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Solution-processed Ultrathin SnS$_2$-Pt Nanoplates for Photoelectrochemical Water Oxidation

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**ABSTRACT:** Tin disulfide (SnS$_2$) is attracting significant interest due to the abundance of its elements and its excellent optoelectronic properties in part related to its layered structure. In this work, we detail the preparation of ultrathin SnS$_2$ nanoplates (NPLs) through a hot-injection solution-based process. Subsequently, Pt was grown on their surface via *in-situ* reduction of a Pt salt. The photoelectrochemical (PEC) performance of such nanoheterostructures as photoanode toward water oxidation was afterward tested. Optimized SnS$_2$-Pt photoanodes provided significantly higher photocurrent densities than bare SnS$_2$ and SnS$_2$-based photoanodes previously reported. Mott-Schottky analysis and PEC impedance spectroscopy (PEIS) were used to analyze in more detail the effect of Pt on the PEC performance. From these analyses, we attribute the enhanced activity of the SnS$_2$-Pt photoanodes here reported to a combination of the very thin SnS$_2$ NPLs and the proper electronic contact between Pt nanoparticles (NPs) and SnS$_2$.  

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1. INTRODUCTION

The conversion of solar energy into electric power or solar fuels such as hydrogen is a particularly relevant economic and social challenge. Toward this goal, since the report by Fujishima and Honda, photoelectrochemical (PEC) water splitting has become a promising route to produce environmentally friendly and potentially cost-effective hydrogen through the absorption and conversion of solar energy by a suitable semiconductor.

Owing to its composition, SnS$_2$, an indirect bandgap n-type semiconductor with a gap energy of 2.18–2.44 eV, has been proposed as a potentially advantageous absorber material free of rare, costly and toxic elements. SnS$_2$ displays a characteristic 2D hexagonal structure with tin atoms sandwiched between two close-packed sulfur atoms, and with the adjacent sandwiches being held together by weak Van der Waals forces. Such layered material has been used in a range of applications, including batteries, photocatalysis, sensors and FETs. Surprisingly, taking into account its well-fitted properties, the use of SnS$_2$ for PEC water oxidation has been not thoroughly investigated.

The main flaws of SnS$_2$ are a relatively low electrical conductivity and a moderate absorption coefficient in the visible part of the solar spectrum, what limits its photoactivity. To solve these limitations, a number of strategies have been developed: i) introduce extrinsic dopants to adjust the SnS$_2$ band gap and modulate its charge carrier concentration; ii) introduce co-catalysts on the surface of SnS$_2$ to enhance its activity, e.g. Pt; and iii) reduce the SnS$_2$ thickness taking into account that thin SnS$_2$ nanosheets with exposed (001) facets display higher photocatalytic activities.

In this last direction, several methods have been used to prepare SnS$_2$ nanostructures with a variety of morphologies, trying to maximize the exposed surface. e.g. nanoflakes, nanowires, nanoleaves and microspheres. A particularly interesting example is the exfoliation of SnS$_2$ bulk powders into single-layers, which showed a promising although still moderate performance in PEC water splitting. This approach had as main drawback its relatively low production throughput due to the long processing time and low yield.

Herein, we present a simple solution-based route to produce (001)-faceted SnS$_2$ NPLs. These NPLs are loaded with Pt NPs via an in-situ reduction process. The resulting SnS$_2$-Pt heterostructures are used as photoanode here for PEC water oxidation under simulated sun light. The performance of this new material is further characterized using Mott-Schottky analysis and PEIS.
2. EXPERIMENTAL SECTION

Chemicals. All chemicals were used as received, without additional purification. Tin(IV) chloride pentahydrate (SnCl₂·5H₂O, 98%), sulfur powder (99.8%), tetrahydrofuran (THF, ≥99%), 1,2-
hexadecanediol (90%), 1,2-dichlorobenzene (DCB, 99%) and diphenyl ether (≥99%) were purchased from Sigma-Aldrich. Platinum(II) acetylacetonate (98%), oleylamine (OAm, 80-90%) and oleic acid (OAc, 70%) were purchased from Acros. 1-Octadecene (ODE, 90%) was purchased from Alfa-Aesar. Toluene, hexane, isopropanol and ethanol were of analytical grade and obtained from various sources. All the aqueous solutions were prepared using Milli-Q water (18.2 MΩ).

