This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Facile Synthesis of Novel MoS$_2$@SnO$_2$ Hetero-nanoflowers and Enhanced Photocatalysis and Field Emission Properties

Jinzhu Li, Ke Yu,* Yinghua Tan, Hao Fu, Qingfeng Zhang, Weitao Cong, Changqing Song, Haihong Yin, and Ziqiang Zhu

A novel hierarchical MoS$_2$@SnO$_2$ hetero-nanoflower was successfully synthesized by a facile two-step hydrothermal method without using any additives or surfactants. One possible growth mechanism of the hetero-nanostructure was presented in detail based on OH$^-$ ion-dependent experimental facts. Due to the formation of the p-n junctions and the increased specific surface area in the composites, an outstanding photocatalytic activity of the as-prepared sample was obtained by monitoring the photodegradation of methylene blue (MB). According to the data, after irradiation for 100 min, the remaining MB in solution is about 26% for MoS$_2$ nanoflowers and 9.5% for MoS$_2$@SnO$_2$ hetero-nanoflowers. Moreover, an excellent field emission performance was obtained from MoS$_2$@SnO$_2$ hetero-nanoflower relative to the pure MoS$_2$ with the turn-on field decreasing from 4.2 V$\mu$m$^{-1}$ to 3.4 V$\mu$m$^{-1}$ and the threshold field decreasing from 6.2 V$\mu$m$^{-1}$ to 5.2 V$\mu$m$^{-1}$, which is mainly contributed to the increased field emission points and MoS$_2$-SnO$_2$ heterojunction.

1. Introduction

Over the last few years, aroused by the discovery of graphene, two-dimensional (2D) nanomaterials have been largely researched in the field of industrial and scientific for their unique properties and wide potential applications.\(^1\)\(^-\)\(^4\) Recently, more and more researchers are paying attention to the layered MoS$_2$ which has a similar structure to graphene.\(^5\)\(^-\)\(^7\) Each layer of the MoS$_2$ nanosheets is consists of molybdenum atoms sandwiched between two layers of hexagonally close-packed sulfur atoms, that the adjacent atomic sandwiches are held together by weakly van der Waals forces.\(^8\)\(^-\)\(^9\) MoS$_2$ nanoflowers, as typical three-dimensional (3D) metal sulfide microspheres, are composed of 2D nanosheets, have became particularly interesting due to their enhanced structural complexity and the potential to exploit the functionalities of these nanomaterials, making it a up-and-coming candidate for many useful applications, such as outstanding photoluminescence,\(^10\)\(^-\)\(^11\) lithium battery cathodes,\(^12\) sensors,\(^13\) and hydrogen storage medias\(^14\)\(^-\)\(^15\) etc. However, photocatalytic and field emission abilities of MoS$_2$ nanoflowers are not productive enough for large scale applications in industry because of the relatively narrow band gap (1.8 eV), a rapid recombination rate of photogenerated electrons and holes and lacking of effective emission sites. However, lots of previous studies reveal the fact that forming hetero-nanostructure can give the nanomaterials a better performance in vacuum electronics, optoelectronics and other aspects because of the generation of hetero-junction, enlarged specific surface area and so on, such as MoS$_2$/CdS,\(^16\) MoS$_2$/TiO$_2$,\(^17\) and MoS$_2$/MWNT.\(^18\)

SnO$_2$, as one of the most successful n-type semiconductors, due to its low-cost and low-toxic property, wide band gap (E$_g$ = 3.8 eV) and stable chemical properties,\(^19\) has been widely studied in gas sensors,\(^20\) lithium ion batteries\(^21\) and field emission devices.\(^22\) Therefore, we pay great attention to the MoS$_2$@SnO$_2$ system connecting two chemically stable and inexpensive multifunctional semiconductor materials together. In this system, MoS$_2$ works as narrow band gap (1.8 eV) p-type semiconductor\(^16\) and SnO$_2$ serves as wide band gap (3.8 eV) n-type semiconductor,\(^23\) result in a same Fermi energy level at the interface and constructing the p-n heterojunctions. This p-n junction will make a contribution to specific charge-transfer kinetics and separation of electron-hole pairs, giving advanced performances for photocatalytic. Meanwhile SnO$_2$ nanoparticles which adhered on the surface of MoS$_2$ will increase the emission point and the formed p–n heterojunction can help the separation of the electron–hole pairs which can give a larger promotion in field emission properties. Hence, the nano-heterojunction MoS$_2$@SnO$_2$ composite with high-efficiency photovoltaic and vacuum electronic properties need to be explored. In our previous study, many heterojunction composites were synthesised by using photodeposition-based technique,\(^24\) electrochemical synthesis\(^25\) and ultrasonic treatment\(^26\) etc, these methods are not facile enough and always hindered by the experimental conditions.

