Efficient charge transfer at a homogeneously distributed $(NH_4)_2Mo_3S_{13}$ / WSe_2 heterojunction for solar hydrogen evolution

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Supplementary information



Supplementary Figure 1. (a) SEM image of the WSe₂ film with the marked grain boundaries with the lateral sizes of 2-6 μ m. Scale bar is 1 μ m. (b) Optical image of a WSe₂ film coated with ATM (15 cycles). Scale bar is 100 μ m. (c) Optical image of delaminated, rolled ATM flakes. (d) A 30-40 nm thick ATM layer on top of FTO after 11 cycles of spin coating. Scale bar is 200 nm.



Supplementary Figure 2. Photoelectrochemical thinning (functionalization) of the ATM-WSe₂ film (300 nm) on a TiN:O back contact in 0.5 M H_2SO_4 upon chopped illumination (AM 1.5) with increasing IV-cycling number (a) with Pt counter electrode 8 cycles, (b) with carbon (C) counter electrode 8 cycles and further 2 cycles with Pt counter electrode. The inset shows the photocurrent onset potential of about 0.7 V. (c) Optical absorption spectra of ATM layers with different thicknesses on FTO. Tauc plots for (d) a 690 nm thick ATM layer on FTO and (e) a 350 nm thick WSe₂ layer on quartz glass.

Surface photovoltage of WSe₂, Pt-WSe₂ and ATM-WSe₂ on TiN:O back contact

Supplementary Fig. 3 shows the in-phase and phase-shifted by 90° SPV spectra. As remark, the in-phase signals or the phase-shifted by 90° signals are very fast or slow, respectively, with respect to the modulation period. The SPV signals of the TiN:O substrate are of the order of the noise and can be neglected, i.e. the substrate was not photoactive. The in-phase signals were negative, i.e. photogenerated electrons were separated preferentially towards the external surface. The in-phase signals were much larger for the WSe₂/TiN:O and Pt-WSe₂/TiN:O samples, i.e. fast charge separation and recombination dominated the relaxation of the SPV signals. In contrast, the phase-shifted by 90° signals were of the same order as the in-phase signals for the ATM-WSe₂/TiN:O sample, i.e. the ATM surface layer led to a strong retardation of charge separation and relaxation of SPV signals. The phase-shifted by 90° signals even increased with increasing photon energy and reached the maximum at about 2.7 eV whereas the in-phase signals reached the maximum at about 1.6 eV (excitonic A transition) and decreased with further increasing photon energy for ATM-WSe₂/TiN:O. Therefore, the disordered ATM layer contributed to photogeneration and caused a slow response. At photon energies below the excitonic A transition, the phase-shifted by 90° signals were positive (about 2 µV) for Pt-WSe₂/TiN:O and WSe₂/TiN:O but negative for ATM-WSe₂/TiN:O. This difference can be interpreted by injection of electrons photogenerated at the ATM/WSe₂ interface into WSe₂.

The maximum in-phase signals of ATM-WSe₂/TiN:O were about 2.7 or 3.1 times larger than for WSe₂/TiN:O or Pt-WSe₂/TiN:O, respectively. The in-phase signals at photon energies below the excitonic A transition were much smaller than the maximum in-phase signals. Therefore, photogeneration from defect states did not contribute to fast charge separation and relaxation processes.



Supplementary Figure 3. In-phase (a) and phase-shifted by 90° (b) modulated surface photovoltage spectra of the TiN:O substrate, ATM-WSe₂/TiN:O, WSe₂/TiN:O and Pt-WSe₂/TiN:O (red lines and circles, black lines and squares, blue lines and triangles and green lines and stars, respectively).



Supplementary Figure 4. (a) Evaluation of the valence band edge position of the pristine WSe₂, Pt-WSe₂, ATM-WSe₂ and Pt-ATM-WSe₂ films by XPS. Linear lines show the valence edge positions. (b) Band alignment for the ATM-WSe₂ film. (c) Ultraviolet photoelectron spectroscopy (UPS) measurement of WSe₂ via a He I photon source with the energy E = 21.21 eV. Here, the work function (WF) of WSe₂, secondary electron cutoff (*SEC*), E_f - Fermi level (1.07 eV).



Supplementary Figure 5. Chopped linear scanning voltagram (LSV) curves for (a) ATM and WSe₂ films and (b) the LSV curve exhibiting the highest photocurrent density of 5.6 mA cm⁻² at 0 V vs. RHE for an ATM coated 350 nm thick WSe₂ film on a TiN:O back contact in 0.5 M H₂SO₄ upon illumination (AM 1.5).



Supplementary Figure 6. Chopped photocurrent density versus time (light/dark times were 10 sec each) of a 320 nm thick ATM/WSe₂ photocathode at 0 V_{RHE} in 0.5 M H₂SO₄, illumination AM 1.5.



Supplementary Figure 7. XPS spectra of pristine and tested (during 2 hours upon illumination) ATM-WSe₂ films for (a) molybdenum 3d regions. (b) sulfur 2p region showing the presence of $2p_{3/2}$ and $2p_{1/2}$ doublets: first doublet (pink) corresponds to terminal ligands S_2^{2-} and apical ligand S^{2-} and second doublet (violet) arises from the bridging ligands S_2^{2-} of [Mo₃S₁₃] ²⁻ clusters. The S/Mo elemental ratio calculated from the integrated peak area of XPS spectra is 3.75.



Supplementary Figure 8. EDX mapping of the ATM-WSe₂ film surface coated photochemically by Pt nanoislands during 540 sec at open circuit potential in 0.1 M HCl solution, illumination AM 1.5.



Supplementary Figure 9. Chopped linear scanning voltagram (LSV) curves for Pt/ATM, ATM/WSe₂ and Pt/ATM/WSe₂ on a TiN:O back contact in 0.5 M H_2SO_4 upon illumination (1.5AM). The Pt was photodeposited at open circuit potential under light exposure (AM 1.5) during 360 sec.

Functionalization of the ATM/WSe₂ photocathodes

The photocurrent density for ATM/WSe₂ photocathode increases with the IV cycling (Supplementary Figure 2a). The brown color of the ATM film becomes more transparent after cycling (etching, it can be seen, when the sample is tilted at a certain angle), approaching the gray color of WSe₂, i.e. the ATM film is slightly dissolved. The XPS data in Fig.2a,b show that the W and Se peaks appear weakly after IV cycling (functionalization), which means that the optimum ATM thickness is 10 nm or below according to XPS probe depth. The circular area (1) shows the uncoated WSe₂ sample; the circular area (2) shows the ATM/WSe₂ tested for 7 cycles which becomes more transparent; the circular area (3) shows after stability test during 115 min in sulfuric acid, which depicts the obvious etching of the ATM from the WSe₂ surface.



Supplementary Figure 10. Image of the ATM/WSe₂/TiN:O photocathode tested (1) uncoated region of WSe₂, (2) tested at 7 cycles and (3) after 115 min of chopped light testing at 0 V vs. RHE.