

Cite this: *RSC Adv.*, 2019, 9, 33747

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

Qianyuan Chen,^{ab} Zhongchi Wang,^a Keqiang Chen,^{id b} Qiang Fu,^d Yueli Liu,^{id c} Yupeng Zhang,^{id *b} Delong Li^{*b} and Chunxu Pan^{id *ad}

The growing demands for reproducible and clean sources of power has prompted the exploitation of novel materials for solar-energy conversion; in any case, the improvement of their conversion efficiency remains a big challenge. We report a mixed-dimensional heterostructure to synchronously enhance charge separation and light-absorption of the photoanodes via the introduction of two-dimensional reduced graphene oxide and zero-dimensional CuSbS₂ quantum dots on one-dimensional TiO₂ arrays. The experimental results show that the graphene sheets with a low Fermi level and a superior electron mobility accept photo-excited electrons from TiO₂ and enable fast electron transportation; while the CuSbS₂ quantum dots promote the visible light-absorption of the photoanode. The synergistic effects in this mixed-dimensional (1D–2D–0D) heterostructure photoanode induce a markedly raised photoconversion efficiency of 1.2% at 0.3 V and a photocurrent density of 5.5 mA cm^{−2} at 0.4 V. Furthermore, the photocurrent density of the mixed-dimensional heterostructure exceeds previously reported TiO₂-based photoanodes in neutral media. The improved photoelectrochemical properties are attributed to the synergistic-effect-induced highly organized, mixed-dimensional architectures. It is expected that the mixed-dimensional heterostructure photoanode will be a potential candidate for applications in environmental remediation and energy fields.

Received 9th September 2019
Accepted 14th October 2019

DOI: 10.1039/c9ra07237c

rsc.li/rsc-advances

1 Introduction

Solar energy is regarded as a feasible alternative to fossil fuels because of its promise for addressing environmental remediation and energy conversion. Therefore, the ability to efficiently harness and utilize solar energy is of great importance. Since its use for water photolysis by Fujishima and Honda in 1972, TiO₂ has garnered considerable attention in solar cells and photoelectrochemical devices.^{1–6} However, TiO₂ exhibits several drawbacks, such as the fast recombination of photo-excited carriers and a low-degree of quantum efficiency (monochromatic incident photon-to-electron conversion efficiency). Meanwhile, TiO₂ can only convert less than 5% of the full solar

spectrum and this limits the use of solar energy as a primary source of energy because TiO₂ is a wide band-gap semiconductor (3.2 eV).^{7–12}

Great efforts have been made including the geometry and band structure engineering to solve these problems. For instance, one-dimensional (1D) TiO₂ including TiO₂-tubes, TiO₂-rods, TiO₂-fibers, TiO₂-belts, and TiO₂-wires recently have attracted wide interest for photoelectrical applications because of their large surface area for light-absorption, as well as an axial transport of photo-generated carriers with fast transport property.^{13–18} In addition, forming a Schottky or p–n junctions to realize band structure engineering is another effective approach, which aims to widen the visible light-absorption and hinder from the recombination of electrons and holes to improve the photon-to-energy conversion efficiency.^{19–21} For example, coupling 1D TiO₂ with narrow bandgap zero-dimensional (0D) quantum dots could enhance the photoconductivity by photogating effect. Furthermore, the dangling-bond surfaces of 2D graphene materials offer flexibility in integrating different dimensioned materials into mixed-dimensional heterostructures for next-generation electronic/optoelectronic devices.²² The introduction of two-dimensional (2D) materials such as graphene into the 1D TiO₂, will promote the carrier transfer efficiency. The synergistic effect fully exploits the extraordinary electron transport characteristics of 2D graphene

^aSchool of Physics and Technology, MOE Key Laboratory of Artificial Micro- and Nano-structures, Wuhan University, Wuhan 430072, China. E-mail: cxpan@whu.edu.cn

^bInstitute of Microscale Optoelectronics, College of Electronic Science and Technology, Shenzhen Key Laboratory of Flexible Memory Materials and Devices, Shenzhen University, Shenzhen 518060, China. E-mail: ypzhang@szu.edu.cn; ldlong19890809@163.com

^cState Key Laboratory of Silicate Materials for Architectures, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, 430070, China

^dCenter for Electron Microscopy, Wuhan University, Wuhan 430072, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra07237c

and further makes large contribution to the highly promoted photoelectrochemical performance of the mixed-dimensional heterostructures device. It is thus of strategic interest to synthesize the 0D quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures with appropriate composition and well-designed structure.^{23–27} The interface in this mixed-dimensional heterostructure is less constrained due to the absence of the need for lattice matching, resulting in effective interaction.

Recently, copper antimony sulfide (Cu–Sb–S) quantum dots have gained significant attention in solar cells and photoelectrochemical devices.²⁸ As a p-type semiconductor with a high light-absorption coefficient (over 105 cm^{−1} at visible wavelength), copper antimony sulfide quantum dots are made up from environmentally-friendly and earth-abundant elements, the major phase of Cu–Sb–S has a bulk band-gap in the range of 1.0–1.8 eV; this type of non-toxic quantum dots have a high potential for photosensitization of 1D TiO₂. Specifically, graphene is widely used in photocatalysis for its unique atomic-thick 2D structure and super physicochemical properties. When combined with 0D the quantum dots/1D TiO₂ heterostructure, owe to 2D graphene higher work function which induces photogenerated electron transfer from the conduction band of the semiconductor to graphene. In other word, 2D graphene acts as an electron shuttle.²⁹ To enhance the surface reaction kinetics, introduction of RGO into the 0D quantum dots/1D TiO₂ to create mixed-dimensional (0D–1D–2D) heterostructures which provide new reaction pathways to cut down kinetic barriers.