In this paper, we fabricate MoS$_2$@SnO$_2$ hetero-nanoflowers composite for the first time, and report a facile route for synthesizing the composite which is based on MoS$_2$ nanoflowers by a two-step low temperature hydrothermal method without using any additives or surfactants. The experimental reagents are simple and easy to get and the reaction conditions are simple and
controllable. In addition, the functional behavior of the obtained hetero-nanoflowers in photocatalysis and field emission applications are presented in detail. We measured the photocatalytic and field emission properties of MoS\textsubscript{2}@SnO\textsubscript{2} hetero-nanoflowers and compared them with those of pure MoS\textsubscript{2} samples. The experiment results indicate that the fabricated MoS\textsubscript{2}@SnO\textsubscript{2} hetero-nanoflowers have a significant performance improvement in these properties.

2. Experimental section

2.1 Synthesis of MoS\textsubscript{2} nanoflowers

In our experiments, the MoS\textsubscript{2} nanoflowers were synthesized in a Teflon-lined autoclave via a hydrothermal route. All the chemical reagents used in the experiment were analytical grade without further purification. The procedure of the preparation was as follows: Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O (1.0 g) and thioacetamide (1.2 g) were used as Mo and S sources, respectively, dissolved in a beaker with 80 ml deionized water. The solution was stirred about 20 min to form a transparent solution, and then adjust the pH value to an acid environment by using oxalic acid (0.4 g). Transfer the solution to a 100 ml stainless-steel autoclave with a Teflon liner after the oxalic acid was dissolved absolutely. The autoclave was sealed and heated at 200 °C for 24 h without shaking or stirring during this period. Collected black precipitate after the autoclave cooled down to room temperature and washed with deionized water and 95% ethanol several times in order to remove any impurities, after that dried in a vacuum at 60 °C for 5 h to obtain black powders. For the sake of getting a more crystalline product, the as-prepared sample was annealed at 850 °C for 2 h under the protection of pure argon.

2.2 Synthesis of MoS\textsubscript{2}@SnO\textsubscript{2} hetero-nanoflowers

The synthesis of MoS\textsubscript{2}@SnO\textsubscript{2} hetero-nanoflowers were also used a one-step hydrothermal method. The as-fabricated MoS\textsubscript{2} (0.1 g) was dissolved in glass beaker with 80 ml deionized water and stirred 20 min to ensure the black powders was completely dispersed in the solution. SnCl\textsubscript{4}·5H\textsubscript{2}O (1.05 g, 3 mM) and NaOH (0.84 g, 21 mM) as Sn and O sources respectively, dissolved in the solution quickly due to their strong deliquescence. After magnetic stirring for 30 min, a suspension was obtained and transferred into a stainless steel autoclave with Teflon-lined, which was heated at 180 °C for 2 h. After being cooled down to the room temperature, the resultant was washed with deionized water and 95% ethanol several times until the impurities were all cleaned away. Finally, the as-prepared sample was obtained at 850 °C for 5 h under the protection of pure argon.

2.3 Characterization

The crystal structures of the products were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) using monochromatized Cu-K\textalpha radiation (\(\lambda=1.5418\) Å). The diffraction patterns were collected in the 20 scanning range from 10° to 80° with 0.02° per step. The structures and morphologies of the as-prepared samples were characterized by field emission scanning electron microscopy (FESEM, JEOL-JSM-6700F) at an accelerating voltage of 20 kV and transmission electron microscopy (TEM, JEOL-JEM-2100) at an accelerating voltage of 200 kV. TEM of the samples were prepared by adding a drop of the colloidal solution onto a standard holey carbon-coated copper grid. The grids were dried in air at room temperature.

