

Supporting Information

Title TiO₂/graphene/CuSbS₂ mixed-dimensional array with high-performance photoelectrochemical properties

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Characterization methods

The morphology and microstructure of the samples were characterized via scanning electron microscope (SEM; Sirion, FEI, Netherlands), and high-resolution transmission electron microscopy (HRTEM; JEM 2010 FEF HRTEM, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS; Genesis 7000, EDAX Inc., USA). The crystalline phases were detected via an X-ray diffractometer (XRD; D8 Advance, Bruker AXS, Germany) with an angular range from 20-80°. Raman measurements were conducted on a Raman spectrometer (Raman; Jobin Yvon LabRAM HR, HORIBA, France) with a laser excitation source ($\lambda_{ex}=488$ nm). The elemental compositions were analyzed via X-ray photoelectron spectroscopy (XPS; AXIS-Ultra instrument, Kratos Analytical, England) with a monochromatic Al K α X-ray beam (225 W, 15 Ma, 15 kV). The UV-Vis diffuse reflectance spectra (DRS) of the samples were measured with the diffuse reflectance accessory of UV-Vis spectrophotometer (UV-2550; Shimadzu, Kyoto, Japan), in which BaSO₄ was used as a background between 200-800 nm. The photoluminescence measurements were conducted on a Raman spectrometer (Raman; Jobin Yvon LabRAM HR, HORIBA, France) with a laser excitation wavelength at $\lambda_{ex} = 325$ nm.

Photoelectrochemical performance

Photoelectrochemical measurements were performed on an electrochemical analyzer (CHI-660C, CH Instruments Co.) in a standard three-electrode configuration with different photoelectrodes, i.e., pristine TiO₂, TiO₂/graphene, and the TiO₂/graphene/CuSbS₂ composites. In addition, the Na₂SO₄ (0.1 mol L⁻¹) aqueous solution was used as an electrolyte.

The counter electrode and the reference electrode were a Pt rod and saturated calomel electrode (SCE), respectively. The working area of the electrode was fixed at 1 cm², and the distance between the working electrode and the light source (300 W xenon arc lamp coupled to an AM 1.5 G filter) was 15 cm. The surface photocurrent spectra (SPC) were collected by measuring the photocurrent under chopped light irradiation (20 s light/dark cycles).

Preparation of GO

GO was synthesized from natural graphite (~325 mesh, 99.95%) by a modified Hummers method: (1) The mixture of graphite powders (1.0 g), K₂S₂O₄ (0.5 g) and P₂O₅ (0.5 g) were put into an 80 °C solution of concentrated H₂SO₄ (98%, 10 ml) for 4 h. Then, the dark mixture was filtrated by deionized water for several times and dried in a stove; (2) The pre-oxidized graphite was put into 15 ml H₂SO₄ (98%), and 4 g KMnO₄ was gradually added with stirring and cooling with an ice-water bath; (3) 30 ml deionized water was added to the solution after stirring for 2 h at 35 °C; (4) The solution was kept at 85 °C for 30 min, and then, H₂O₂ (30%) was added to the solution until the color of the mixture turned to bright yellow. The GO was obtained after filtration, pickling, washing, and drying.

