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.
Keplerate-type Polyoxometalate/Semiconductor Composite Electrode with Light-enhanced Conductivity towards High Efficient Photoelectronic Devices

Shasha Xu,†‡ Yanhua Wang,†‡ Yue Zhao,§ Weilin Chen,∥ Jiabo Wang,∥ Lifei He,∥ Zhongmin Su,∥ Enbo Wang∥‡ and Zhenhui Kang*∥‡

Metal oxide semiconductor (MOS) photoelectrodes hold great promise for new energy and environment applications, from water splitting to photovoltaic devices. Here, we show an efficient polyoxometalate assistance strategy for the design and fabrication of MOS composite photoelectrode with light enhanced conductivity. Four type MOS based photoelectrodes were fabricated by a simple wet chemistry method through bonding TiO$_2$, SnO, WO$_3$, ZnO with keplerate-type polyoxometalate $\{(\text{NH}_4)_2\text{Mo}_6\text{O}_{18}\}^{2+}$, respectively. In these photoelectrodes, $\{(\text{Mo}_{132})\}$ may act as photo-induced electron acceptor/donor to accelerate electron transfer and then improve their conductivity efficiently. We further demonstrated that the 5%$\{(\text{Mo}_{132})\}/\text{TiO}_2$ modified photoanode, in dye-sensitized solar cells (DSSCs), exhibits the power conversion efficiency (PCE) of 7.94% (31% improvement compared with the TiO$_2$-based cell (6.06%).

Introduction

The metal oxide semiconductor (MOS; i.e., TiO$_2$, ZnO and WO$_3$) electrodes, with the characteristic of photoelectrical response, hold great promise for the new energy and photovoltaic devices application, such as, water photoelectrocatalysis, light emission, dye- and quantum-dots-sensitized solar cells, etc. Generally, for photovoltaic devices application, a good conductivity (and/or photovoltaic) and visible light induced photoelectrical response of these MOS photoelectrodes will enhance their performance and usable capacity greatly. Recent progress has been achieved in the development of MOS based photoelectrodes for high performance photovoltaic devices. For examples, using the electron acceptor to transfer the electrons quickly from the conduction band (CB) of MOS to external circuit, reducing the electron recombination and enhancing the overall power conversion efficiency (PCE). Meanwhile, the interfacial electron transfer in nanosized materials also varies with the size and the morphology of the materials; and then, various nanostructured semiconductors have been designed with short charge diffusion length, high crystallinity and more charge separation sites, but less defects have been fabricated. Moreover, the formation of a semiconductor hetero-junction is also extensively applied to improve the charge separation and transformation. However, many MOS photoelectrodes (i.e., TiO$_2$ and WO$_3$) still suffer from the poor conductivity and low PCE, which are greatly limited by the low electron diffusion coefficient and the high interfacial electron-hole recombination.

Polyoxometalate (POM), as a nanosized multi-functional species, should be an ideal candidate for photovoltaic application. Our previous studies have shown that POM, in MOS based solar photovoltaic system, can act as the electron acceptor or the electron donor to raise the PCE. Motivated by the strong photoelectric activities of POM, we further expect that combining a suitable POM species with MOS as a way to construct MOS composite photoelectrode with light enhanced conductivity for high performance photovoltaic devices. Achim Müller, the famous scientist, has made outstanding contributions in the high-nuclear clusters field.

In that POM family, keplerate-type species, $\{(\text{NH}_4)_{12}\text{Mo}_{27}\text{O}_{90}\text{O}_{12}(\text{H}_2\text{O})_{27}\}$ $\{(\text{Mo}_{132})\}$ clusters capture our attentions as the photo-induced electron acceptor or electron donor to enhance the conductivity of MOS photoelectrodes owing to its strong absorption in visible light, high stability and unique photoelectric properties. Here, we show a general and efficient POM assistance strategy for the design and fabrication of MOS composite photoelectrodes with light enhanced conductivity. Four kinds of MOS film electrodes.
were fabricated by combining (Mo132) with MOS, denoted as (Mo132)/MOS (TiO2, ZnO, WO3, and SnO2). In these composite photoelectrodes, (Mo132) clusters act as photo-induced electron acceptor/donor to accelerate electron transfer, improve the electron lifetime and retard the recombination, and then lead to the photo-enhanced conductivity. Further, (Mo132)/TiO2 composite photoelectrodes were introduced into the DSSCs as the photoanode. The 5%-Mo132/TiO2 photoanode exhibits the PCE of 7.94%, increased by 31% compared with the TiO2-based cell (PCE, 6.06%).