In this work, negative charged graphene oxide (GO) was self-assembled on rutile TiO₂ arrays; then, the composite was annealed at 450 °C in an N₂ atmosphere for 2 h to improve the adhesion between graphene and TiO₂.¹⁰ Finally, the 1D TiO₂/2D graphene/0D CuSbS₂ quantum dots prepared by wet chemical method, followed by annealing at 200 °C for 60 min in argon (Ar) to obtain ternary 1D TiO₂/2D graphene/0D CuSbS₂ nanocomposites. To increase the interfacial contact between the 1D TiO₂ arrays, 2D graphene and the 0D CuSbS₂ quantum dots, the graphene sheets were fragmented between the quantum dot/TiO₂ heterostructure by tuning the concentration of the spin-coated GO.²⁵ As a consequence, the contact area and interaction between graphene and the other two phases was markedly increased. The experimental results show that the ternary composites exhibited excellent photoelectrochemical properties under solar light irradiation; the peak current reached 6 mA cm^{−2} and the photo-energy conversion efficiency was 1.2%. Furthermore, the graphene sheets not only reduced the open potential of photocurrent but also improved the stability of the CuSbS₂ quantum dots under prolonged irradiation. In a word, it is expected that mixed-dimensional heterostructure photoanode will be a promising candidate for applications in environmental remediation and energy fields.

2 Experimental section

2.1 Materials

The natural graphite powder, 325 mesh, 99.95% was bought from Alfa Aesar. The fluorine-doped tin oxide (FTO) was bought

from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. (Zhuhai, China). The copper(I) iodide (CuI, 98%), antimony(III) chloride (SbCl₃, 99%), sodium chloride (NaCl, 99.9%), phosphorus pentoxide (P₂O₅, 99.9%), potassium thiosulfate (K₂S₂O₄, 99.9%), potassium permanganate (KMnO₄, 99.9%), titanium(IV) butoxide (Ti(OBu)₄, 99%), *N,N'*-diphenylthiourea (98%), diphenyl ether (99%), oleylamine (OLA, 80–90%), hexane (C₆H₁₄, 99%), absolute ethanol (C₂H₆O, 99%), propan-2-ol (C₃H₈O, 99%), acetone (C₃H₆O, 99%), hydrochloric acid (HCl, 20 wt%), sulfuric acid (H₂SO₄, 98%), hydrogen peroxide (H₂O₂, 30%), were purchased from Shanghai Chemical Reagents Company without any further treatment. Deionized water was used for all the experiments.

2.2 Preparation of the CuSbS₂ quantum dots

A typical hot-injection method was used for the preparation.²⁸ 1.5 mM copper(I) iodide and 1.5 mM antimony(III) chloride were loaded into a 50 ml three-neck flask containing 30 ml oleylamine. The mixture was heated to 100 °C under an Ar atmosphere, and then a clear slight yellow solution would emerge. Afterwards, the temperature of the solution was increased to the target temperatures (150 °C) and 4.5 ml 1 M *N,N'*-diphenylthiourea dissolved in diphenyl ether was subsequently injected into the mixture as quickly as possible. The solution was cooled to room temperature after 5 min. The mother liquor (1 ml) was added into methanol (3 ml) and centrifuged at 8000 rpm for 3 min. Hexane (4 ml) was used to redisperse the nanocrystals, and the precipitates were separated by centrifugation at 8000 rpm for 3 min. The product was further purified by several precipitation/dispersion cycles.

2.3 Preparation of the TiO₂/graphene/CuSbS₂ composites

Fig. 1 illustrates the fabrication process of the ternary TiO₂/graphene/CuSbS₂ composites. The fluorine-doped tin oxide (FTO) substrate (10 mm × 30 mm) was ultrasonically cleaned and then the highly ordered TiO₂ nanorod arrays were grown on the FTO substrate *via* the hydrothermal method. Briefly, 0.45 ml titanium(IV) butoxide (Ti(OBu)₄, 99%) and 0.6 g sodium chloride (NaCl, 99.9%) were added into 30 ml diluted hydrochloric acid (HCl, 20 wt%). Then, the above precursor (30.45 ml) was transferred into a 100 ml Teflon-lined stainless steel autoclave and for hydrothermal growth at 170 °C for 8 h. The resultant samples (TiO₂ nanowire arrays) were rinsed with deionized water and dried at 70 °C in air.

Graphene oxide (GO) was prepared *via* the modified Hummers and Offeman's method,²⁸ the preparation process is given in the ESI.† The TiO₂/GO composites were prepared by spin-coating a GO aqueous solution (1 mg ml^{−1}, 350 μl) onto the TiO₂ nanowires array substrate. Then, the composite was annealed at 450 °C in an N₂ atmosphere for 2 h to improve the adhesion between graphene and TiO₂.

The TiO₂/graphene composite was immersed in the CuSbS₂ quantum dots (3 mg ml^{−1}) for 12 h (the preparation of CuSbS₂ quantum dot was given in the ESI†), after the solvent evaporated completely, the sample was taken out and annealed at 200 °C in argon (Ar) for 60 min.