2.4 Photocatalytic measurements

For investigating the photocatalytic of the as-prepared products, methylene blue (MB) was selected because of the strong adsorption to metal oxide surface, strong absorption in the visible region and excellent stability under various pH conditions. The maximum optical absorption peak of methylene blue at 664 nm was used to monitor the concentration of the solution which was catalyzed by the samples at room temperature. The procedure was as follows: Chosen the as-prepared MoS\textsubscript{2} nanoflowers (0.01 g) and MoS\textsubscript{2}@SnO\textsubscript{2} (0.01 g) hetero-nanoflowers as the photocatalyst respectively and added to a cylindrical container with 100 ml MB aqueous solution (10 mg L\textsuperscript{-1}). Before irradiation, covered the container with aluminized paper to keep the mixed solution stay in dark, stirred for 20 min to ensure the establishment of an adsorption-desorption equilibrium of the MB on the samples’ surface. In order to minimize the heat effect, the photo reactor was fixed in a glass container which was cooled by flowing water and air conditioning. An 20 W tungsten halogen lamp (\(\lambda \geq 340\) nm) was used to irradiate the solution and then analyzed the MB concentration, every 20 minutes a total of 6 times, by a UV-vis spectrophotometer (UNICO 2802).

2.5 Field emission measurement

For the field emission experiment, the synthesized MoS\textsubscript{2} nanoflowers and MoS\textsubscript{2}@SnO\textsubscript{2} hetero-nanoflowers were prepared on the silicon substrate by the method of screen-printing, respectively. After that, they were dried in vacuum at 50 °C for 5 h. The silicon substrate with the nanomaterials was regarded as the cathode, which was separated from a phosphor–indium tin oxide (ITO)/glass anode by two Teflon spacers with a fixed thickness of 200 μm. Field emission properties were measured in a vacuum chamber with a high vacuum level of about 5×10\textsuperscript{-7} Pa at room temperature. The measured emission area was 1×1 cm\textsuperscript{2}. In the measurement, the turn-on field is determined as the field produces a current density of 1 μAcm\textsuperscript{-2}, and the threshold field is the field produces a current density of 0.1 mAcm\textsuperscript{-2}.

3. Results and discussion

3.1 Characterization of the as-fabricated samples

The purity and crystalline phase of the hydrothermally synthesized MoS\textsubscript{2} nanoflowers, SnO\textsubscript{2} nanoparticles and MoS\textsubscript{2}@SnO\textsubscript{2} hetero-nanoflowers were analyzed by a powder X-ray diffractogram. Fig. 1 shows the XRD patterns of the samples, which displays diffraction peaks in the range of 10-80°. Fig. 1 black curve could be clearly pointed out the pure hexagonal phase of MoS\textsubscript{2} (JCPDS 37-1492) with lattice constants of a=b=3.16 Å, c=12.29 Å. The diffraction peaks at 2θ=14.4°, 33.1°, 39.7° and 58.5° can be assigned to the (002), (100), (103) and (110) faces, and there are no peaks for other impurities being found in the spectra, revealing there is only MoS\textsubscript{2} with a high purity. The red
curve of the pattern mainly consists of mainly SnO₂ peaks. Meanwhile all diffraction peaks from the tetragonal SnO₂ (JCPDS 71-0652) are also observed. The intense peaks of the XRD pattern indicate that the SnO₂ nanoparticles were well crystallized. The XRD pattern for the MoS₂@SnO₂ hetero-nanoflowers is shown as blue curve in Fig. 1, distinct lattice planes corresponding to the SnO₂ NPs and MoS₂ nanoflowers revealed the presence of individual components of SnO₂ and MoS₂. The schematic crystal structures of MoS₂ and SnO₂ are showed in Fig. 1b. The sandwiched structure of MoS₂ crystal was stacked together by weak van der Waals interactions with an interlayer spacing of 6.15 Å, and the layer structure of MoS₂ is the main reason for its many amazing functionalities such as high electron mobility and quantum Hall effects etc.  SnO₂ nanoparticles adhered to the surface of MoS₂ nanosheet. We consider the combination of MoS₂@SnO₂ nanocomposite is ascribed to the nano-reunion effect. In order to reveal the specific surface area of the samples, we obtain two distinct hysteresis loops at a relative pressure of 0.1–0.9 in the N₂ adsorption–desorption isotherm (Fig. 2), which indicates the presence of a flower-like structure. A Brunauer–Emmett–Teller (BET) surface area is 24.6 m² g⁻¹ for the MoS₂@SnO₂ binary nanoflowers and 17.2 m² g⁻¹ for the MoS₂ nanoflowers (the table in the inset). It is obviously that the specific surface area of MoS₂@SnO₂ binary nanoflowers is larger than that of MoS₂ nanoflowers.