Results and discussion

Properties of (Mo132)

(Mo132), a nanoball reported by Achim Müller in 1998, has a fascinating and special structure with more than 500 atoms and the highest Euclidean symmetry.30-32 The anion of (Mo132) is a spherical icosahedral cluster (a nanoball), which is composed of 12 (Mo11) fragments with a central bipyramidal (MoO5) unit to form a cage structure (see Fig. S1†). About (Mo132), most previous reports mainly focused on its structure and basic catalytic properties.30 Here, some basic electrochemical and photoelectric properties of (Mo132) were further investigated in our experiments. Scanning electron microscopy (SEM) image (Fig. 1a) and transmission electron microscopy (TEM) profile (upper inset in Fig. 1a) of the prepared (Mo132) display that (Mo132) nanoballs can be self-assembled to be the aggregates with the size ranging between 1 and 2.5 μm. Energy dispersive spectrometry (EDS) further demonstrates the existence of Mo, C and O in the (Mo132) aggregates (down inset in Fig. 1a). The UV-vis absorption of (Mo132) exhibits a broad optical absorption band nearly covering the whole of UV and visible regions (Fig. 1b), which is beneficial for solar energy harvesting. The UV light absorption is attributed to the charge transfer from oxygen to metal and the visible absorption is due to Mo d-d transitions and Mo5- Mo6 intervalence charge transfer transition in the (Mo132) framework.33 The electron energy levels of (Mo132) were also studied by the cyclic voltammetry (CV), solid diffuse reflection method, as well as the ultraviolet photoemission spectroscopy (UPS) techniques. The lowest unoccupied molecular orbital (LUMO) energy level of POM is formally a combination of d orbitals centering on the metal atoms, which could be estimated from the first reduction applied potential of the CV.34 It can be confirmed from Fig. 1c that the LUMO level of (Mo132) corresponds to -0.52 V vs Ag/AgCl, which is equal to -0.33 V vs NHE and -4.17 eV vs vacuum. The band gap energy (Eg) of (Mo132) was acquired from the diffuse reflectance UV-vis spectrum. Fig. 1d reveals the plot of K-M function F against energy E of (Mo132). The Eg of (Mo132) was estimated to be 1.61 eV by measuring the x-axis intercept of an extrapolated line from the linear regime of the curve.35 The UPS measurement of (Mo132) was carried out to gain more insight into the energy levels. As shown in Fig. 1e, the work function (Wf) of the (Mo132) is calculated to be about 2.84 eV by subtracting the width of the secondary electron cutoff (18.38 eV) from the excitation energy (21.22 eV). The ionization energy (Iu, the onset of the band of occupied orbital) of (Mo132) is about 2.96 eV, and then the highest occupied molecular orbital (HOMO) of (Mo132) with respect to vacuum level can be calculated from -Wf + Iu, which is -5.80 eV.34,35 On the basis of the UPS and UV-vis spectrum results, the LUMO of (Mo132) can be got to be -4.19 eV, which is well agreement with the result gained from the CV test (-4.17 eV vs vacuum). Fig. 1f shows the energy levels of (Mo132), the reported theoretical calculation data of (Mo132),36 and the band structure of common MOSs. It suggests that the energy levels (HOMO/LUMO) of (Mo132) are in a medium position of band structure (VB/CB) of common MOss, which satisfy the necessary condition for (Mo132) improving the conductivity of (Mo132)/MOS composite electrodes by the electron acceptation or donation. In addition, the TG curve and IR spectra of (Mo132) (Fig. S2†) demonstrate that the skeleton structures of (Mo132) remain stable below 210°C, indicating a good stability of (Mo132)/MOS composite during the fabrication.
(MoO$_{123}$)/TiO$_2$ Composite Photoelectrodes