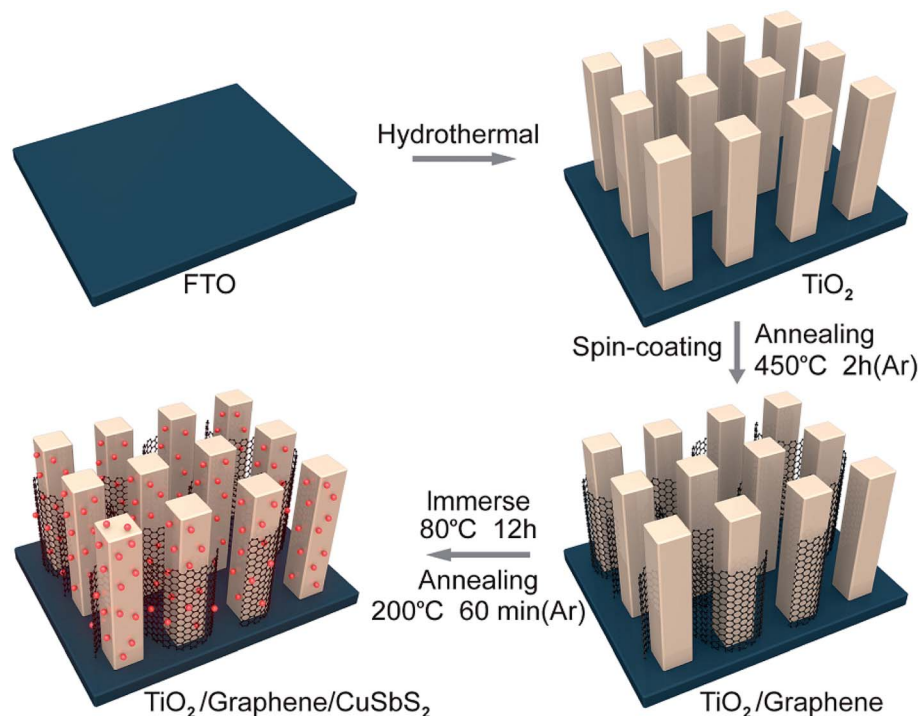


Fig. 1 Schematic diagram of the preparation of the 0D CuSbS_2 quantum dots/1D TiO_2 nanowires/2D graphene (mixed-dimensional) heterostructures.

3 Results and discussion

3.1 Morphology and structure analysis

The scanning electron microscope (SEM) morphologies of pure 1D TiO_2 and the 1D TiO_2 /2D graphene composite are shown in Fig. 2(a) and (b), while the 0D CuSbS_2 quantum dots/1D TiO_2 nanowires/2D graphene (mixed-dimensional) heterostructures are shown in Fig. 2(c). The 1D TiO_2 arrays were prepared on the FTO substrate, as is shown in Fig. 2(a) the average diameter of 1D TiO_2 arrays is 50–100 nm. The transparent fragmented graphene sheets were overlaid on the prepared 1D TiO_2 arrays and made full use of the large gaps in the 1D TiO_2 arrays. As a result, a large contact area between 1D TiO_2 arrays and the graphene sheets was achieved (Fig. 2(b)). For the 1D TiO_2 nanowires/0D CuSbS_2 quantum dots composites, the CuSbS_2 quantum dots are firmly attached to the TiO_2 nanowires without any agglomeration (Fig. S2(a)†). Similarly, the CuSbS_2 quantum dots are uniformly distributed on the 1D TiO_2 nanowires/2D graphene heterostructures, as shown in Fig. 2(c) (inset is TEM image of 0D CuSbS_2 quantum dots). The TEM image further shows the morphology of a single rod of the 0D CuSbS_2 quantum dots/1D TiO_2 nanowires/2D graphene (mixed-dimensional) heterostructures (Fig. S2(b)†). The EDS spectra shows uniform signals for the Ti, O, C, Cu, Sb, and S elements (Fig. 2(d)), which indicates the homogeneous distribution of the graphene and CuSbS_2 quantum dots on the TiO_2 nanowires.

Fig. 2(e) shows the XRD patterns of the mixed-dimensional heterostructures. The diffraction peaks of SnO_2 at 2θ values of 26.578° , 37.768° , 51.755° and 65.740° (JCPDS no. 46-1088)

initiated from the FTO substrate, and the diffraction peaks at 2θ values of 27.446° , 36.085° , 54.322° and 62.5° correspond to the (110), (101), (211) and (002) planes of rutile phase of TiO_2 arrays, respectively (JCPDS no. 21-1276).¹³ In the $\text{TiO}_2/\text{CuSbS}_2$ and $\text{TiO}_2/\text{graphene}/\text{CuSbS}_2$ composites, the diffraction peaks at 2θ values of 28.47° and 32.09° correspond to the (101) and (201) planes of CuSbS_2 quantum dots, respectively, which correspond with the HRTEM results.³⁰ One should note that the rutile phase structure of the TiO_2 nanowires shows little change after heat treatment because of its high stability. Additionally, the CuSbS_2 quantum dots are stable in the ternary composites, and the graphene sheets exhibited no influence on the CuSbS_2 quantum dots.²⁸

The Raman spectra are shown in Fig. 2(f). The peaks at 450 cm^{-1} and 610 cm^{-1} identify the E_g and A_{1g} vibration modes of rutile TiO_2 , respectively.²⁶ Two bands located at 1350 cm^{-1} (D band) and 1595 cm^{-1} (G band) demonstrate the presence of graphene.^{31–34} Generally speaking, the G band originates from the first order scattering of the E_{2g} mode, indicating the sp^2 hybridized carbon atoms; the D band is assigned to the A_{1g} symmetry vibration of the K-point, revealing the sp^3 defects in graphitic structure. Furthermore, the I_D/I_G ratio is a critical indicator of the defect density or average size of the sp^2 domains in graphene.³¹ The intensity ratio (I_D/I_G) of graphene oxide (GO) in the TiO_2/GO composite was 0.97, the intensity ratio (I_D/I_G) decreased to 0.80 ($\text{TiO}_2/\text{graphene}$) after thermal treatment, which indicated the good reduction of graphene oxide. However, the value in the $\text{TiO}_2/\text{graphene}/\text{CuSbS}_2$ composites is 0.85, which demonstrated the high surface defect density of the graphene sheets. This phenomena is ascribed to the large