3.2 Morphology of the MoS₂ nanoflowers

The microstructure and morphology of the as-prepared MoS₂ nanoflowers were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the results of which are shown in Fig. 3. The surface morphology of the flower-like MoS₂ could be clearly observed from Fig. 3a and b, a set of typical SEM images at different magnifications. As shown in Fig. 3a, every MoS₂ nanoflower with an average diameter of 1 to 2 μm. The surface of the nanoflowers with a large amount of petals, which were tightly aggregated, could be observed clearly in Fig. 3b. From the inset in Fig. 3b, high-magnification of a single MoS₂ nanoflower could be seen that the petals (2D nanosheet) align together disorderly with much interspace pointing towards a common inner center to form the spherical product.

In the Fig. 3c and d, TEM and HRTEM measurement were performed for the sake of a further investigation on the morphology and crystallographic features of MoS₂ nanoflowers. The flower petals could be observed in Fig. 3c. We can see that the petals was constructed by a combination of 4–9 MoS₂ layers and has an interlayer separation of 0.64 nm. The inset of Fig. 3c exhibits the low magnification of a single nanoflower. A local high resolution TEM image is showed in Fig. 3d that the synthesized nano-petal was grown in high densities. The selected-area HRTEM from the inset of Fig. 3d shows the lattice fringes of the samples with a well-defined crystal structure, and the lattice spacing corresponded to the (002) plane.
3.4 Formation process and mechanism of the as-synthesized products

In order to investigate the formation process and mechanism of the MoS2@SnO2 hetero-nanoflowers, the reagent dependent experiments with different amount of NaOH from 0.72 g (18 mM) to 1.08 g (27 mM), namely the molar ratio of SnCl4·5H2O to NaOH from 1:6 to 1:9 were performed (Fig. 5), while the amount of MoS2 (0.1 g), SnCl4·5H2O (1.05 g, 3 mM) and the reaction conditions (time is 16 h and temperature is 180 °C) were kept and fixed. When a relative low amount of NaOH was used (0.72 g), the obtained products show that there are several white SnO2 quantum dots attached on the surface of MoS2 petals (Fig. 5a). With the increase of the molar ratio from 1:7 to 1:9, more and more SnO2 can be observed on the surface of MoS2 (Fig. 5b-d). Fig. 5b exhibits the nanoflower-nanoparticle architecture described above. From c to d, the MoS2 nanoparticles are almost all covered with SnO2 nanorods. As the amount of OH- increased, the SnO2 grew from short-nanorod to long-nanorod.

In our case, the formation of SnO2 adhering on the MoS2 can be expressed by the formula as follows:

\[
\text{Sn}^{4+} + 6\text{OH}^- \rightarrow \text{Sn(OH)}_6^{2-}
\]

\[
\text{Sn(OH)}_6^{2-} \rightarrow \text{SnO}_2 + 2\text{OH}^- + 2\text{H}_2\text{O}
\]

Summing up in a total reaction is:

\[
\text{Sn}^{4+} + 4\text{OH}^- \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O}
\]

In our studies, the morphology of SnO2 attached on MoS2 is related to the reaction time, reaction temperature\(^{29}\) and reagent dosage.\(^{29}\) When the reaction time and temperature are fixed, the amount of NaOH will play a key role\(^{30}\) in the morphology of SnO2 attaching on the MoS2 nanoflowers, namely the concentration of the OH- determines the morphology of the MoS2@SnO2 products. The higher OH- ion concentration accelerates the nucleation process and results in a higher nuclei concentration.\(^{30}\) According to the description made by Peng and Peng,\(^{31}\) the growth of elongated nanocrystals can be promoted after combining with relatively high chemical potential. However, too high OH- ion concentration will play an opposite role. This is due to the total volume of aqueous solution used in the experiment is fixed and with the increasing of the OH- ion, the concentration of Sn\(^{4+}\) will decrease. So the molar ratio of SnCl4·5H2O to NaOH is also a key role in this case.