Synthesis of SnS₂ nanoplates. In a typical synthesis, SnCl₂·5H₂O (2 mmol) was dissolved in THF (1 mL) in a 50 mL three-neck round flask. ODE (16 mL), OAc (4 mL) and OAm (2 mL) were then added and stirred at room temperature for 10 min. A syringe inserted into the solution was used to bubble Ar. The solution was then heated up to 140 °C and kept at this temperature for 1h to remove low boiling-point impurities. Then the obtained clear brown solution was heated to 220 °C. At this temperature, 4 mL of a S-OAm stock solution, pre-prepared by dissolving sulfur powder (4 mmol) into OAm (4 mL) under sonication, was quickly injected into the reaction flask with a syringe. The mixture was maintained at this temperature for 1h and afterward quickly cooled down using a cold water bath. The resulted product was centrifuged at 6000 rpm for 4 mins after adding toluene (15 mL), and then washed three times with toluene and ethanol by dispersion-precipitation cycles. The obtained pale yellow product was dried under vacuum for its posterior use and characterization. Around 280 mg of material was obtained in each batch, which corresponded to a 80% material yield after purification.

Synthesis of SnS₂-Pt nanoheterostructures. Phenyl ether (10 mL), 1,2-hexadecanediol (43 mg), OAm (0.2 mL) and OAc (0.2 mL) were loaded into a 25 mL three-neck reaction flask and kept at 140 °C for 30 min with Ar bubbling through a syringe. Depending on the relative SnS₂/Pt ratio targeted, 2 mg (SnS₂-Pt-2), 5 mg (SnS₂-Pt-5), 10 mg (SnS₂-Pt-10), or 20 mg (SnS₂-Pt-20) of platinum(II) acetylacetonate was added into a SnS₂ dispersion containing 100 mg of SnS₂ NPs (containing ca. 20 % organics) within 4 mL of DCB. These values correspond to a nominal molar concentration of 1.2% (SnS₂-Pt-1.2), 2.9% (SnS₂-Pt-2.9), 5.8% (SnS₂-Pt-5.8) and 11.6 % (SnS₂-Pt-11.6), respectively. The solution was then sonicated at 45 °C for 30 mins to homogenize. This mixture was quickly injected into the reaction flask at 200 °C and maintained at this temperature for 10 mins. A cold water bath was then used to quench the reaction. The product was washed with hexane and ethanol by multiple dispersion-precipitation cycles.

Ligand exchange. The native organic ligands were displaced from the NP surface using a NH₄SCN solution. Briefly, 10 mL of a hexane solution containing the NPs (5 mg/mL in hexane) was mixed with
5 mL of 0.13 M NH₄SCN solution (0.5 g NH₄SCN in 50 mL acetone). The mixture was then shaken for several minutes with a vortex and finally centrifuged out at 4000 rpm for 3 mins. The resulted product was further washed with 10 mL acetone twice to remove residual NH₄SCN.

**Sample characterization.** Powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 ADVANCE X-ray diffractometer (Bruker, Karlsruhe, Germany) operating at 40 kV and 40 mA with Ni-filtered (2 μm thickness) Cu Kα1 radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) characterization was carried out on a ZEISS LIBRA 120 (Carl Zeiss, Jena, Germany), operating at 120 kV. High-resolution TEM (HRTEM) images were obtained using a field emission gun FEI Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai microscope by using a GATAN QUANTUM filter. For TEM characterization, samples were prepared by drop casting a solution of NPs on a 200 mesh copper grid. SEM analysis was done in a ZEISS Auriga microscope (Carl Zeiss, Jena, Germany) with an energy dispersive X-ray spectroscopy (EDX) detector at 20 kV to study composition. X-ray photoelectron spectroscopy (XPS) was carried out on a SPECS system (SPECS GmbH, Berlin, Germany) equipped with an Al anode XR50 source operating at 150 mW and a Phoibos 150 MCD-9 detector (SPECS GmbH, Berlin, Germany). The pressure in the analysis chamber was kept below 10⁻⁷ Pa. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). Binding energy (BE) values were centered by using the C 1s peak at 284.8 eV. Fourier transform infrared spectroscopy (FTIR) was performed on an Alpha Bruker FTIR spectrometer with a platinum attenuated total reflectance (ATR) single reflection module. FTIR data were typically averaged over 24 scans. UV-Vis absorption spectra were recorded on a PerkinElmer LAMBDA 950 UV-Vis spectrophotometer (PerkinElmer, Waltham, MA, USA). Steady state photoluminescence (PL) spectra were recorded on a high resolution photoluminescence spectrofluorometer (Horiba Jobin Yvon Fluorolog-3).