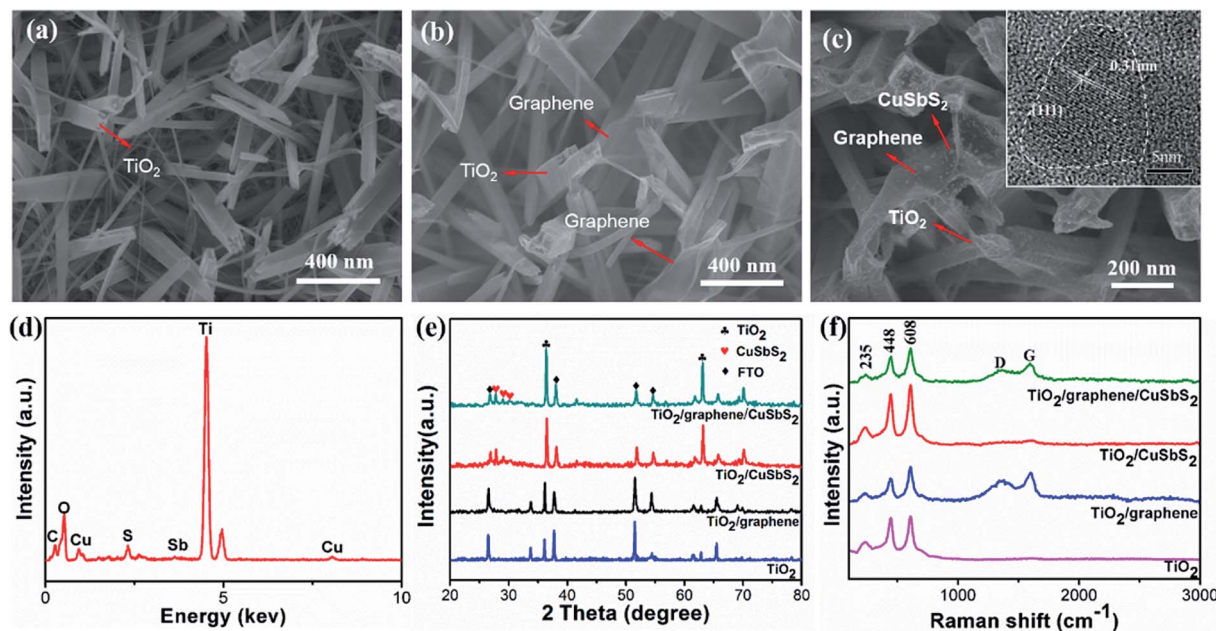


Fig. 2 SEM morphologies of (a) 1D TiO₂ nanowires arrays, (b) 1D TiO₂ nanowires/2D graphene composite and (c) the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures (inset is TEM image of 0D CuSbS₂ quantum dots); (d) EDX profile of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures; (e) XRD patterns and (f) Raman spectra of the samples.

contact area between graphene and the CuSbS₂ quantum dots, which induce strong interactions and led to the increased I_D/I_G value.¹⁹

3.2 Optical properties

The light-absorption properties of the material is a crucial factor for photoanodes. Fig. 3(a) shows the UV-Vis absorption spectra of the mixed-dimensional heterostructures. The TiO₂ arrays exhibit strong absorption in the ultraviolet region and had an absorption edge at ~ 410 nm, which corresponded to a band-gap of 3.11 eV. The 1D TiO₂/2D graphene composite shows a higher absorption in the visible region than simplex TiO₂ arrays, this might be ascribed to the intense visible light-absorption of graphene sheets. However, a red shift of the

absorption edge was observed because the sp^2 orbit of graphene monished the energy between the Ti (3d) and O (2p) orbits. For the 0D quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) composites, light-absorption ranged from the ultraviolet to the visible.^{35,36} Significantly, the 0D quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) composites exhibit a more intense absorption in the visible region, this might be ascribed to the large contact area between graphene and the CuSbS₂ quantum dots, which promote the synergistic effects on light-absorption.

The PL behavior originates from the recombination of photoinduced electron-hole pairs. Fig. 3(b) illustrates the PL emission spectra of the samples; the TiO₂ array exhibited two dominant peaks at 467 nm and 416 nm, these PL signals

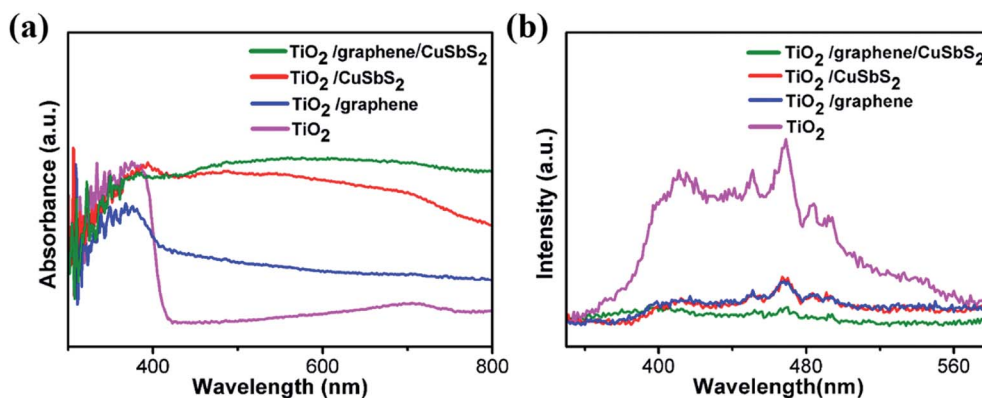


Fig. 3 (a) UV-Vis diffuse reflectance spectra and (b) PL spectra of the samples.



originate from the charge transfer and band-gap transitions of TiO_2 due to oxygen vacancies which trap the electrons.^{37,38} The PL intensity of the 1D TiO_2 nanowires/2D graphene and 1D TiO_2 nanowires/0D CuSbS_2 decline sharply because of the marriage of the graphene sheets and the fabricate the heterostructure, which observably benefit electron-hole separation.³⁹ Moreover, a further fluorescence decrease was observed for the 0D quantum dots/1D TiO_2 nanowires/2D graphene (mixed-dimensional) heterostructures photoanode, this might be attributed to the following: (1) the narrow band gap of the CuSbS_2 quantum dots promoted the intense absorption of visible light; the potentials of the conduction band (CB) of CuSbS_2 were more positive than TiO_2 , and the photo-generated electrons transferred to TiO_2 because of the potential dissimilarity; (2) the higher work function of the graphene sheets promote the transfer of the photo-generated charge carriers at the interface.