Morphology observation and characterization of CuSbS₂ quantum dots

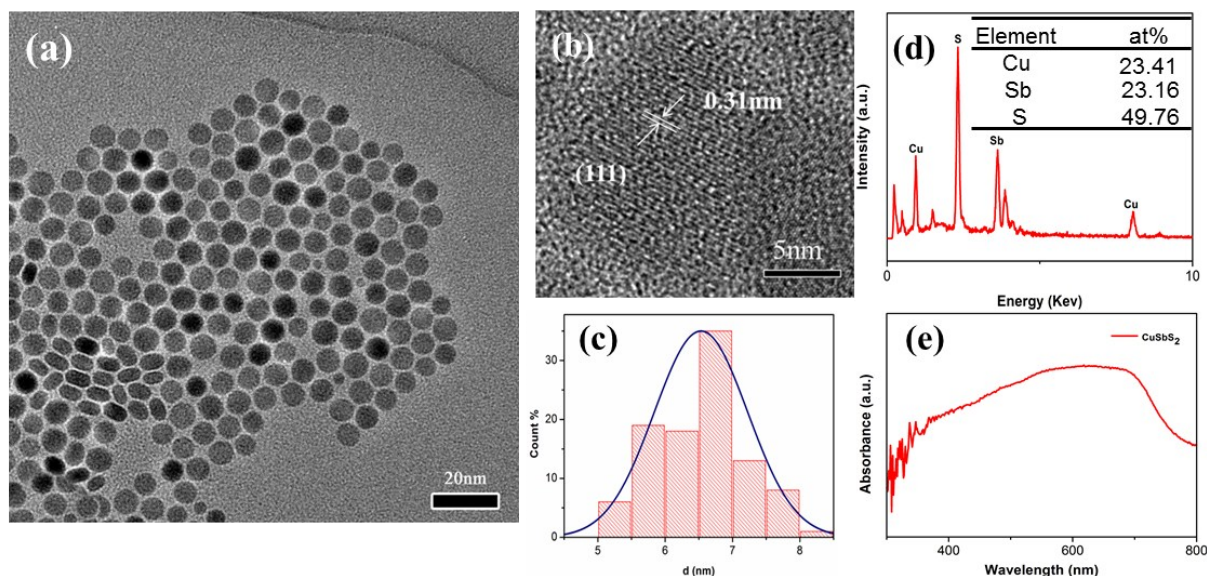


Fig. S1 CuSbS₂ quantum dots: (a) TEM image (low resolution), (b) TEM image (high resolution); (c) Size distribution histograms; (d) EDS profile; (e) UV-Vis spectra.

Fig. S1(a) shows the TEM images of the CuSbS₂ quantum dots, apparently, they are uniformly distributed without any agglomeration. HRTEM observation reveal that the interplanar distance of 0.31 nm is corresponding to (111) plane of the CuSbS₂ quantum dots (JCPDS 65-2416), as shown in Fig. S2(b). The average particle size of the CuSbS₂ quantum dots were calculated to be 6.7 nm (Fig. S2(c)), and its uniform particle size were correspond with the TEM image. The composition of CuSbS₂ quantum dots was characterized as well. The Cu/Sb/S molar ratio of 23.41: 23.16: 49.76 was obtained from the energy dispersive X-ray (EDX) spectroscopy (Fig. S2(d)). It can be seen that the light-absorption range of CuSbS₂ quantum dots covered from 300 to 800 nm, in addition, it shows extremely strong absorption in visible light region, this phenomena not only indicate its narrow band gap characteristic, but also reflect an extremely sensitive response to visible light, as shown in Fig. S2(e).

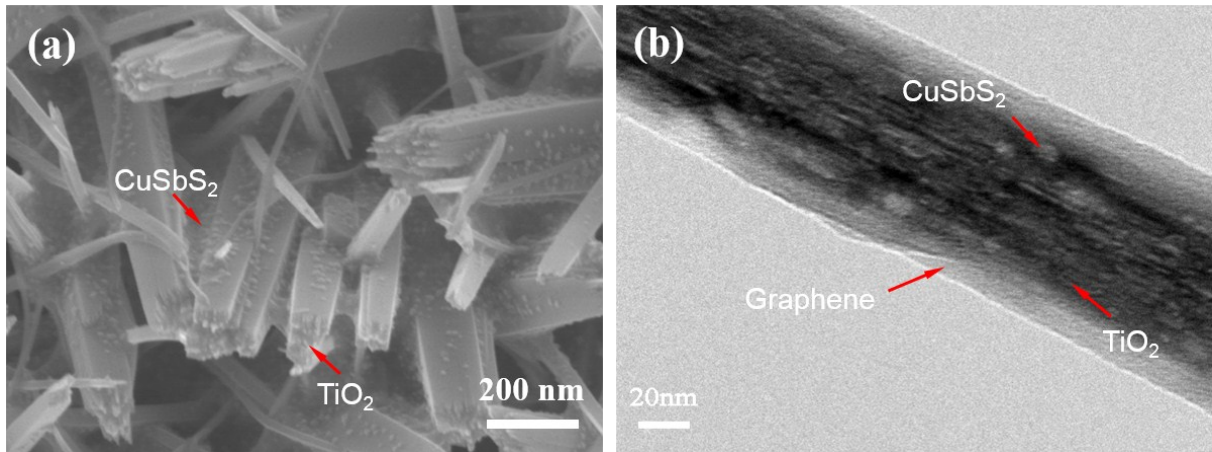


Fig. S2 (a) SEM images of 1D TiO₂ nanowires/0D CuSbS₂ quantum dots composite;

(b) TEM image of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures.