**Photoelectrochemical measurements.** PEC characterization was performed in a three-electrode system using an electrochemical workstation (Metrohm Autolab). A Pt mesh (2 cm² surface area) and Ag/AgCl (3.3 M KCl) were used as the counter and reference electrodes, respectively. To prepare the working electrode, 2 mg of NPs and Nafion (20 μL, 5wt%) were dispersed in water-isopropanol (0.4 mL) with a volume ratio of 3:1 by sonicating 1h until obtaining a homogeneous ink. Depending on the amount of catalyst we wanted to test, 50 μL-300 μL ink was drop casted onto an FTO (fluorine doped tin oxide, 1cm*1.8cm) substrate and then annealed at 200 °C for 20 min after solvent evaporation. Before deposition, the FTO glass was washed with acetone-isopropanol (1-1 volume), ethanol, and then deionized water. After ink deposition, part of the material was wiped out from the FTO substrate to leave a clean area for electrical connection. An active area of 1cm x 1cm was left for PEC tests. An aqueous
solution of Na$_2$SO$_4$ (0.5 M, pH = 7) was used as the electrolyte. The electrolyte was purged with Ar for 30 min prior to the measurement. The incident light source was provided by 8 radially distributed 35 W xenon lamps, providing a total irradiance power on the sample of ca. 100 mW/cm$^2$. The following formula was used to convert the potentials to the reversible hydrogen electrode (RHE) standard scale:

$$E_{\text{vs. RHE}} = E_{\text{Ag/AgCl}^+} + E_{\text{Ag/AgCl}^+}^0 + 0.059^* \text{pH} = E_{\text{Ag/AgCl}^+} + 0.623 \text{ (V)}$$

For PEIS measurements, the frequency was swept from 1 MHz to 50 mHz with a sinusoidal amplitude of 25 mV under the same conditions used for photocurrent measurements. An equivalent circuit modeling software ZView (Scribner Associates) was used to fit the PEIS data. Mott-Schottky analysis was performed under dark conditions.
3. RESULTS AND DISCUSSION

SnS$_2$ NPs were produced from the reaction of tin chloride with elemental sulfur dissolved in OAm at 220 °C (see experimental section for details). Figure 1 shows representative TEM and SEM micrographs of the SnS$_2$ NPs produced following this synthesis procedure. SnS$_2$ NPs displayed hexagonal plate-like geometry with a diameter of around 150 nm and a thickness of ca. 6 nm (Figure 1a,b, S1). Such NPLs were much thinner than previously reported solution-processed SnS$_2$ NPs.$^{29,34-36}$ XRD patterns showed the SnS$_2$ NPLs to have a hexagonal phase and pointed at the (001) facet as the dominantly exposed (Figure 1c). HRTEM characterization confirmed SnS$_2$ NPLs to have a hexagonal crystallographic phase (space group =P-3m1) with a=b=3.6460 Å, c=5.8960 Å, and revealed them to be ~10 layers thick along the [001] direction. Additional EELS chemical composition analysis (Figure 1e) showed a uniform distribution of Sn and S through the whole SnS$_2$ NPL.

The process of formation of SnS$_2$ NPLs was analyzed through the XRD characterization of the product precipitated from aliquots extracted at different reaction times (Figure S2a). We observed that after few minutes reaction, mainly S was present in the precipitated powder, obtained from the reversible reaction of formation of oleylammonium polysulfides from the reaction of sulfur and OAm.$^{37,38}$ With time, SnS$_2$ was directly formed and S was gradually consumed along the 1h reaction. Sulfur could react with Sn(IV)-OAm directly, or in the form of oleylammonium polysulfides. We actually believe that both reactions took place simultaneously. No Sn-S intermediate phase could be detected.

