Fabrication of layered (CdS-Mn/MoS₂/CdTe)-promoted TiO₂ nanotube arrays with superior photocatalytic properties

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Abstract: A novel (CdS-Mn/MoS₂/CdTe)-sensitized TiO₂ nanotube arrays (NTAs) photoelectrode has been prepared by electrodeposition, successive ionic layer adsorption and reaction (SILAR) coupled with hydrothermal method. When a ZnS layer was added on the top of CdS-Mn/MoS₂/CdTe/TiO₂, a notable red-shift and high absorption was observed in the visible light region. The photocurrent density (mA/cm²) systematically increases from TiO₂ NTAs (0.43), CdTe/TiO₂ (1.09), MoS₂/CdTe/TiO₂ (1.80), CdS-Mn/MoS₂/CdTe/TiO₂ (2.40), to ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ (3.41) under visible light irradiation, due to the type-II semiconductor heterostructures comprising multiple components with a staggered band offset. Such a heterostructure possesses an enhanced photocatalytic performance towards degradation of organic contaminant, e.g. P-Nitrophenol (PNP) and Rhodamine B (RhB).

Keywords: Stepwise level; MoS₂ nanosheet; TiO₂ NTAs; Hydrothermal; SILAR; Electrodeposition; Photocatalytic.

1. Introduction

Recently, MoS₂ are being investigated with great attention [1, 2], due to its large intrinsic band gap, high carrier mobility and specific surface areas, exotic electronic properties, etc. It have shown great promise for sensors, transistors, catalysis, photodetectors, lithium ion batteries, and energy storage applications. It has been reported that the band-gap of MoS₂ can be tuned from an indirect band-gap (1.2 eV for bulk form) to a direct bandgap (1.9 eV for monolayer) with the decrease in layer thickness [1]. CdTe is a direct band gap semiconductor with $E_g = 1.4672$ eV (~ 1.5 eV), which is well matched to the solar spectrum for photovoltaic performance [3]. Using Mn-CdS quantum dots (QDs) in solar cells has been proven to be a powerful strategy to extend the lifetime of charge carriers to boost the efficiency. The Mn-doped-CdS shows a red-shift in the absorption compared with the undoped CdS, which corresponds to a bandgap of 2.4 eV [4]. As is reported, developing TiO₂-based photocatalysts is a clean, economical and environment friendly approach, whether for the decomposition of organic pollutants or the water-splitting for hydrogen production using solar energy [5, 6]. However, it is well known that anatase TiO₂ has a band gap of 3.2 eV, which can solely absorb the UV light, accounting for only 4% of the total sunlight, thus greatly limiting its practical applications. It is highly desirable to develop photocatalysts with high catalytic activities under the visible light. To achieve this goal, numerous strategies, including the impurity doping and growth of TiO₂-based heterostructures [7, 8], have been developed. The photocatalytic efficiency of TiO₂-based photocatalysts has been enhanced by broadening their lightharvesting

1 window to the visible range. In addition, various semiconductor nanocrystals
2 heterostructures, such as MoS₂/TiO₂ [9], Ag₂O/TiO₂ [8], CdTe/CdSe [10], MoS₂/WS₂
3 [11], ZnS/CdS [12], CuS/ZnS [13], CdS/MoS₂ [14], MoO₃/MoS₂ [15],
4 P/Ag/Ag₂O/Ag₃PO₄/TiO₂ [16], and (CdS/CdSe/ZnS)-sensitized TiO₂ [17], have been
5 reported. By coupling energy band matching semiconductors structures, the efficient
6 charge separation can be obtained, which leads to the improved photocatalytic activity
7 and efficiency. For example, Zhou et al. [9] reported the synthesis of few-layer MoS₂
8 nanosheet-coated TiO₂ nanobelt heterostructures for enhanced photocatalytic
9 activities. Chuang et al. [10] prepared a CdTe/CdSe core/shell nanoheterostructures
10 for the potential applications in photoelectrochemical cells. Xu et al. [11] reported the
11 fabrication of monolayer MoS₂/WS₂ QDs as efficient electrocatalysts for
12 photoelectrochemical hydrogen generation. Hu et al. [12] prepared ZnS-CdS
13 nanoparticle hybrids with enhanced photoactivity. Zong et al. [14] reported the
14 compound of CdS/MoS₂ with enhanced photoactivity for hydrogen generation under
15 visible light irradiation. Zhu et al. [16] reported the synthesis of
16 P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst with superior photocatalytic activity and
17 stability. Lee et al. [17] reported the fabrication of TiO₂ mesoporous for multilayered
18 semiconductor (CdS/CdSe/ZnS)-sensitized solar cell and the introduction of the ZnS
19 layer as a potential barrier, which has been demonstrated to be an efficient interface
20 treating strategy for performance improvement [18].