3.3 Photoelectrochemical performance

Fig. 4(a) shows the results of linear sweep voltammograms (LSV). It can be seen that the TiO_2 arrays exhibit the lowest photoresponse, with a photocurrent density of 1 mA cm^{-2} at 0.4 V and an onset potential of 0.05 V ; the 0D quantum dots/1D TiO_2 nanowires exhibited a comparable onset potential, along with an increase in the photocurrent density (2.6 mA cm^{-2} at 0.4 V) contrast to the pristine TiO_2 arrays. This indicates that the CuSbS_2 quantum dots were able to improve the photoresponse of the pristine TiO_2 arrays, which could be ascribed to its high light-absorption coefficient as well as its narrow band-gap. For the 1D TiO_2 nanowires/2D graphene, a reinforced photocurrent density (1.5 mA cm^{-2} at 0.4 V) and a cathodic shift of the onset potential relative to the pristine TiO_2 arrays were observed. For

the 0D CuSbS_2 quantum dots/1D TiO_2 nanowires/2D graphene (mixed-dimensional) heterostructures photoanode, the onset potential of the sample exhibit a marked negative shift. This indicated that the accumulation of photo-generated carriers at the interface is significantly reduced and could be attributed to the high charge transfer characteristics of the graphene sheets, as well as the large contact area between the graphene and the CuSbS_2 quantum dots.^{40,41} Additionally, the photocurrent density (5.2 mA cm^{-2} at 0.4 V) increase rapidly alongside the increase of the bias voltage, which was two times higher than that of the 0D quantum dots/1D TiO_2 nanowires (under the same bias voltage). Significantly, the photocurrent density is not saturated with increasing bias, this suggest an excellent light response and a high separation of photo-generated carriers in the 0D CuSbS_2 quantum dots/1D TiO_2 nanowires/2D graphene (mixed-dimensional) heterostructures, which is caused by the synergistic effects between graphene and the CuSbS_2 quantum dots.

The photoconversion efficiency (η) of each photoanode was calculated based on the current voltage curve as a function of the applied voltage (Fig. 4(b)), as shown by the followed formula:⁴¹

$$\eta = J \times 1.23(1.23 - E_{\text{RHE}})/P_{\text{light}} \quad (1)$$

$$E_{\text{RHE}} = E_{\text{SCE}} + E_{\text{SCE}}^{\ominus} + 0.059 \times \text{pH} \quad (2)$$

where J is the photocurrent density (mA cm^{-2}), P_{light} is the incident light intensity (100 mw cm^{-2}), E_{RHE} is the testing voltage relative to the reversible hydrogen electrode (RHE), E_{SCE} is the testing voltage relative to the SCE, and E_{SCE}^{\ominus} is the standard electrode potential of saturated calomel electrode (SCE) at 25°C . The 0D CuSbS_2 quantum dots/1D TiO_2 nanowires/2D

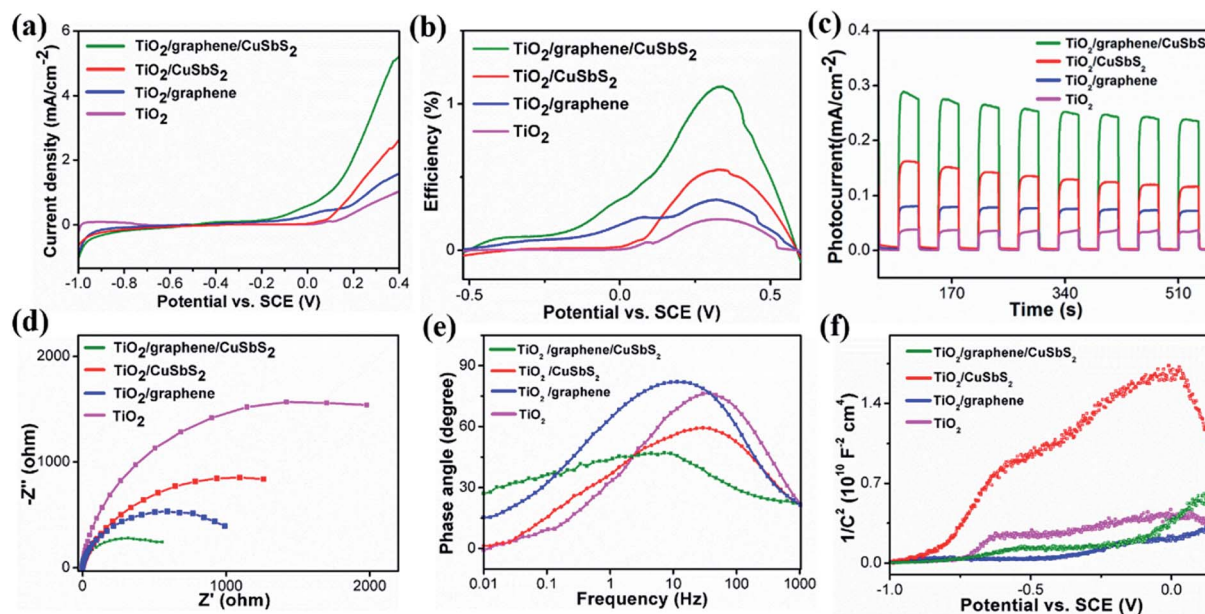


Fig. 4 Photoelectrochemical properties of the samples: (a) current-voltage curves, (b) photoconversion efficiency curves, (c) $I-t$ curves at a potential of 0.1 V , (d) electrochemical impedance spectra, (e) Bode phase plots, (f) Mott-Schottky plots.



graphene (mixed-dimensional) heterostructures photoanode exhibits a highest photoconversion efficiency of 1.2% at 0.3 V, which is observably larger than that of the 1D TiO₂ nanowires/2D graphene (0.34%), the 0D quantum dots/1D TiO₂ nanowires (0.54%), and pristine TiO₂ (0.2%). The PEC property of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode clearly demonstrated that a synergistic effect is achieved by the integration of 2D graphene and 0D CuSbS₂ quantum dots with 1D TiO₂ nanowires.