The influence of the OAc/OAm ratio was analyzed through the XRD and TEM characterization of the products obtained under different amounts of these two surfactants (Figure S4). Pure OAm resulted in the formation of both SnS and SnS$_2$ phases due to the partial reduction of the Sn$^{4+}$ precursor by OAm. Only with the addition of a sufficient amount of OAc, pure SnS$_2$ phase could be formed. When no OAm was added, the Sn precursor could not be totally dissolved in the ODE-OAc initial solution. Under these conditions, large (~1 μm) flower-like SnS$_2$ structures were formed at 220 °C, after injecting the sulfur precursor (S-ODE in this case), as observed from representative SEM and TEM micrographs in Figure S5. The microstructures of SnS$_2$ samples show difference with/without OAm addition because OAm was not only necessary to bring Sn and S into the solution, but it also played a role as surfactant promoting the asymmetric growth of SnS$_2$ into NPLs, probably by preferential binding at (001) facets, and preventing the NPLs aggregation. Without OAm, urchin-like structures were obtained (Figure S5). On the other hand, OAc facilitated the formation of the SnS$_2$ phase.$^{34}$ With no OAc, a mixture of SnS$_2$ and SnS phases was systematically obtained (Figure S4).
SnS$_2$-Pt nanoheterostructures were produced by the growth of Pt nanodomains on the surface of preformed SnS$_2$ NPLs through the reduction of Pt(II) acetylacetonate (see experimental section for details). EDX analyses showed the final Pt concentration on the SnS$_2$ NPL surface to follow the nominal precursor ratios, pointing at a high yield of Pt deposition. When increasing the nominal amount of Pt, from 1.2%, to 2.9% and 5.8%, the diameter of the Pt domains in the SnS$_2$-Pt nanoheterostructures increased from ~1 nm, to ~3 nm and ~5 nm (Figure 2), respectively. Pt nanodomains were found uniformly distributed on the NPLs surface. However, at higher Pt concentrations, e.g. when introducing a nominal 11.6% of Pt (Figure S6b), the Pt size did not significantly further increase with respect to SnS$_2$-
Pt-5.8 but some Pt aggregation started to occur. HRTEM and EELS chemical compositional maps further confirmed the homogeneous distribution of Pt NPs through the SnS$_2$ surface and their average crystal domain size (Figure 3, S6c). XRD analyses showed the Pt metallic peaks at high Pt concentration, but no additional phase (Figure S6a).

**Figure 2.** TEM images of a) SnS$_2$ NPLs and SnS$_2$-Pt nanoheterostructures with increasing amounts of (b) Pt: 1.2 mol%, (c) 2.9 mol% and (d) 5.8 mol%.

XPS analyses provided slightly higher Pt concentrations than those nominally introduced and measured by EDX. As an example, the Pt concentration in the sample with a nominal composition of 2.9% was 3.8 mol% (Figure S7). As expected, XPS analysis showed the Pt to be in a metallic state. The Sn:S ratio was found at 0.6, which also pointed at a slightly Sn-rich surface. XPS analysis of bare SnS$_2$ (Figure S8) showed the same Sn/S atomic ratio, 0.6, proving the addition of Pt not to affect the SnS$_2$ composition. The Sn-rich surface could be ascribed to an intrinsically off-stoichiometry of SnS$_2$ surfaces, particularly (001) facets, or to a slight oxidation of the SnS$_2$ NPLs that had been exposed to air. Nevertheless, only one chemical environment was identified for Sn in both SnS$_2$ and SnS$_2$-Pt samples, and this was compatible with a Sn$^{4+}$ chemical state in a SnS$_2$ environment.
To promote an efficient transport of charge carriers within SnS$_2$-Pt NPL-based films, before film preparation, original insulating organic ligands were removed using a 0.13 M NH$_4$SCN solution (see experimental section for details). After ligand exchange, samples could not be re-dispersed in non-polar solvents such as hexane. Additionally, the bands corresponding to the C–H signal of OAm and OAc (2851-2923 cm$^{-1}$) completely disappeared from the FTIR spectrum (Figure S9), which indicated the effective removal of organic ligands from the NC surface. Subsequently, SnS$_2$-Pt NPLs were drop-casted on FTO substrates to test their performance as photoanode for PEC oxygen evolution.
All samples showed activity toward PEC water oxidation under simulated solar light (Figure 4). Figure 4a and 4b display the I-V curves and transient photocurrent (external bias of 1.23 V vs. RHE) under chopped visible-light illumination. As expected, the addition of Pt increased the PEC activity, being the SnS$_2$-Pt-2.9 photoanode the one providing the highest photocurrent densities. The values obtained with this catalyst were superior to most SnS$_2$-based photocatalysts previously reported (Table S2), particularly when compared with materials deposited from solution on top of FTO/ITO substrate (See Ref. 1-4 in Supporting Information, SI). Although SnS$_2$-based materials directly grown from a conducting substrate like FTO (Ref. 6,7 in SI) and Ti foil (Ref. 8), generally showed an improved contact between sample materials and current-collector and a related lower contact resistance.

