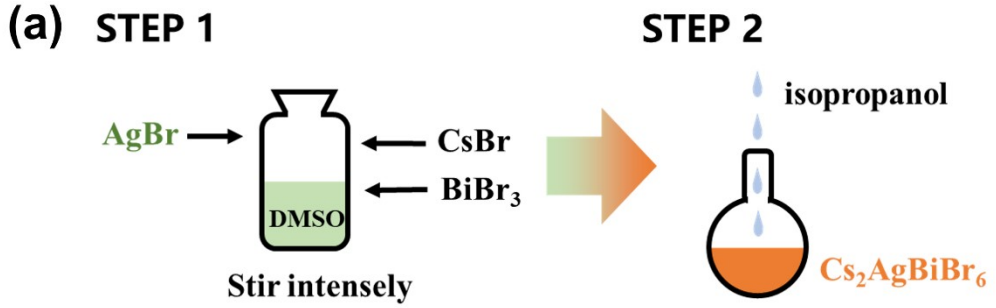

Fig. S1 Schematic illustration of synthetic procedures of $Cs_2AgBiBr_6$.

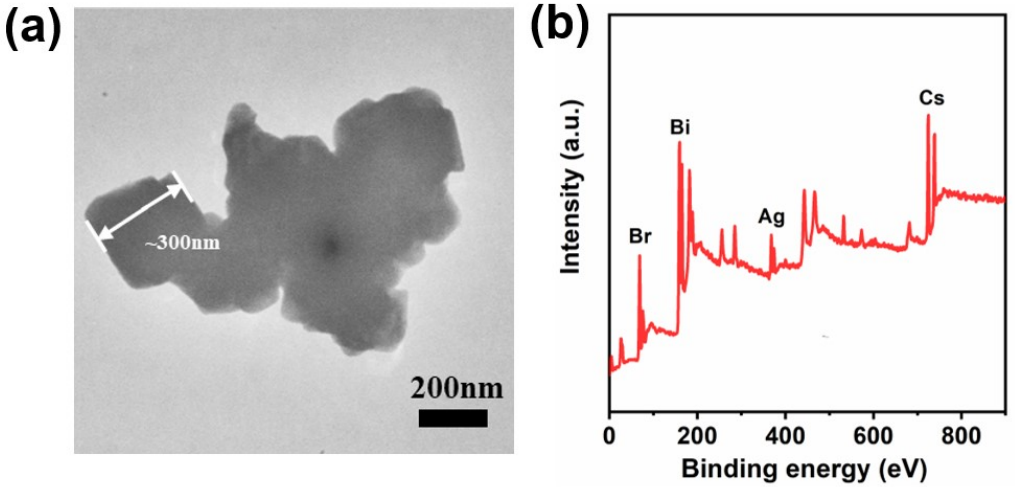

Fig. S2 (a) TEM image of $Cs_2AgBiBr_6$ NCs; (b) Survey XPS spectrum of the sample.

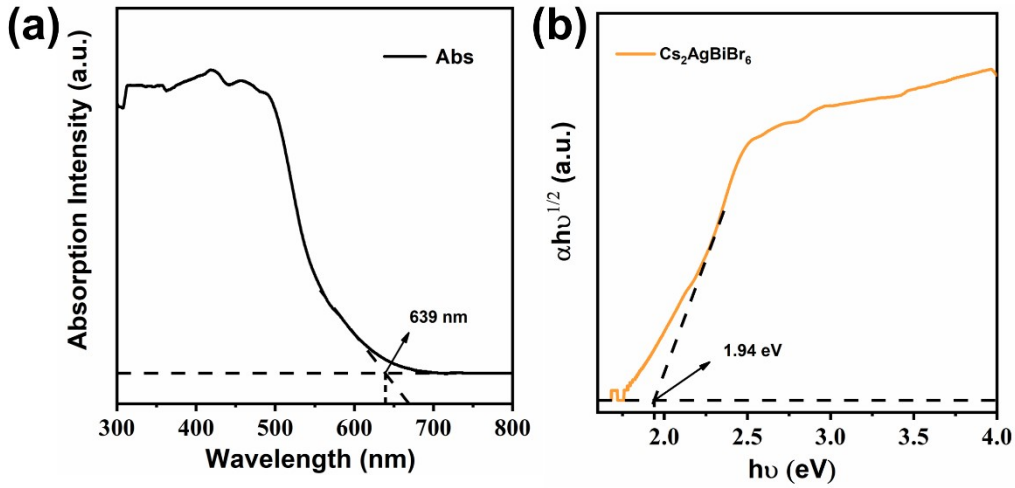

Fig. S3 (a) UV-vis spectrum of $Cs_2AgBiBr_6$ XPS (b) $(\alpha h\nu)^{1/2}$ versus hν curves.

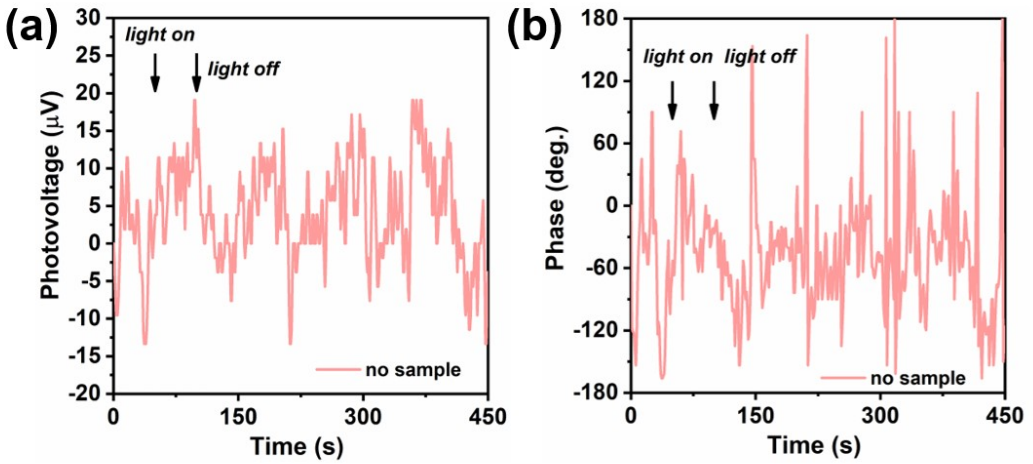

Fig. S4 Blank SPV spectra without the testing sample under 405 nm laser irradiation (a) photovoltage intensity (b) corresponding phase spectrum

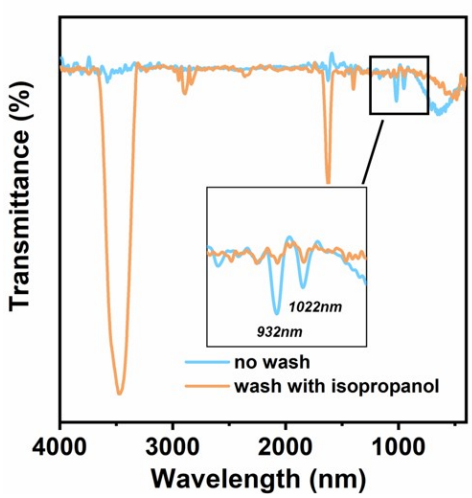

Fig. S5 FT-IR spectra of $Cs_2AgBiBr_6$ with and without washing with isopropanol

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