In the first set of experiments, we studied the photo-electronic chemical properties of (MoO$_{123}$)/MOS composite photoelectrodes. Briefly, the TiO$_2$ paste prepared by mixing (MoO$_{123}$) and the calcined TiO$_2$ with the mass percentage of 5% (5% (MoO$_{123}$); 95% TiO$_2$) was fabricated to be the composite photoelectrode (5% (MoO$_{123}$)/TiO$_2$ photoelectrode), and the pure TiO$_2$ for comparison. The SEM image (Fig. 2a) of 5% (MoO$_{123}$)/TiO$_2$ photoelectrode indicates that it consists of spherical and granular particles with size in range from 20 to 100 nm. Furthermore, the EDS mapping (Fig. 2b) demonstrates the existence of Ti, Mo, O, and C which confirms that (MoO$_{123}$) and TiO$_2$ are uniformly distributed in the composite photoelectrodes. X-ray diffraction (XRD) was carried out to monitor the TiO$_2$ phase changes in the 5% (MoO$_{123}$)/TiO$_2$ composite photoelectrodes. The characteristic peaks of TiO$_2$ can be discovered from the XRD patterns of calcined TiO$_2$ and 5% (MoO$_{123}$)/TiO$_2$ (Fig. 2c), which are in agreement with those of anatase TiO$_2$ (JCPDS, 21-1272), indicating that the crystal shape of TiO$_2$ was not changed after the modification with (MoO$_{123}$). The diffraction peaks for (MoO$_{123}$) are not effectively detected from the XRD patterns of 5% (MoO$_{123}$)/TiO$_2$ due to the lower content of (MoO$_{123}$) or its amorphous state. The X-ray photoelectron spectrum (XPS) of TiO$_2$, (MoO$_{123}$) and 5% (MoO$_{123}$)/TiO$_2$ composite was employed to further analyze the surface composition and chemical environment of Ti and Mo atoms. As shown in Fig. S3† and Fig. 2d, the XPS spectra of 5% (MoO$_{123}$)/TiO$_2$ clearly reveals the presence of O (1s), Ti (2p), C(1s) and Mo (3d). For pure TiO$_2$, the energy regions of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ are located at 457.8 and 463.4 eV. While, both of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ energy regions shift towards the lower binding energy and locate at 457.4 and 463.2 eV for 5% (MoO$_{123}$)/TiO$_2$ composite.\(^{39,40}\) Fig. 2e clearly illustrates that the characteristic Mo3d doublet is composed of the 3d$_{5/2}$ and 3d$_{3/2}$ levels. In the lower group curves of the XPS of (MoO$_{123}$), the peaks located at 231.9 eV and 235.1 eV are assigned as Mo$^{5+}$, while the peaks at 234.1 eV and 231.1 eV are attributed to Mo$^{4+}$.\(^{41,42}\) Furthermore, the XPS peaks of Mo in 5% (MoO$_{123}$)/TiO$_2$ also shift towards a lower binding energy compared with the pure (MoO$_{123}$). All these XPS results indicate that the (MoO$_{123}$) has indeed been combined with TiO$_2$ in the 5% (MoO$_{123}$)/TiO$_2$ composite, but not the physical mixture of (MoO$_{123}$) and TiO$_2$. Fig. 2f represents the powder UV-vis absorption of TiO$_2$, 5% (MoO$_{123}$)/TiO$_2$ and pure (MoO$_{123}$). Pure TiO$_2$ only absorbs UV light (<387 nm) without any absorption in the visible and infrared regions. While the strong UV and visible absorption could be observed for 5% (MoO$_{123}$)/TiO$_2$ composite.