When increasing the Pt loading, the PEC current density at 1.23 V vs. RHE increased from 16.84 $\mu$A/cm$^2$ for SnS$_2$, to 112 $\mu$A/cm$^2$ for SnS$_2$-Pt-2.9, to later decrease at higher Pt concentrations, e.g. 36.18 $\mu$A/cm$^2$ for SnS$_2$-Pt-5.8. The reduced photocurrent at high Pt loading was associated to: 1) a poor electronic/catalytic properties of the Pt with increased particle size; 2) the excessive electron-hole recombination centers resulting from higher Pt loading, thereby limiting the extraction of electrons with the external bias; 3) a strong light absorbance by Pt that partially shadowed the semiconductor from the light. Photoresponse times were on the order of 0.1 s for all samples, indicating a relatively rapid charge transport toward the substrate. The SnS$_2$-Pt-2.9 photoanode displayed transient spikes that increased with the photocurrent. These spikes were typically attributed to the charge accumulation and recombination at the interface, evidencing limitations on the charge transfer process to the electrolyte.

The amount of catalyst used to produce the film had a notable influence on the photocurrent response (Figure 4c and S10a). Excess amounts of catalysts resulted in a low illumination of the material close to the electrodes, where a more efficient charge extraction takes place. On the contrary, too small amounts limit the total surface area available for PEC oxygen evolution, also resulting in lower photocurrents. XRD (Figure S10b), SEM and TEM (Figure S11) characterization demonstrated that no crystallographic phase change took place during PEC measurements.

Long term stability of the SnS$_2$-Pt-2.9 photoanode was tested under chopped simulated solar light (on/off every 10 s). The results showed that around 60 % of the initial current density was preserved after 2000 s and then became almost steady, indicating an acceptable stability (See Figure S12a). Bubbles could be easily seen around the photoanode and Pt mesh, which was respectively ascribed to the O$_2$ and H$_2$ generation from water during test, as well as the inside wall of the PEC cell (Figure S12b).
Figure 4. (a) Linear sweep voltammogram curves under chopped AM 1.5G illumination for PECs. (b) Corresponding amperometric i-t curves under chopped illumination at an applied potential of 1.23 V vs. RHE (0.6 V vs. Ag/AgCl, 3.3 M KCl). (c) Amperometric i-t curves from films of different thicknesses produced from different ink amounts. (d) Comparison of the PEC performance obtained from different samples.