As seen in the pictures, higher amount and molar ratio of NaOH can induct the MoS2 almost all covered with SnO2 nanorods, leading to the decrease of specific surface area and lose

attached to the upper surface, lower surface and inner space of MoS2 petals. The sizes of the SnO2 nanoparticles are within the range of 15 to 20 nm.

As can be seen from the High magnification TEM image (Fig. 4c), a petal of molybdenum disulfide nanoflowers is inlayed with several SnO2 nanoparticles. The inset of Fig. 4c shows the selected area electron diffraction (SAED) pattern and HRTEM image of the SnO2 nanoparticles. The measured lattice spacing of 0.26 nm corresponds to the d-spacing of the (101) and (10̅1) crystal planes of the SnO2, as shown in the HRTEM image (inset in Figure 4c, right upper). Moreover, the corresponding SAED pattern (inset in Fig. 4c, right lower) derived from single SnO2 nanoparticle of which is the corresponding HRTEM image can confirm the single-crystalline form of SnO2 nanoparticles. Enlarged TEM view of the SnO2 nanoparticles adhered to the MoS2 nanosheets are shown in Fig. 4d. The red circle exhibits the stratified structure of MoS2 attached with the nanoparticle (a black shadow) which presents a strong demonstrate to the hetero-architecture of MoS2@SnO2. SEM and TEM analysis of the obtained material revealed the formation of the 3D hierarchical hetero-architecture meanwhile, the MoS2 nanoflowers and the SnO2 nanoparticles can be clearly observed from Fig. 4a to d. It is obvious that for the MoS2@SnO2 composites, the SnO2 nanoparticles are covered with cubic nanoparticles, which further reveals that these MoS2@SnO2 hetero-nanoflowers are assembled from MoS2 nanoflowers.
UV-vis light region, which similar to the spectrum of sunlight, can minimize the surface energy so that the nanoparticles were found adhering on the surface MoS$_2$ nanoflowers. The SnO$_2$ nanoparticles adhere to MoS$_2$ which we have described in Ch 3.3. The MoS$_2$ nanoflowers are covered with short-nanorod (c) and long-nanorod (d) SnO$_2$ when the ratio is 1:8 and 1:9 respectively.

Therefore, in order to obtain the ideal hetero-nanoflowers, the amount of NaOH and the molar ratio of SnCl$_4$·5H$_2$O to NaOH should be adjusted in a proper value (0.84 g, 1:7).

On the basis of the above result, we proposed a possible growth mechanism for MoS$_2$@SnO$_2$ nanoflowers, as illustrated in Scheme 1. As shown in Fig. 5 and Scheme 1, the growth mechanism could not be attributed to Ostwald-ripening, it is not suitable to explain the growth of SnO$_2$ by classical crystal growth mechanism. A different theory of crystal growth which called “oriented attachment”, proposed by Penn and Banfield, may give out an explanation to the growth of SnO$_2$ adhering on the MoS$_2$ nanoflowers in our samples. They hold the idea that eliminating surface energy is the impetus for the aggregation of SnO$_2$ nanoparticles and nanorods. Consistent with our observations through the growth of SnO$_2$. Firstly, through the dehydration of Sn(OH)$_6^{2-}$ and then epitaxially, the SnO$_2$ quantum dots grow on the surfaces of the MoS$_2$ petals (Scheme 1b). With the increase of the amount and molar ratio of NaOH, the quantum dots are enlarged into particles (Scheme 1c). As the process going on, SnO$_2$ nanoparticles will find a direction which could minimize the surface energy so that the nanoparticles were found served as "seeds" for the growth of nanorods, which has been promoted by higher OH$^-$ concentration. Finally the SnO$_2$ short-nanorods are formed (Scheme 1d) on the surface of MoS$_2$ surface and continue to grow in the vertical to generate the long-nanorods with a higher OH$^-$ concentration (Scheme 1e).