The photocurrent response and electrochemical impedance spectroscopy (EIS) are the valuable measurements to study the conductivity of the surface-modified electrodes, in particular regarding the electron-transfer characteristics.\(^{43}\) The photocurrent transient experiments have been carried out under the simulated solar illumination for the 5% (MoO$_{123}$)/TiO$_2$ and the TiO$_2$ film electrodes to investigate the conductivity of the electrodes with the introduction of (MoO$_{123}$). Fig. 3a presents the photocurrent changes of the film electrodes when the irradiation is switched on and off. The photocurrent density of pure TiO$_2$ is approximately 0.015 mA·cm$^{-2}$, and this weak photocurrent response may be due to its fast electron-hole recombination and weak absorption in the visible area. Strikingly, the photocurrent response intensity of the 5% (MoO$_{123}$)/TiO$_2$ (about 0.059 mA·cm$^{-2}$) is four times higher than that of pure TiO$_2$. Furthermore, the photocurrent at different irradiance is shown in Fig. 3b, the 5% (MoO$_{123}$)/TiO$_2$ film electrode shows a higher photocurrent response for different light intensities compared to the pure TiO$_2$ which also testifies that the conductivity of TiO$_2$ is virtually enhanced by the incorporation of (MoO$_{123}$). The reason may be that (MoO$_{123}$) can compensate the weak absorption of TiO$_2$ in the visible region.

The investigations of EIS presented in the forms of a typical Nyquist plots are to understand the difference in the electronic properties of 5% (MoO$_{123}$)/TiO$_2$ and TiO$_2$ film electrodes (Fig. 3c). The semicircle diameter at high frequency corresponds to the charge-transfer resistance ($R_{ct}$), and a straight line at low frequency attributes to diffusion process, which represents the so-called Warburg impedance.\(^{44}\) The analog circuit diagram of equivalent circuit used to fit the impedance measurement has been illustrated in Fig. S4†. The diameter for arc radius of the 5% (MoO$_{123}$)/TiO$_2$ electrode is smaller than the TiO$_2$ electrode, which indicates that the conductivity is enhanced by the modification of TiO$_2$ with...
(Mo$_{132}$) may enhance the injection and transport of electrons, and then retard the electrons recombination in the TiO$_2$ film electrode. The surface photovoltage spectrum (SPS) and the photoluminescence (PL) were also further utilized to survey the charge transfer process at the interface of TiO$_2$ and (Mo$_{132}$) in the electrode. The SPS of pure TiO$_2$ suggests a peak around 360 nm (Fig. 3d), which may be ascribed to the charge separation upon only UV light excitation. The 5% (Mo$_{132}$)/TiO$_2$ composite reveals higher photovoltage in the visible region than pure TiO$_2$ (Fig. 3d), which demonstrates that the modification of (Mo$_{132}$) could broaden the optical response range of TiO$_2$. While the SPS response of 5% (Mo$_{132}$)/TiO$_2$ (9.72 mV) displays lower photovoltage in the UV region than pure TiO$_2$ (20.82 mV), which may be attributed to the photogenerated charge transfer between (Mo$_{132}$) and TiO$_2$ particles. The electrons accepted by the (Mo$_{132}$) will recombine with the holes of TiO$_2$, leading to the lower photovoltage and enhancing the conductivity of the TiO$_2$. In addition, the change of PL intensities can reveal the photogenerated charge-carrier recombination rate in semiconductors. The PL of pure TiO$_2$ appears a fluorescence emission band at 500 nm upon the excitation at 390 nm (Fig. 3e), which is efficiently quenched (upon the same excitation wavelength) with the introduction of (Mo$_{132}$) to TiO$_2$ demonstrating that the photo-induced electrons may transfer from TiO$_2$ to (Mo$_{132}$) clusters. It can be concluded that the charge recombination is suppressed by the incorporated (Mo$_{132}$). The LUMO of (Mo$_{132}$) is lower than the CB of TiO$_2$, so (Mo$_{132}$) can be used as the electron acceptor to accept the electrons from TiO$_2$, which is a favorable exothermic process (Fig. 3f). The photogenerated electrons in the excited state can be extracted and transferred to (Mo$_{132}$). So (Mo$_{132}$) may increase the mobility of electrons in the TiO$_2$ and enhance the conductivity of the electrode.