To gain insight into the charge carrier behavior at the semiconductor-liquid interface, PEIS measurements were carried out. Figure 5a shows the Nyquist plots corresponding to the SnS2-based anodes containing increasing amounts of Pt. At first sight, the decrease in the diameter of the semi-arc with the increased Pt loading suggested a decrease in the film resistance. A quantitative analysis of the electrochemical properties of the electrodes was attempted by fitting the Nyquist plots with equivalent circuits. Given the components and processes assumed to occur in these electrodes, we considered a general equivalent circuit containing a series resistance (Rs) and three RC components with the following contributions (Figure 5b): i) capacitance of the bulk SnS2 (Cbulk) and resistance of hole trapping to the surface states (Rtrap); ii) capacitance of the surface states (CSS) and resistance for charge transfer to the electrolyte through the surface states (RCSSS); and iii) charge transfer resistance from the valence band to Pt particles (Rcbd), capacitance associated to the surface Pt particles (Cp) and charge transfer resistance from Pt particles to the electrolyte (Rct, Pt). The Bode plot (Figure S13) obtained for the different samples
displayed a broad band, probably composed by two nearby peaks, indicating that a two-time constant equivalent circuit could describe sufficiently well the impedance response. Therefore, two simplified equivalent circuits (Figure 5c,d) were used to fit the Nyquist plots. For the sake of the analysis, the electrochemical parameters extracted from the fitting were plotted as a function of Pt loading in Figure 5e. In terms of the charge transfer resistance, bare SnS₂ and SnS₂-Pt-1.2 presented very high values, which resulted in low photocurrents. When the Pt loading increased (SnS₂-Pt-2.9 and SnS₂-Pt-5.8), the charge transfer resistance at the surface dropped dramatically, evidencing the improved catalytic activity provided by the Pt NPs. It is worth noting that $R_{\text{ct,bulk}}$ ($R_{\text{trap}}$) values are much lower than those of $R_{\text{ct,Pt}}$ ($R_{\text{ct,SS}}$), which was a sign that charge transfer was limited by the electrode/electrolyte interface instead of bulk. Interestingly, it was found that the lowest charge transfer resistance was achieved for SnS₂-Pt-2.9, in good agreement with the best performance obtained for this material. Further increase of the Pt loading led to an increase in $C_{\text{Pt}}$ and $R_{\text{ct,bulk}}$, whereas $R_{\text{ct,Pt}}$ remained virtually unchanged. These findings suggest that the decreased performance for high Pt loading (Figure 4a) did not originate from a deterioration of the catalytic activity of the Pt overlayer since $R_{\text{ct,Pt}}$ barely changed, but potentially from a worse charge transfer from the SnS₂ to the larger Pt NPs, given the increased $R_{\text{ct,bulk}}$. Likewise, the larger $C_{\text{Pt}}$ could be accounted for by the increased coverage and size of the Pt nanoparticles. To provide more details about the water oxidation mechanism on SnS₂-Pt nanoheterostructures, EIS was carried out in the dark and under illumination on a representative SnS₂-Pt-2.9 photoanode (Figure S14). Data extracted from fitting is displayed in Table S1. First, the value of $R_{\text{ct,bulk}}$ in the dark (around 2.8 kΩ) is higher than that under illumination (1.9 kΩ). This is not surprising given that under illumination the increased carrier density will decrease the film resistance. Second, the value of $R_{\text{ct,Pt}}$ decreases significantly under illumination which is consistent with the increased current. Indeed, the negligible faradaic dark current suggests that charges at this applied potential are unable to drive the water oxidation reaction, whereas under illumination the more oxidizing holes can successfully trigger the interfacial reaction. Third, the value of $C_{\text{Pt}}$ increases under illumination, which could be accounted for by the role of Pt as a reservoir of photogenerated holes at the interface. This result together with the increased photocurrent observed when coating SnS₂ with Pt provides compelling evidence that water oxidation occurs primarily via Pt sites rather than through the valence band of SnS₂. Similar behavior has also been found on other photoanodes such as hematite and copper ferrite. Additionally, Mott-Schottky analysis was performed on two representative samples, bare SnS₂ and SnS₂-Pt-2.9, under dark conditions. A Randles circuit was used to extract $C_{\text{bulk}}$ from impedance response to construct Mott-Schottky plot in Figure 5f. The positive slope of the $C^{-2}$-E plots indicated that both bare SnS₂ and SnS₂-Pt-2.9 are n-type semiconductors. The introduction of an optimal Pt loading positively shifted the flat band potential ($V_{\text{fb}}$) from 0.24 V to 0.14 V.
vs RHE. This implied a better photocurrent onset potential for SnS$_2$-Pt-2.9 and was consistent with Gong and co-workers reporting on surface modified hematite photoanodes.$^{48}$

Figure 5. (a) Nyquist plots measured under simulated sunlight irradiation with corresponding fitting curves of the bare SnS$_2$ and SnS$_2$-Pt nano-heterocomposites at a bias of 0.6 V (vs Ag/AgCl). (b) Proposed full equivalent circuit used for interpretation of SnS$_2$-Pt photoanode. Simplified equivalent circuit used for fitting impedance response of SnS$_2$ (c) without and (d) with Pt loading. (e) $R_{ct,bulk}$, $R_{ct,ss}/R_{ct,Pt}$ and $C_{ss}/C_{Pt}$ values fit from impedance response of SnS$_2$ photoanode as a function of Pt loading. (f) Mott–Schottky plots of SnS$_2$ NPLs and SnS$_2$-Pt-2.9 nanoheterostructures measured in the dark.