4. Photodegradation of MB

MoS$_2$ has photocatalytic properties in the visible region and SnO$_2$ may utilize the ultraviolet light, and hopefully the MoS$_2$@SnO$_2$ composites would present photocatalytic activity across the whole UV-vis light region, which similar to the spectrum of sunlight, and have a good potential in applications. In our case, the MB is used to monitor the photocatalytic activities of the two as-prepared samples because of the characteristic of absorption peak at 663 nm. In the experiment, bare MoS$_2$ nanoflower and MoS$_2$@SnO$_2$ hetero-nanoflower samples were employed as reference catalysts, and the corresponding absorption spectra were shown in Fig. 6a and b, respectively. As the irradiation proceeded, the intensity of the main absorption peaks of MB continued to decrease. Obviously, the MB solution containing MoS$_2$@SnO$_2$ exhibited a much faster peak-descending rate than pure MoS$_2$ nanoflower. Meanwhile, in the inset of Fig. 6b, the dexter container exhibits more dilute than the counterpart in the inset of Fig. 6a, which were influenced by the same environment condition and irradiation time.

It is apparent that the photocatalytic ability of the MoS$_2$@SnO$_2$ hetero-nanoflowers was much better than that of the MoS$_2$ nanoflowers. The dependencies of the degradation efficiency on irradiation time for the samples which are represented by the concentrations of the MB solution at 663 nm with the maximum absorption, are presented in Fig. 6c. The degradation efficiency is defined as C/C$_0$ in which C and C$_0$ stand for the remnants and initial concentration ratio of MB respectively. According to the data, before the light irradiation, the mixed solution of the photocatalyst (as-prepared samples) and MB was stirred in dark to establish the adsorption/desorption equilibrium of MB on the surfaces of samples. Clearly, the remaining MB in both solutions, indicating that MoS$_2$@SnO$_2$ nanoflowers present stronger adsorption ability than the MoS$_2$ samples, due to the larger specific surface area. After the dark period, both of the samples were irradiated for 100 min in the same conditions, the remaining MB in solution is about 26% for the MoS$_2$ nanoflower and 9.5% for the MoS$_2$@SnO$_2$ hetero-nanoflower, indicating that the MoS$_2$@SnO$_2$ hetero-nanoflower structure possess a better photocatalytic performance.

Based on the above experimental results and previous studies, enlarged specific surface area will play a key role to the enhanced photodegradation activities. It is generally accepted that the catalytic process is mainly related to the adsorption and desorption processes on the surface of the catalyst. The high specific surface area of the nanocatalyst results in more unsaturated surface coordination sites exposed to the reactants. The enlarged specific surface area of MoS$_2$@SnO$_2$ hetero-nanoflowers is due to the SnO$_2$ nanoparticles which are covered on the surface MoS$_2$ nanoflowers. The SnO$_2$ nanoparticle has a...
the holes transfer to the valance band of MoS$_2$. Therefore, the surface area of the MoS$_2$@SnO$_2$ nanoflowers will be much larger than that of MoS$_2$ nanoflowers. We can get the same result from the UV-vis light photodegradation of MoS$_2$@SnO$_2$ composites.

After the separation of the electrons and holes, the surface area by themselves. When the SnO$_2$ nanoparticles are growing on the surface of MoS$_2$ to form the composite, the surface area of the MoS$_2$@SnO$_2$ nanoflowers will be much larger than that of MoS$_2$ nanoflowers. We can get the same result from the result of Fig.2 and the enlarged specific surface area is highly advantageous for photocatalytic activity.