(Mo$_{132}$/MOS (ZnO, WO$_3$, SnO$_2$) Photoelectrodes

In (Mo$_{132}$/TiO$_2$ system, we show that (Mo$_{132}$) acts as the photo-induced electron acceptor to accelerate electron transfer and then improve their conductivity efficiently. Here the question is whether (Mo$_{132}$) is a general functional species for the high performance (Mo$_{132}$/MOS composite photoelectrodes or not. Similar to TiO$_2$, ZnO is also a wide band gap (about 3.20 eV) MOS. Similar experiments of (Mo$_{132}$) modified ZnO film electrodes (Fig. S5† and S6†) with a weight ratio of 5% were also studied under simulated solar illumination. In Fig. S6a†, the investigation of EIS also proves that (Mo$_{132}$) may act as the electron acceptor to inhibit the recombination of electron-hole, thus improving the conductivity of the 5% (Mo$_{132}$/ZnO) film electrode. WO$_3$ is a MOS material (band gap about 2.70 eV) with the CB edge (−5.24 eV vs vacuum) lower than the LUMO of (Mo$_{132}$). The XRD patterns of WO$_3$ film (Fig. S7†) indicate that it is the monoclinic phase. In the following experiments, the (Mo$_{132}$/WO$_3$) composite photoelectrode was fabricated by combing (Mo$_{132}$) and WO$_3$ nanocrystals with a weight ratio of 5%. The SEM of WO$_3$ and 5% (Mo$_{132}$/WO$_3$) film electrodes

![Image](image_url)
illustrate the morphology of film surface. As shown in Fig. S8a†, the fairly uniform-sized WO$_3$ nanocrystals are distributed well on the surface. Also, the similar morphology of the 5%{Mo$_{132}$}/WO$_3$ film is shown in Fig. S8b†, suggesting that the {Mo$_{132}$} did not influence the morphology of WO$_3$. The photocurrent response and EIS experiments of 5%{Mo$_{132}$}/WO$_3$ and pure WO$_3$ film electrodes have been carried out to study the conductivity of the {Mo$_{132}$}-modified WO$_3$ film electrodes. It can be observed that the photocurrent density (approximately 0.16 mA·cm$^{-2}$) of the 5%{Mo$_{132}$}/WO$_3$ film electrode increases by about 0.02 mA·cm$^{-2}$ than that of pure WO$_3$ (0.14 mA·cm$^{-2}$) (Fig. 4a). In addition, the EIS investigations (Fig. 4b) indicate that the semicircle diameter at high frequency of the 5%{Mo$_{132}$}/WO$_3$ film electrode is smaller than that of the WO$_3$ electrode, which reveals that the charge-transfer resistance on the electrode surface is decreased with the introduction of {Mo$_{132}$}. The PL experiment was also carried out to understand the efficiency of charge trapping and transfer in the semiconductor. The PL signal intensity at 480 nm for the 5%{Mo$_{132}$}/SnO$_2$ film electrode is increased by about 0.01 mA·cm$^{-2}$ than that of pure SnO$_2$ (0.14 mA·cm$^{-2}$) (Fig. S9†). The scheme of the photo-induced electron transfer (Fig. S10a†) depicts the EIS measurements with 5%{Mo$_{132}$} film electrodes. The power conversion efficiency ($\eta$) of 711 mV and a fill factor ($\eta_{\text{FF}}$) of 16.78 mA·cm$^{-2}$, an open circuit voltage ($V_{\text{oc}}$) of 114.5 mV and a fill factor (FF) of 0.66, resulting in the $\eta$ of 6.06% (see Table 1). It indicates an overall PCE improvement up to 31% compared with the TiO$_2$-based cell (6.06%). The increase of $J_{\text{sc}}$ may be due to more efficient electronic injection, smoother transfer and high efficient collection. The improvement of $V_{\text{oc}}$ may be ascribed to the reduced charge recombination. Further, 5%{Mo$_{132}$}/TiO$_2$ can also decrease the onset of dark current to different extent (Fig. 6c), which may be attributed to the contribution of {Mo$_{132}$} preventing the electrons flowing back to the electrolyte or dyes from {Mo$_{132}$}/TiO$_2$ photoelectrode. Fig. 6d depicts the EIS measurements with 5%{Mo$_{132}$}/TiO$_2$.