Fig. 4(c) shows the transient photocurrent densities of mixed-dimensional heterostructures photoanode with bias potentials of 0.1 V under identical incident power intensities. It is found that all the mixed-dimensional heterostructures photoanode exhibit a relatively high photocurrent density rate constant compared to those of their counterparts due to the synergistic effect involving the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode. The photocurrent density of the TiO₂ array is higher than that of 1D TiO₂ nanowires/2D graphene; however, the magnitude of the photocurrent density is 20 μ A. This is because of the limited use of the solar spectrum by the TiO₂ arrays, which led to low light to energy conversion. For 1D TiO₂ nanowires/0D CuSbS₂ quantum dots, the photocurrent intensity of the heterojunction increase significantly to 147 μ A, which indicate that the narrow band-gap CuSbS₂ quantum dots could efficiently harness incident solar light. However, the photocurrent density is not stable, after 600 s of illumination the intensity is attenuated to 115 μ A. It is important to highlight that the photocurrent density of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode represent the highest value among these four photoanodes, and the photocurrent rises and falls rapidly with changes between the light-on and light-off states. Although charge relaxation was observed, this phenomenon disappeared gradually with prolonged duration. Additionally, the photocurrent density increased to 287 μ A, which indicate that the graphene sheets not only effectively modulated the transport of charge carriers but also improve the stability of the CuSbS₂ quantum dots under extended illumination. This can be attributed to the large interfacial contact area between graphene and CuSbS₂ quantum dots. To the best of our knowledge, the photocurrent density of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene mixed-dimensional heterostructures photoanode is highest among other reported TiO₂-based photoanodes (Table S1†) and is also the maximum of the other reported photoanodes in a neutral medium.

Electrochemical impedance spectroscopy (EIS) studies was carried out to investigate charge transport behavior in these photoanodes. Generally, a smaller semicircle diameter in the plot suggests a lower charge transfer resistance. As shown in Fig. 4(d), the novel ternary 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode has the smallest semicircle diameter among the investigated samples. This indicate a low charge transfer resistance as well as a high electrochemical activity. The main reason for this is that graphene not only promotes the mass

transfer process but also improves electron transport, which rapidly increases the carrier concentration. The Bode curves of the samples are fitted from the EIS curves to further study the effects of graphene on carrier modulation, as shown in Fig. 4(e). The mid-frequency characteristic peak of TiO₂/graphene/CuSbS₂ shift markedly to a lower frequency, which reveal a more rapid electron mobility process. In addition, the lifetime of electrons τ_{eff} can be extracted *via* the following equation:^{42,43}

$$\tau_{\text{eff}} = 1/2\pi f_{\text{min}} \quad (3)$$

The electron lifetime is only determined by the minimum frequency (f_{min}) of the mid-frequency. In actual calculations, we reverse the minimum frequency (f_{min}) of Bode plots peak as a function of electron lifetime. The electron lifetime for the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode is 26.5 ms, 1D TiO₂ nanowires/0D CuSbS₂ quantum dots is 5.1 ms, 1D TiO₂ nanowires/2D graphene is 15.9 ms, and for pristine TiO₂ is 4.3 ms. The electron lifetime of the novel ternary 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures was the highest among the samples, and it was almost 5 times higher than that of 1D TiO₂ nanowires/0D CuSbS₂ quantum dots. In this regard, the incorporation of graphene sheets play a vital role in modulating photo-excited carrier transport in the composites.

The semiconducting properties of the obtained samples were investigated by measuring the Mott-Schottky plots, as shown in Fig. 4(f). The positive slopes of the plots for all the samples indicate formation of an n-type TiO₂ semiconductor. Additionally, the charge carrier density was calculated from the slope according to the following equation:⁴⁴

$$N_d = (2/e\epsilon_0\epsilon)[d(1/C^2)/dV]^{-1} \quad (4)$$

where N_d is the charge carrier density, e is the elementary electron charge, ϵ_0 is the permittivity in vacuum, and ϵ is the dielectric constant. The charge carrier density for the samples are $1.64 \times 10^{18} \text{ cm}^{-3}$ (TiO₂), $5.57 \times 10^{18} \text{ cm}^{-3}$ (TiO₂/graphene), $0.79 \times 10^{18} \text{ cm}^{-3}$ (TiO₂/CuSbS₂), and $5.08 \times 10^{18} \text{ cm}^{-3}$ (TiO₂-graphene/CuSbS₂); the results corresponded with the Bode plots, which further demonstrated the strong modulation of the charge carriers by graphene. The highly interconnected and the synergistic effects at 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures contribute to this distinguished photoelectrochemical performance. The flat band potential is obtained by extrapolating the Mott-Schottky plot to $1/C^2 = 0$ to obtain the intercept. An evident positive shift could be observed after the incorporation of graphene sheets, while a negative shift occurred after the incorporation of CuSbS₂ quantum dots. Generally, the positive shift of the flat band potential for TiO₂ indicate a decrease in the bending of the band edges, and this could facilitate charge transfer at the electrode/electrolyte interface. The results can be ascribed to the lower Fermi level of graphene, which facilitate the transportation of charge carriers and reduce the band bending between the electrode and the electrolyte interface.