Besides, the enhanced photodegradation activities in MoS$_2$@SnO$_2$ hetero-nanoflowers may be also attributed to the synergetic effect and specific charge-transfer kinetics. For MB can only be catalyzed by MoS$_2$ in visible light because the energy gap of MoS$_2$ is relatively narrow and the recombination rate for the excited electron-hole pairs is too fast, conducting a low efficiency of photodegradation. However, the formation of the MoS$_2$@SnO$_2$ structure formed a p-n junction, which will result in the MoS$_2$ and SnO$_2$ having a same Fermi energy level at the interface. Thus a staggered band offset and a built-in internal electric field was formed near the interface as shown in Fig. 6d. The positive and negative charges regions lead to the formation of the internal electric field which promoted the separation of photogenerated electrons and holes in the composite. When the MoS$_2$@SnO$_2$ nanoflowers were irradiated by UV-vis light, electrons of MoS$_2$ and SnO$_2$ were excited by visible and ultraviolet light, respectively. Therefore the photocatalytic abilities can be elevated by more photogenerated carrier pairs. Because the conduction band and the valence band of SnO$_2$ both lie below the energy band of MoS$_2$ in this composite (see in Fig. 6d), the excited electrons can easily cross the interface and transfer to the conductive band of SnO$_2$ nanoparticles, likewise the holes transfer to the valance band of MoS$_2$. Therefore, the mitigation in electron and hole pairs' recombination benefits from the photogenerated electrons and holes, which are separated efficiently at the interface, and photocatalytic abilities can thus be improved eventually.

After the separation of the electrons and holes, the surface hydroxyl groups (or H$_2$O) capture the holes (h$^+$) at the catalyst surface, generating OH$^-$ radicals. Water react with superoxide radicals (O$_2^-$) which come from the reaction between dissolved oxygen molecules (O$_2$) and conduction band electrons (e$^-$), to yield hydroperoxyl radicals (HO$_2^-$). Then, oxydol (H$_2$O$_2$) and hydroxyl radicals (OH$^-$), which are powerful oxidizing agents to decompose the organic dye, can be produced. These chemical reactions can be written as:

\[
\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^{-} \\
\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^-
\]

\[
\text{O}_2^\cdot + \text{H}_2\text{O} \rightarrow \text{HO}_2^\cdot + \text{OH}^- \\
\text{HO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- \\
\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{OH}^\cdot + \text{OH}^{-}
\]

5. Field emission studies

Field emission properties of the as-prepared samples were measured by the method described in the experimental section. The field emission properties of MoS$_2$ are far less reported than those of semiconductor nano-materials, such as ZnO, Cu$_2$S and MWNT, etc., not to mention MoS$_2$@SnO$_2$ composites. Because the composite have numerous sharp edges of MoS$_2$ and large proportion of nano-prorusions, the field emission will be greatly improved. So we therefore studied the field emission properties of both the MoS$_2$ nanoflower and MoS$_2$@SnO$_2$ hetero-nanoflower. Fig. 7a shows the characteristic emission current density versus applied electric field for several bias voltage sweeps. We obtain the J-E curves which can indicate our samples have a good repeating ability of the emission process. The turn-on field (defined as the field which is required to produce a current density of 1μA cm$^{-2}$) and threshold fields (defined as the field where the current density reaches 0.1mA cm$^{-2}$) for the MoS$_2$ nanoflowers are about 4.2 and 6.2 Vμm$^{-1}$, respectively. For the MoS$_2$@SnO$_2$ hetero-nanoflowers, these field properties are about 3.4 and 5.2 Vμm$^{-1}$. It is shown that the field emission property for the MoS$_2$@SnO$_2$ nanoflowers hybrid emitters has a distinct improvement comparing with that of the MoS$_2$ nanoflowers.

The Fowler-Nordheim (F-N) plots corresponding to the date in Fig. 7a are shown in Fig. 7b. It is interesting that the F-N plots of both of these two samples are in straight lines, which indicates that the emitting electrons are mainly originated from barrier tunneling electrons excited by the electric field. The field enhancement factor can be calculated from the slope of the F-N plot by employing the F-N equation:

\[
\ln(J/E^2) = (1/\beta)\ln(\phi) + \ln(\beta J^3/\phi)
\]

where $\beta$ is the field enhancement factor, $\phi$ is the emitter material’ work function, J is the emission current intensity and E is the applied electric field. The A and B are constants with the values of 1.56 × 10$^{-10}$ A V$^{-2}$ eV$^{-1}$ and 6.83 × 10$^3$ eV$^{3/2}$ V μm$^{-1}$, respectively. The slope has an inverse ratio to the field enhancement factor $\beta$, which is given by

\[
\beta_{\text{slope}} = \frac{\beta J^3}{\phi}
\]

According to early research, the work functions of MoS$_2$ and SnO$_2$ are 5.96 eV and 4.5 eV. From the slopes of F-N plots, the field enhancement factor $\beta_{\text{slope}}$ (for MoS$_2$ nanoflowers) and $\beta_{\text{C}}$ (for
MoS$_2$@SnO$_2$ composites) are estimated to be 2098 and 2814. Obviously, $\beta_\text{MoS}_2$ is much larger than $\beta_{\text{MoS}_2@\text{SnO}_2}$ from the results above. The evident difference in $\beta$ may be attributed to a large proportion of free open thin edges and a good deal of nano-protrusions on the composites.