21 According to previous reporters, ideal type-II semiconductor heterostructures
22 comprise two components with a staggered band offset [19]. Spatial separation of the

1 electron and hole wave functions within such type-II semiconductor heterostructures
2 can result in a long-lived charge transfer (CT) state that has desirable characteristics for
3 applications such as light emitters, lasers, photocatalysts, and photovoltaic devices [20].
4 J. Cai et al [21] reported the fabrication of CdTe/CdS–TiO₂NTA electrode with a
5 stepwise structure of band-edge levels because of their harmonious bandgaps. To sum
6 up, combining TiO₂ with CdTe, MoS₂, CdS-Mn and ZnS semiconductors could largely
7 improve the photocatalytic activity of the co-sensitized electrode, due to the step-like
8 band edge structure which benefits the separation of electron-hole pairs.

9 To the best of our knowledge, there is no report about the codoping of TiO₂ with
10 CdTe, MoS₂, CdS-Mn and ZnS. It is important to pay attention to this multilayered
11 semiconductor-sensitized TiO₂ with a stepwise structure of band-edge levels. The
12 bandgaps of TiO₂ NTAs, CdS, MoS₂, and CdTe are 3.2, 2.4, 1.9, and 1.5eV,
13 respectively [22-24]. Herein, we developed a novel visible-light-driven
14 ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ photocatalyst by pulse electrodeposition and SILAR
15 processes coupled with hydrothermal method. It was demonstrated that
16 ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ exhibited excellent photocatalytic activity to
17 completely degrade PNP in about 20 min and about 80 min to degrade RhB. Our
18 findings provide a feasible way to design and engineer advanced nanostructures with
19 extremely high separation efficiency of photo-excited electron–hole pairs. Moreover,
20 it had extremely high photocatalytic ability and stability in the degradation of organic
21 contaminant, e.g. Rhodamine B and PNP under simulated solar light.

22

2. Experimental

2.1. Materials and methods

Titanium foils (250 μm thick, 99.8%) were purchased from Aldrich (Milwaukee, WI). NaF, NaHSO₄, NaTeO₃, CdSO₄, Na₂SO₃, Na₂S, Cd(NO₃)₂, Zn(NO₃)₂, Mn(CH₃COO)₂, sodium molybdate (Na₂MoO₄·2H₂O), thioacetamide (C₂H₅NS), P-Nitrophenol (PNP), rhodamine B (RhB), KOH and H₂SO₄ of analytic grade were purchased from Aladdin (Shanghai Aladdin biological technology co., LTD) and used as received. Twice-distilled water was used throughout this experiment.

Titanium foil was cut into 1.0 cm $\times$ 3.5 cm strips. Strips were ultrasonically cleaned in acetone and ethanol each for 5 min, respectively. The cleaned titanium strips were anodized at a constant potential of 20 V in an electrolyte containing 0.1 M NaF and 0.5 M NaHSO₄ at room temperature for 3 h in a two electrode configuration with a platinum cathode and the Ti strip as the anode. After oxidation, the amorphous TiO₂ NTAs were crystalline and photolytic active by annealing in air at 500 $^{\circ}\text{C}$ for 3 h with heating and cooling rates of 2 $^{\circ}\text{C min}^{-1}$.