To further investigate the recombination behavior of photoinduced electron-hole pairs in bare SnS$_2$ and SnS$_2$-Pt-2.9 nanoheterostructures, PL spectra were measured. The PL measurements of bare SnS$_2$ and SnS$_2$-Pt-2.9 nanoheterostructure were carried out under the excitation wavelength of 390 nm. As shown
in the PL spectra (Figure S15b), bare SnS$_2$ exhibited the radiative interband recombination peak at 543 nm, which was consistent with the SnS$_2$ band gap (2.25 eV, Figure S15a). In addition, an emission shoulder appeared at 455 nm, which we related to the radiative recombination of exciton absorption.$^{35}$ Compared with the PL intensity of bare SnS$_2$, a significantly decreased PL emission, especially for the emission from radiative interband recombination, was observed for SnS$_2$-Pt-2.9 nanoheterostructures. These results demonstrate that a reduced photogenerated hole-electron recombination existed in SnS$_2$ photoanodes, assigned to the facilitated charge separation by the introduction of Pt. The suppressed charge recombination in SnS$_2$ photoanode benefited achieving high photocurrent responses. A simplified PEC water oxidation mechanism on SnS$_2$-Pt nanoheterostructures is summarized in Figure 6. As shown in Figure 6a, photogenerated electrons from SnS$_2$ NPLs are transferred to the FTO and from it to the Pt mesh for H$_2$ evolution. Photogenerated holes are injected from the SnS$_2$ NPLs to the OH$^-$ groups through the Pt nanodomains. The flow direction of electrons and holes is schematized in the energy-band diagram in Figure 6b. We consider the SnS$_2$ conduction band minimum (CBM) of SnS$_2$ to be 0.1 V above the flat band potential (0.24 V vs NHE for SnS$_2$ as measured from M-S).$^{49,50}$ Therefore, the CBM of SnS$_2$ without external bias was around 0.14 V vs NHE. Under a positive bias, the CB and VB shifted toward positive values, facilitating the photogenerated holes transfer to OH$^-$ groups in solution through Pt domains. On the other hand, the photogenerated electrons transferred to the counter electrode (a Pt mesh) to reduce H$^+$ into H$_2$. A relatively fast separation of the photogenerated charge carriers reduced opportunity of charge recombination thus promoting performance in SnS$_2$-Pt nanoheterostructures compared with SnS$_2$ NPLs. Pt NPs played a significant role in electron-hole separation and facilitating charge transfer to the hydroxyl groups, thus resulting in a superior performance of SnS$_2$-Pt nanoheterostructures when compared with bare SnS$_2$. However, a clear deterioration of the performance was observed when larger Pt NPs were deposited. Overall, these results suggest that new strategies, capable of decoupling both particle size and coverage during the Pt deposition, would be essential to further enhance the performance of this system, targeting a narrow size distribution for the Pt NPs and a high coverage.
Figure 6. a) Cartoon and b) Energy band schematic diagram of SnS$_2$-Pt nanoheterostructures for water oxidation in a PEC cell.

4. CONCLUSIONS

In summary, ultrathin SnS$_2$ NPLs were produced via colloidal hot injection synthesis route, and the roles of surfactant OAm and OAc were investigated. Subsequently, metallic Pt was uniformly deposited on the surface via an in-situ reduction method. Such SnS$_2$-Pt nanoheterostructures showed significantly enhanced PEC current response under simulated sunlight compared to bare SnS$_2$ NPLs. The decreased performance observed for high Pt loadings appeared to be related to a deterioration of the charge transfer from the SnS$_2$ to the larger Pt NPs according to the PEIS data. The intimate contact between Pt NPs and SnS$_2$ NPLs was the key to obtain a useful semiconductor-noble metal synergetic effect through an efficient charge transfer of the photogenerated carriers from the semiconductor to the metal to promote solar energy conversion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: **********.

Electronic supplementary information (ESI) available: Additional experiments, XRD, TEM, SEM, EDX, XPS, FTIR, PEC tests, bode plots, (ahv)$^2$-hv plots and PL.

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Notes
The authors declare no competing financial interest.

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