Field emission stability for MoS$_2$ and MoS$_2@$SnO$_2$ hybrid emitters is shown in Fig. 7c, which is represented by plotting the emission current density versus a function of time with original emission current density of 500 $\mu$A cm$^{-2}$. For both field emission sources, no obvious degradation of current density was observed during 240 min. As revealed in Fig. 7c, the emission current fluctuation of MoS$_2@$SnO$_2$ composites was with $\pm4\%$ which exhibits a better emission stability than that of MoS$_2$ nanoflowers was $\pm7\%$. It could be attributed to the fact that SnO$_2$ has excellent chemical stability and can protect the emitter from ion bombardment during operation. From the inset of Fig. 7c, field emission images of the MoS$_2$ (sample I in the inset) and MoS$_2@$SnO$_2$ nanoflower hybrid emitter (sample II in the inset) which were operated at an electric field of 6.5 V $\mu$m$^{-1}$ are shown to us. The emission spot density for the MoS$_2@$SnO$_2$ nanoflower hybrid emitters (the ESD could be estimated at about 10$^3$ cm$^{-2}$) are higher than that of the MoS$_2$ emitters (the ESD could be estimated at about 10$^2$ cm$^{-2}$) apparently. Meanwhile, the light spots on the fluorescent screen became more uniform and denser.

Large number of SnO$_2$ nanoparticles, which serve as emitters on the surface of the MoS$_2$, may be the reason of the improvement of the light emitting quality.

The schematic energy band diagram of the MoS$_2$-SnO$_2$ heterojunction under an applied voltage is shown in Fig. 7d. The MoS$_2$-SnO$_2$ heterojunction helps in the separation of the electron-hole pairs. Because the MoS$_2$ and SnO$_2$ have different work functions, when they come into contact, there is a formation of a p-n heterojunction at their interface. In order to achieve thermal equilibrium in this junction with different work functions, electrons will flow from MoS$_2$ to SnO$_2$ nanoparticles and gather on the surface of the SnO$_2$ nanoparticles, then emit to a vacuum. On the other hand, the MoS$_2@$SnO$_2$ hetero-nanoflower has more nano-protrusions because the petals are covered with massive SnO$_2$ nanoparticles, it will have relatively more field emission points than the MoS$_2$ nanoflower. Thus, the enhancement of the MoS$_2@$SnO$_2$ hetero-nanoflower is stronger.

### 6. Conclusion

In summary, novel MoS$_2@$SnO$_2$ hetero-nanoflowers were successfully synthesized by a facile two-step hydrothermal method. After the initial growth of MoS$_2$ nanoflowers, SnO$_2$ was synthesized directly on the as-prepared MoS$_2$ followed by a vacuum drying process. The UV-vis photocatalytic properties and field emission of both samples were measured and compared. It is demonstrated that coupled MoS$_2@$SnO$_2$ photocatalysts was obviously more active than MoS$_2$ through a photocatalytic degradation of methylene blue. Meanwhile by using the MoS$_2@$SnO$_2$ hybrid nanostructure, a more efficient field emission performance was obtained with a low turn-on and threshold field, high emission spot density and good stability. The enhanced properties contributed to the increased specific surface area, nano-heterojunctions between MoS$_2$ and SnO$_2$ and more field emission points in the MoS$_2@$SnO$_2$ composite. Research shown here offers a promising candidate for the practical applications such as high efficiency sunlight photocatalysts and field emission based flat panel displays.

### Acknowledgments

The authors acknowledge financial support from the NSF of China (Grant Nos. 61204018, 61274014), Innovation Research Project of Shanghai Education Commission (Grant No. 13zz033), Education Committee of Jiangsu Province (Grant No. 12KJD510011), and Project of Key Laboratory of Polar Materials and Devices (Grant No. KFKT2014003).

### Notes and references