Given the discussion above, a mechanism for the photoelectrochemical mechanism of the novel ternary 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures is proposed and shown in Fig. 5. First, electron-hole pairs are generated in the 1D TiO₂ nanowire arrays under illumination. Based on the structure analysis, the band energy difference between these mixed-dimensional induce both electron transfer from the 1D TiO₂ nanowire arrays to 2D graphene and hole capture by CuSbS₂ quantum dots. There should be a synergistic effect in the composites. This opposite transmission of electrons and holes inhibits the surface recombination of photogenerated charge carriers. The super-fast migration of electrons to the current collector was performed in 2D graphene due to its superior electron mobility, which remarkably suppresses the bulk electron-hole recombination and enhances the charge separation efficiency.²⁹ We thus believe that in our mixed-dimensional heterostructures materials, the highly interconnected and the synergistic effects at different dimensional contribute to this distinguished photoelectrochemical performance. Then, a large number of photogenerated carriers (electrons and holes) are formed due to the quantum effect of the CuSbS₂ quantum dots, the average size of CuSbS₂ quantum dots (around 6.7 nm) is smaller than their double Debye length of the electrons, which makes the whole quantum dots become the depletion layer, and this distinguishing feature is of high absorption coefficient because of the tiny amount electron injection. Subsequently, the large specific surface area of graphene accelerates mass transfer between the electrode and electrolyte, which prompts the transfer of photogenerated holes to the electrolyte. The synergistic effect fully exploits the extraordinary electron transport characteristics of 2D graphene and further makes large contribution to the highly promoted photoelectrochemical performance of the mixed-dimensional heterostructures device.⁴⁵ Finally, the photogenerated electrons migrate to the surface of graphene because of its lower Fermi

level. Under a certain bias, the electrons collected on the graphene eventually flow to the negative pole through the TiO₂ nanowire array under an external electric field.

4 Conclusions

An innovative ternary 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures photoanode was prepared *via* a simple and economic process where graphene sheets were fragmented between 1D TiO₂ nanowires and 0D CuSbS₂ quantum dots. The resulting ternary nanocomposites exhibit dramatically enhanced photoelectrochemical properties, including a large photocurrent density and an extended charge carrier lifetime. The enhancement could primarily be attributed to the fragmented graphene sheets; the high work function of the graphene sheets facilitates the migration of the photo-excited charge carriers, and the synergistic effects between graphene and the 0D CuSbS₂ quantum dots simultaneously enhances the absorption and conversion of solar energy. The demonstration of such the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene mixed-dimensional heterostructures proposed here would open up a wide area of opportunities for designing high-performance photoelectrochemical device. This kind of ternary nanocomposites exhibits broad application potential in areas such as CO₂ conversion, water splitting, gas sensors, and solar-energy conversion.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported by the Science and Technology Innovation Commission of Shenzhen (No. JCYJ20180305125345378, JCYJ20170303170542173), the National Nature Science Foundation of China (No. 51702219, 11174227), Shenzhen Nanshan District Pilotage Team Program (LHTD20170006), and Chinese Universities Scientific Fund.

References

- 1 P. Yan, G. Liu, C. Ding, H. Han, J. Shi, Y. Gan and C. Li, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3791–3796.
- 2 Y. Yang, S. Niu, D. Han, T. Liu, G. Wang and Y. Li, *Adv. Energy Mater.*, 2017, **7**, 1700555.
- 3 X. Jiang, Y. Zhang, J. Jiang, Y. Rong, Y. Wang, Y. Wu and C. Pan, *J. Phys. Chem. C*, 2012, **116**, 22619–22624.
- 4 Y. Zhang and C. Pan, *J. Mater. Sci.*, 2011, **46**, 2622–2626.
- 5 L. Wei, S. Chen, Y. Yang, Y. Dong, W. Song and R. Fan, *RSC Adv.*, 2016, **6**, 100866.
- 6 T. Su, Y. Yang, Y. Jiang, Y. Shi, R. Fan and W. Cao, *RSC Adv.*, 2016, **6**, 99251.
- 7 M. Ge, C. Cao, J. Huang, S. Li, Z. Chen, K. Zhang, S. S. Al-Deyab and Y. Lai, *J. Mater. Chem. A*, 2016, **4**, 6681–6772.

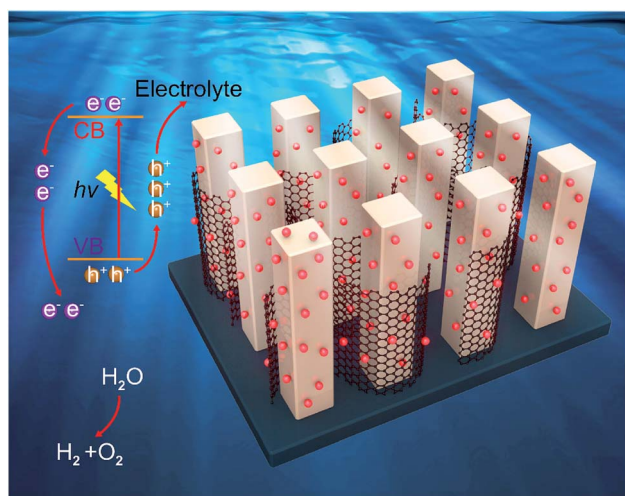


Fig. 5 Photoelectrochemical mechanism of the 0D CuSbS₂ quantum dots/1D TiO₂ nanowires/2D graphene (mixed-dimensional) heterostructures.