\{Mo$_{132}$\}/TiO$_2$ Photoelectrodes Based DSSCs

We further demonstrated the application of 5%{Mo$_{132}$}/TiO$_2$ photoanode in dye-sensitized solar cells (DSSCs). Fig. 6a presents the scheme of DSSC based on 5%{Mo$_{132}$}/TiO$_2$, which consists of a film of dye (N719)-sensitized {Mo$_{132}$}/TiO$_2$ photoelectrode, a Pt counter electrode and the electrolyte containing the redox pairs (I$^-$/I$_3$). Fig. 6b presents the UV-vis absorption spectra of {Mo$_{132}$} and N719. Notably, {Mo$_{132}$} has a good absorption in the visible area at 450 nm, which is expected to make up for the visible absorption of dye N719. The performance of the {Mo$_{132}$}/TiO$_2$ DSSCs were investigated under simulated AM 1.5 illumination (at 100 mW·cm$^{-2}$) and in the dark, respectively. The power conversion efficiency ($\eta$) of the {Mo$_{132}$}/TiO$_2$ DSSC has the pronounced enhancement compared to the pure TiO$_2$ DSSC. The {Mo$_{132}$}/TiO$_2$ DSSC exhibits a short circuit current density ($J_{\text{sc}}$) of 16.78 mA·cm$^{-2}$, an open circuit voltage ($V_{\text{oc}}$) of 114.5 mV and a fill factor (FF) of 0.66, resulting in the $\eta$ of 6.06%. The increase of $J_{\text{sc}}$ may be due to more efficient electron injection, smoother transfer and high efficient collection. The improvement of $V_{\text{oc}}$ may be ascribed to the reduced charge recombination. Further, 5%{Mo$_{132}$}/TiO$_2$ can also decrease the onset of dark current to different extent (Fig. 6c), which may be attributed to the contribution of {Mo$_{132}$} preventing the electrons flowing back to the electrolyte or dyes from {Mo$_{132}$}/TiO$_2$ photoelectrode. Fig. 6d depicts the EIS measurements with 5%{Mo$_{132}$}/TiO$_2$. 

\[\text{MO}_x\text{O}_y\text{N}_z\text{S}_m\text{Cl}_n\]
photoanode and the pure TiO₂. The semicircle in high frequency corresponds to \( R_t \), which represents the charge transfer resistance at the counter electrode/electrolyte interface. The second semicircle (\( R_t \)) reflects the electron transport resistance at the photoelectrode/dye/electrolyte interface related to the charge transport/recombination. Here, \( R_t \) is similar since all the cells have the same Pt counter electrode and electrolyte. However, the \( R_t \) of 5\%{Mo\(_{132}\)}/TiO₂ photoanode changes from 4.86 Ω (pure TiO₂) to 6.26 Ω, which indicates that {Mo\(_{132}\)} can retard the charge recombination and result in a smoother and efficient electron transmission in {Mo\(_{132}\)}/TiO₂ photoanode. The bode phase plots are shown in Fig. 6e, the characteristic frequency peak (\( f_{\text{max}} \)) of 5\%{Mo\(_{132}\)}/TiO₂ photoanode at the top of the intermediate frequency arc is 72.20 Hz and the \( f_{\text{max}} \) of TiO₂ is 31.10 Hz, so the calculated electron lifetime (about 2.21 ms) based on the \( f_{\text{max}} \) values, which are coincident with the dark current measurements, demonstrating an improvement on the retardation of carrier recombination. Meanwhile, the electrons recombining can be further evaluated by the open-circuit voltage decay (OCVD), which monitors the decay of \( V_{oc} \) after turning off the illumination in a setting time. As shown in Fig. 6f, it is evident that the DSSC based on 5\%{Mo\(_{132}\)}/TiO₂ photoanode exhibits a slower photovoltage decay rate than that of the pure TiO₂ photoanode, which indicates that the electrons recombining kinetics has been retarded effectively. Further, from the inset of Fig. 6f, we can also conclude that the 5\%{Mo\(_{132}\)}/TiO₂ photoanode has the longer electron lifetime than that of pure TiO₂ photoanode, and will lead to the higher charge collection rate of photogenerated electrons and an improvement in the cell efficiency.