CdTe nanoparticles (NPs) were pulse electrodeposited on the as-prepared TiO₂ NTAs firstly with an electrochemical workstation (IM6ex, Zahner Elektrik, German) in a conventional three-electrode system with the TiO₂ NTAs (on Ti foil) as work electrode, a Pt wire counter electrode and a saturated calomel electrode (SCE) as reference electrode in electrolyte solution: 0.15 and 0.08 mol L⁻¹ for CdSO₄ and NaTeO₃, respectively (pH = 2 adjusted by 1 mol L⁻¹ H₂SO₄) [21]. The pulse on-off time ratio was 0.05:1 with a running voltage of -2 V. The loading amount of the

1 deposit was tuned by adjusting the number of pulse sequence, here, 400 pulse
2 sequences were chosen for deposition [25]. After washing several times with distilled
3 water, the CdTe nanoparticles-modified TiO₂ NTAs (CdTe/TiO₂) were heated in
4 nitrogen atmosphere at 300 °C for 2 h.

5 The formation process of MoS₂/CdTe/TiO₂ heterostructures was described as
6 follows [9]. First, 30 mg sodium molybdate (Na₂MoO₄·2H₂O) and 60 mg
7 thioacetamide (C₂H₅NS) were dissolved in 20 mL deionized water to form a
8 transparent solution. Then the obtained CdTe/TiO₂ was directly immersed into the
9 above solution. The solution was transferred to a Teflon-lined stainless steel autoclave
10 and then heated in an electric oven at 200°C for 24 h. After washing several times
11 with distilled water, the MoS₂ nanosheet-modified CdTe/TiO₂ NTAs
12 (MoS₂/CdTe/TiO₂) heterostructures, was dried at 50 °C for 12 h.

13 SILAR was used to coat MoS₂/CdTe/TiO₂ with CdS-Mn NPs. Briefly,
14 MoS₂/CdTe/TiO₂ substrate was successively immersed into two different solutions for
15 1 min each. First in ethanol solution: 0.05 and 0.0375 mol L⁻¹ for Cd(NO₃)₂ and
16 Mn(CH₃COO)₂ respectively as cation source [17]. This allowed co-adsorption of
17 Mn²⁺ and Cd²⁺ ions. Then in methanol/water (7:3/v:v) solution containing 0.05 mol
18 L⁻¹ Na₂S. Following each immersion, the MoS₂/CdTe/TiO₂ was rinsed for 2 min or
19 longer with pure ethanol and methanol, respectively, to remove excess precursors,
20 before drying. This immersion cycle was repeated five times for the CdS-Mn layer.
21 For ZnS capping, the sensitized photoelectrode was dipped twice into 0.1 mol L⁻¹
22 Zn(NO₃)₂ in ethanol and 0.1 mol L⁻¹ Na₂S in methanol/water (7:3/v:v) solutions with

a soak period of 1 min each. After washing several times with distilled water, the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ heterostructure was heated in nitrogen atmosphere at 300 °C for 2 h.

2.2. Photoelectrochemical measurements and structural characterization

All electrodeposition and electrochemical measurements were performed with a CHI electrochemical analyzer (CHI660E, Shanghai Chenhua Instrument Co. Ltd.) in a standard three-electrode configuration, with the working electrode, a platinum foil counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The electrolyte used is an aqueous solution containing 0.35 mol L⁻¹ Na₂SO₃ and 0.24 mol L⁻¹ Na₂S (pH=11.5). The incident light from a 300 W Xe lamp was filtered to match the AM 1.5G spectrum with a intensity of 79 mW/cm² as measured by a radiometer (OPHIR, Littleton, CO).

Scanning electron microscope (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEOL, JEM 2100) were used to characterize the morphology and dimension of the products. Energy dispersive X-ray (EDX) spectrometer fitted to electron microscope was used for elemental analysis. Light absorption properties were examined using UV-vis diffuse reflectance spectra (DRS, SHIMADZU, UV-2450) within a wavelength range of 200-800 nm. Photoluminescence (PL) spectra were recorded at room temperature using Hitachi F-4600 fluorescence spectrophotometer at an excitation wavelength of 270 nm.