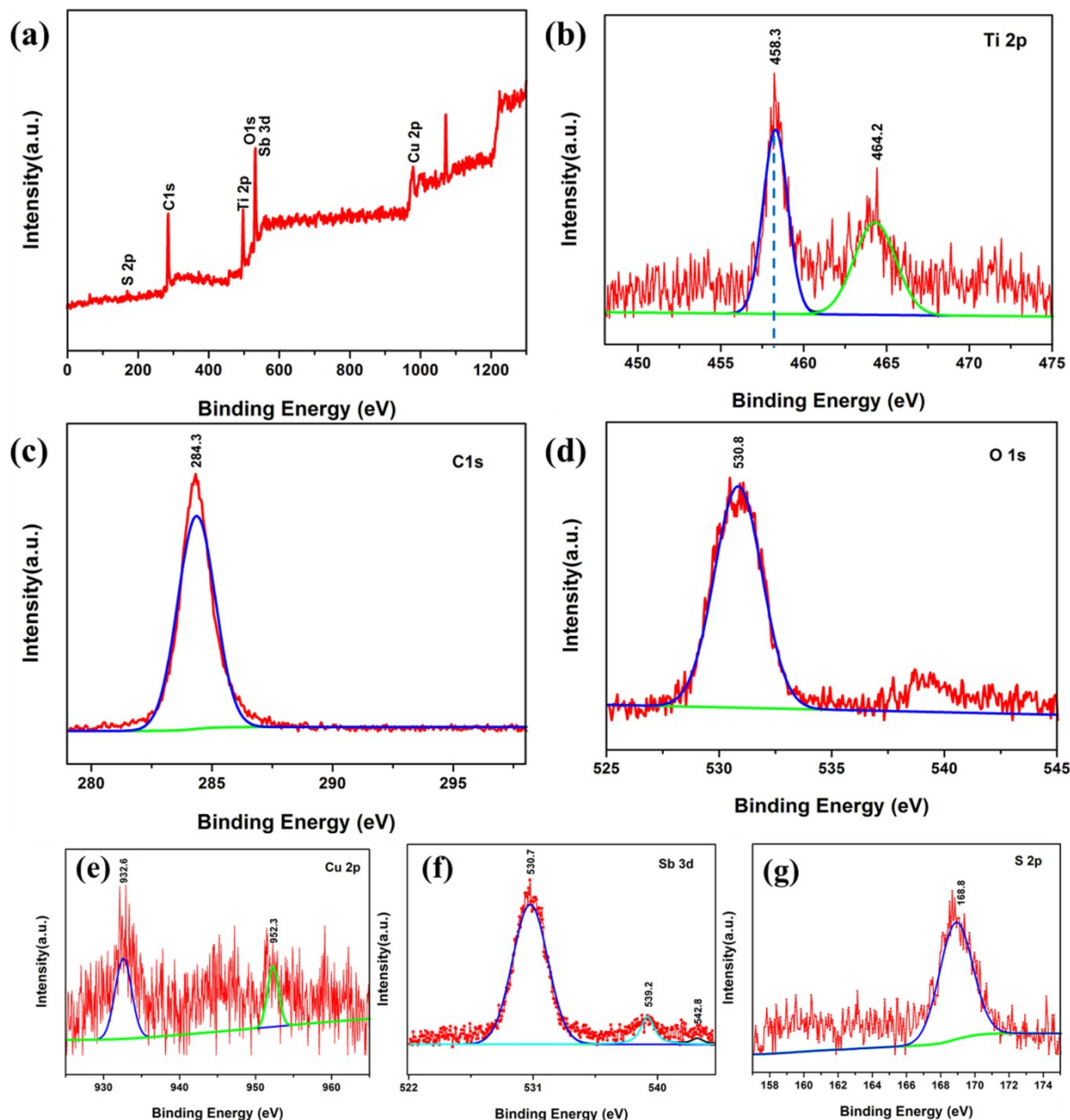


Fig. S3 XPS spectra of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures: (a) Survey; (b) Ti 2p; (c) C 1s; (d) O 1s; (e) Cu 2p; (f) Sb 3d; (g) S 2p.