In the next study, a series of (Mo\(_{132}\))/TiO₂ photoanode-based DSSCs were fabricated and their performance are shown in Fig. S11 and S12. The average performance characteristics obtained from the multiple cells are summarized in Table S1, and the corresponding parameters obtained from the EIS are listed in Table S2. The PCE values of the DSSCs have the pronounced enhancement with the increasing of the content of {Mo\(_{132}\)} from 1%, 3% to 5%, compared to the performance of pure TiO₂, and the best performance of DSSC is the percentage of {Mo\(_{132}\)} up to 5%. However, increasing the content of {Mo\(_{132}\)} up to 7%, the \( R_2 \) of 7\%{Mo\(_{132}\)}/TiO₂ photoanode reduces to 5.04 Ω (Fig. S12a† and Table S2), the performance of DSSCs would decline and is close to pure TiO₂. It may be attributed to the aggregation of the {Mo\(_{132}\)} during the paste making process, and then the electrons massively injected into the electrolyte and no longer collected at the anode.

### Experimental

#### Chemicals and Reagents

All chemicals were commercially purchased and used without further purification. (Mo\(_{132}\)) was prepared according to the literature method.

#### Electrodes Preparation

Firstly, TiO₂ powder was sintered at 450 °C for 30 min. Then the TiO₂ paste was prepared according to the literature by mixing {Mo\(_{132}\)} and the calcined TiO₂ with a series mass percentage of 0%, 1%, 3%, 5%, and 7% to fabricate the film electrodes. The FTO glass plates were pretreated by...
immersed into the 40 mM TiCl₄ aqueous solution at 70 °C for 30 min, and washed with water and absolute ethanol. The electrodes were prepared by coating one layer of paste on the FTO glass plates by screen-printing followed by drying for 5 min at 120 °C. Four-layered paste was coated on every FTO glass. Then, the film electrodes were calcined at 210 °C for 30 min. Subsequently, the resulting sintered film electrodes were post-treated in 40 mM TiCl₄ solution for 30 min at 70 °C and calcined in air at 210 °C for 30 min again. In the meantime, (Mo₁₃₂) modified ZnO, WO₃, SnO₂ in a ratio of 5% electrodes were prepared in the same way.

Solar cells fabrication

The obtained TiO₂ film electrodes were immersed in the 0.2 mM N719 absolute ethanol solution for 24 h. The excess unanchored dyes were rinsed off with absolute ethanol and dried with N₂. Platinum was used as counter electrode. A drop of electrolyte solution composed of 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide and 0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile was introduced between the electrodes by the injector.

Characterization Methods

IR spectrum was recorded in the range of 400-4000 cm⁻¹ region on an Alpha Centaurt FT/IR spectrophotometer with KBr pellet. TG analysis was performed on a PerkinElmer TGA7 instrument at a heating rate of 10 °C min⁻¹ from 25 to 600 °C. X-ray powder diffraction data were collected on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 3-90° with a step size of 0.02°. The diffuse reflectivity spectra were collected on SHIMADZU UV-Vis Spectrophotometer UV-2600 in reflectance mode, which were measured from 200 to 800 nm using barium sulfate (BaSO₄) as a standard with 100% reflectance. Ultraviolet photoelectron spectroscopy (UPS) measurement was performed using the He (21.22 eV) excitation. The morphology of the samples was characterized with SEM (FESEM; XL30, FEG, FEI Company) and TEM (HitachiH-7650). Energy dispersive X-ray spectroscopy (EDS) was obtained from FEI Quanta 200F microscope. X-ray photoelectron spectroscopy (XPS) measurement was performed with a hemispherical analyzer Leybold EA 11. The fluorescence spectra were recorded on the FL900/FS920 steady-state fluorescence spectrometer.