- 8 B. Seger, T. Pedersen, A. B. Laursen, P. C. K. Vesborg, O. Hansen and I. Chorkendorff, *J. Am. Chem. Soc.*, 2013, **135**, 1057–1064.
- 9 Y. Ji, M. Zhang, J. Cui, K. Lin, H. Zheng and J. Zhu, *Nano Energy*, 2012, **1**, 796–804.
- 10 M. Ge, S. Li, J. Huang, K. Zhang, S. S. Al-Deyab and Y. Lai, *J. Mater. Chem. A*, 2015, **3**, 3491–3499.
- 11 Y. Zhang, X. Li, X. Hua, N. Ma, D. Chen and H. Wang, *Scr. Mater.*, 2009, **61**, 296–299.
- 12 C. Gong, K. Hu, X. Wang, P. Wangyang, C. Yan, J. Chu, M. Liao, L. Dai, T. Zhai, C. Wang, L. Li and J. Xiong, *Adv. Funct. Mater.*, 2018, **28**, 1706559.
- 13 J. Su, L. Zhu and G. Chen, *Appl. Catal., B*, 2016, **186**, 127–135.
- 14 Y. Zhang, L. Fei, X. Jiang, C. Pan and Y. Wang, *J. Am. Ceram. Soc.*, 2011, **94**, 4157–4161.
- 15 Y. Zhang, C. Li and C. Pan, *J. Am. Ceram. Soc.*, 2012, **95**, 2951–2956.
- 16 A. Trenczek-Zajac, J. Banas and M. Radecka, *RSC Adv.*, 2016, **6**, 102886.
- 17 L. Jia, J. Xie, C. Guo and C. Li, *RSC Adv.*, 2015, **5**, 62611.
- 18 H. M. Ghartavol, M. R. Mohammadi, A. Afshar, F. C. Hong and Y. Jeng, *RSC Adv.*, 2016, **6**, 101737.
- 19 Z. Lian, P. Xu, W. Wang, D. Zhang, S. Xiao, X. Li and G. Li, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4533–4540.
- 20 S. Y. Chae, P. Sudhagar, A. Fujishima, Y. J. Hwang and O. Joo, *Phys. Chem. Chem. Phys.*, 2015, **17**, 7714–7719.
- 21 I. K. Konstantinou and T. A. Albanis, *Appl. Catal., B*, 2004, **49**, 1–14.
- 22 K. S. Novoselov and A. H. Castro Neto, *Phys. Scr.*, 2012, **T146**, 014006.
- 23 L. Sim, K. Leong, S. Ibrahim and P. Saravanan, *J. Mater. Chem. A*, 2014, **2**, 5315.
- 24 M. Wang, L. Sun, Z. Lin, J. Cai, K. Xie and C. Lin, *Energy Environ. Sci.*, 2013, **6**, 1211.
- 25 S. Yousefzadeh, M. Faraji and A. Z. Moshfegh, *J. Electroanal. Chem.*, 2016, **763**, 1–9.
- 26 Y. Mi, L. Wen, R. Xu, Z. Wang, D. Cao, Y. Fang and Y. Lei, *Adv. Energy Mater.*, 2016, **6**, 1501496.
- 27 Q. Dong, W. Liao, B. Wang and Z. Liu, *RSC Adv.*, 2015, **5**, 33869.
- 28 Y. Liu, H. Wang, K. Chen, T. Yang, S. Yang and W. Chen, *ACS Appl. Mater. Interfaces*, 2019, **11**, 9573–9582.
- 29 F. Ning, M. Shao, S. Xu, Y. Fu, R. Zhang, M. Wei, D. G. Evans and X. Duan, *Energy Environ. Sci.*, 2016, **9**, 2633–2643.
- 30 A. Fujishima, X. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515–582.
- 31 W. Zhang, Y. He, M. Zhang, Z. Yin and Q. Chen, *J. Phys. D: Appl. Phys.*, 2000, **33**, 912–916.
- 32 L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala and A. C. Ferrari, *Nano Lett.*, 2011, **11**, 3190–3196.
- 33 F. Tian, Y. Zhang, J. Zhang and C. Pan, *J. Phys. Chem. C*, 2012, **116**, 7515–7519.
- 34 C. Luo, X. Ren, Z. Dai, Y. Zhang, X. Qi and C. Pan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 23265–23286.
- 35 P. Song, X. Zhang, M. Sun, X. Cui and Y. Lin, *Nanoscale*, 2012, **4**, 1800–1804.
- 36 X. Xiao, R. Hu, C. Liu, C. Xing, C. Qian, X. Zuo, J. Nan and L. Wang, *Appl. Catal., B*, 2013, **140**, 433–443.
- 37 J. Liu, S. Zhang and H. Zhao, *Appl. Surf. Sci.*, 2019, **479**, 247–252.
- 38 G. Zan and Q. Wu, *Adv. Mater.*, 2016, **28**, 2099–2147.
- 39 J. Bai, J. Li, Y. Liu, B. Zhou and W. Cai, *Appl. Catal., B*, 2010, **95**, 408–413.
- 40 L. Gu, J. Wang, H. Cheng, Y. Zhao, L. Liu and X. Han, *ACS Appl. Mater. Interfaces*, 2013, **5**, 3085–3093.
- 41 N. T. Khoa, S. W. Kim, D. Yoo, S. Cho, E. J. Kim and S. H. Hahn, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3524–3531.
- 42 P. E. de Jongh, E. A. Meulenkaamp, D. Vanmaekelbergh and J. J. Kelly, *J. Phys. Chem. B*, 2000, **104**, 7686–7693.
- 43 Y. Lei, G. Zhao, M. Liu, Z. Zhang, X. Tong and T. Cao, *J. Phys. Chem. C*, 2009, **113**, 19067–19076.
- 44 L. Gao, W. Ren, F. Li and H. Cheng, *ACS Nano*, 2008, **2**, 1625–1633.
- 45 J. Kuang, Z. Dai, L. Liu, Z. Yang, M. Jin and Z. Zhang, *Nanoscale*, 2015, **7**, 9252.