Fig. S3 illustrates the XPS profiles of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures. Gaussian deconvolution of the high-resolution spectra was used to verify the chemical bond species and elemental chemical states. From the survey spectra, the sharp photoelectron peaks are obtained at the binding energies of 284.3 eV, 459.1 eV, 530.8 eV and 1021.9 eV, which indicate the existence of C 1s, Ti 2p, O 1s, Cu 2p, Sb 3d and S 2p elements, and the dominant intensity of C 1s is originated from graphene. Significantly, the characteristic peaks with binding energy of 459.1 eV (Ti

2P_{3/2}) and 464.6 eV (Ti 2p_{1/2}) are corresponding to the rutile phase of TiO₂ (Ti⁴⁺),^[1, 2] which exhibit a negative shift of 2 eV, and this phenomena suggest a strong interaction between graphene and the TiO₂ nanowires arrays, as show in Fig. S3(b). The high-resolution C 1s spectrum showed two main components, as shown in Fig. S3(c), i.e., the major peak at 284.3 eV is derived from the sp² carbon atoms of graphene, this result suggest that the thermal reduction of GO is efficient for removing the oxygen functional groups during the thermal treatment.^[3] Significantly, the dominant peak intensity of C=C (284.3 eV) in graphene indicate the highly-ordered sp² carbon network, which is in good accordance with the results exhibit in the Raman spectra. As for the O 1s spectrum, the dominant peaks at 530.8 eV demonstrate a single chemical state of oxygen in the composite. The peak at 530.8 eV is attributed to the lattice oxygen in the TiO₂, which is corresponding to the C 1s species at 284.3 eV.^[4] The featured peaks at 932.6 eV (Cu 2p_{3/2}) and 952.3 eV (Cu 2p_{1/2}) are corresponding to the Cu⁺ (CuSbS₂),^[5] the peak at 530.7 eV (Sb 3d_{5/2}) is consistent with chemical element state of Sb³⁺ (CuSbS₂),^[6] and the characteristic peaks with binding energy of 168.8 eV (S 2p_{3/2}) is corresponding to the S²⁻ (CuSbS₂).^[7]

Table S1 A comparison study of the photoelectrochemical property of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode in this work and previously reported TiO₂-based photonaodes

Photoanode material	Photocurrent density	Light intensity	Testing condition	Reference
TiO ₂ /rGO/NiFe-LDH	1.6 mA cm ⁻² (0.3 V vs. SCE)	100 mW cm ⁻²	0.5 M Na ₂ SO ₄ (pH 6.8)	[5]
GO-decorated TiO ₂	0.767 mA cm ⁻² (1.23 V vs. RHE)	100 mW cm ⁻²	0.5 M Na ₂ SO ₄ (pH 7.0)	[7]
BiVO ₄ /Graphene/TiO ₂	~0.13 mA cm ⁻² (0.8V vs. Ag/AgCl)	100 mW cm ⁻²	0.1 M K ₂ SO ₄ (pH = 6.7)	[8]
AZO/TiO ₂ /Au	1.1 mA cm ⁻² at (0.6 V vs. SCE)	100 mW cm ⁻²	0.1 M Na ₂ SO ₄ (pH = 6.8)	[9]
Disordered surface layer modified TiO ₂	1.18 mA cm ⁻² (0.6 V vs. SCE)	100 mW cm ⁻²	0.5 M Na ₂ SO ₄ (pH 6.8)	[10]
Carbon nitride quantum dots modified TiO ₂	1.34 mA cm ⁻² (0.3V vs. Ag/AgCl)	100 mW cm ⁻²	0.5 M Na ₂ SO ₄ (pH 6.8)	[11]
α-Fe ₂ O ₃ / TiO ₂ nanorod array	3.39 mA cm ⁻² (1.23 V vs. RHE)	100 mW cm ⁻²	1 M NaOH aqueous solution	[12]
CdS quantum-dot /TiO ₂ -based	49.6 μA/cm ⁻² (0.4V vs. SCE)	100 mW cm ⁻²	3 M KOH aqueous solution	[13]
TiO₂/graphene/CuSbS 2	3.91 mA cm⁻² (0.3 V vs. SCE)	100 mW cm⁻²	0.5 M Na₂SO₄ (pH 6.8)	This work

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