Photoelectrochemical measurements

Cyclic voltammogram curve was recorded on a CHI601D Electrochemical Workstation (Shanghai CH Instrument Corp., China), using the composite film assembled FTO glass electrodes as the working electrode, a Pt wire as the counter electrode and the reference was a saturated Ag/AgCl electrode. 0.10 M Na₂SO₄/H₂SO₄ solution with pH=4.00 was used as the supporting electrolyte on the premise of stability of (Mo₁₃₂). Electrochemical impedance spectroscopy (EIS) of the electrodes were measured with an impedance analyzer (Compactstat, IVIUM Tech.) at an open-circuit potential under the condition of simulated solar illumination in 0.10 M KCl solution containing equimolar [Fe(CN)₆]³⁻/⁴⁺ at an ac frequency from 100 kHz to 0.1 Hz. All electrodes were illuminated from the front side using a 300 W Xe lamp equipped with an AM 1.5 G filter (Model 81094, Newport) to simulate the solar spectrum. The photocurrent transient experiments were carried out at a constant bias of 0 V under simulated solar illumination. The illumination area of working electrode was set constant at 0.25 cm². The surface photovoltage spectroscopy (SPS) measurement was carried out on a lab-made instrument, which constitutes a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540) and a photovoltaic cell. The photocurrent-voltage (J-V) characteristics, electrochemical impedance spectroscopy (EIS) measurements of the DSSCs were conducted on an electrochemical workstation, applying a DC bias at open circuit voltage and an AC voltage with the amplitude of 10 mV in dark conditions. Impedance parameters were determined by fitting of the impedance spectra using Z-view software. Open circuit voltage decay (OCVD) of the DSSCs was measured under AM 1.5 simulated solar illumination at 100 mW cm⁻².

Conclusions

We report a general and efficient polyoxometalate assistance strategy for the design and fabrication of POM/MOS composite photoelectrodes with light-enhanced conductivity. Four (Mo₁₃₂)/MOS composite photoelectrodes ((Mo₁₃₂)/TiO₂, ZnO, WO₃, SnO₂) were fabricated and investigated to evaluate the light-enhanced conductivity of these composite photoelectrodes. In (Mo₁₃₂)/MOS composite photoelectrodes, (Mo₁₃₂) acts as photo-induced electron acceptor/donor to accelerate the electron transfer and then improve their conductivity efficiently. Also, the photoresponse property and narrow band gap nature of (Mo₁₃₂) is also helpful for this light-enhanced conductivity process. We further demonstrated that the 5%(Mo₁₃₂)/TiO₂ photoelectrode can be applied in DSSCs as the photoanode. In this system, (Mo₁₃₂) has a good absorption in the visible area at 450 nm, which makes up for the visible absorption of N719. The 5%(Mo₁₃₂)/TiO₂ modified photoanode exhibits the largest electron lifetime (5.12 ms), longer than that of pure TiO₂ (2.21 ms) and a high efficiency up to 7.94%, enhanced by 31% compared with that of pure TiO₂ (6.06%). This work may also provide a new way for getting high performance photoelectrodes in many applications, including solar cells, water splitting devices, photocatalysis and sensors.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21131001), the Open Subject Foundation of Key Laboratory of Polyoxometalate Science of Ministry of Education (No. 130014553), the Science and Technology Research Foundation of the Thirteenth Five Years

Notes and references

We designed and fabricated of POM/MOS composite photoelectrodes with light-enhanced conductivity. \{\text{Mo}_{132}\} clusters act as photo-induced electron acceptor/donor to accelerate electron transfer and then improve their conductivity efficiently. Then the 5\%\{\text{Mo}_{132}\}/\text{TiO}_2 composite photoelectrodes as photoanode in DSSCs exhibit the long electron lifetime (5.12 ms) and high PCE efficiency up to 7.94\%, enhanced by 31\% compared with pure \text{TiO}_2 (PCE, 6.06\%) photoelectrodes.