2.3. Photocatalytic degradation of p-Nitrophenol (PNP) and rhodamine B chloride (RhB)

The photocatalytic decompositions were conducted in a cubic quartz reactor containing 100 mL PNP or RhB at an initial concentration of 20 mg/L with the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ as catalyst under stirring. The concentration change during the degradation procedure was monitored by a UV-vis spectrophotometer (CARY 300 Conc) based on its absorption peak at 321 nm for PNP or 553 nm for RhB, respectively. After measurement, the test sample of 300 µL taken from the solution was immediately put back to the reaction cell to keep the volume constant.

3. Results and discussion

3.1. Characterization of the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂

Fig. 1A shows the TiO₂ NTAs morphology, with a diameter of 50-120 nm and a wall thickness of around 10 nm. They are vertically oriented from the Ti foil substrate, which not only provides accessible accesses for depositing sensitizing nanocrystals (NCs), but promotes the directional charge transport due to the one dimensional feature of the tubes [25]. Fig. 1B shows that the CdTe NPs prepared by pulse electrodeposition are ~7 nm in diameter and are distributed mostly on the opening of the TiO₂ NTAs. Fig. 1C₁ indicates that the CdTe/TiO₂ NTAs are covered with MoS₂ nanosheets prepared by hydrothermal reaction which are as thin as cicada's wings, and are distributed mainly on the top surface of the NTAs (marked with arrows and circle in red). The CdTe NPs are marked with arrows in green. Fig. 1C₂ ~ C₃ are TEM images of the MoS₂ under the different sizes of amplification. CdS-Mn and ZnS NPs were in turn deposited on the MoS₂/CdTe/TiO₂ NTAs by SILAR. The SEM images of

the CdS-Mn/MoS₂/CdTe/TiO₂ NTAs and ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs are shown in Fig. 1(D, E), respectively. No obvious blocking of the entrances is observed.

Fig. 1: SEM and TEM images of as-prepared photoelectrode. SEM images of unmodified TiO₂ NTAs (A), CdTe/TiO₂ NTAs (B), and MoS₂/CdTe/TiO₂ NTAs (C₁). TEM images of the MoS₂ (marked with arrows and circle in red) under the different sizes of amplification (C₂ to C₃). SEM images of CdS-Mn/MoS₂/CdTe/TiO₂ NTAs (D), and ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs (E) .

Fig. 2A depicts the HRTEM image of ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs. The lattice spacing measured is 0.2621 nm corresponding to the (011) plane of the CdTe QDs (JPCDS 41-0941) [22]. The lattice spacing of 0.2852 nm correspond to the

(200) plane of the CdS (well-matched to the reference data JCPDS 80-0019) [26]. The lattice fringe spacing of 0.2346 and 0.2407 nm are assignable to the (004) [27] plane and the (111) plane of anatase(JPCDS21-1272) TiO_2 [21], respectively. From the HRTEM images in Fig. 2A, the lattice fringes of MoS_2 nanosheets can be clearly observed, suggesting the well-defined crystal structure. The fringes with a lattice spacing of 0.2536 nm correspond to the (002) plane of MoS_2 , which agrees well with the recent report (~ 0.28) for 2D layers [28]. The EDX spectrum exhibited in Fig. 2B reveals the characteristic peaks of O, S, Cd, Ti, Mn, Mo and Zn. The Te peak is not detected, probably due to ion-thinning in the course of pro-processing to samples, which causes a loss of ingredients. The nanocrystalline material structure is confirmed with XRD analysis (Fig. 2C) which further indicates the present of MoS_2 、CdTe and CdS.

Fig. 2: HRTEM images of ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs (A). The corresponding EDX analysis (B) and XRD patterns (C).

UV-vis spectra of the different photocatalysts are displayed in Fig. 3A. For comparison, ZnS/MoS₂/CdTe/TiO₂ NTAs photocatalyst was examined (curve e). It can be clearly observed that the absorbance spectrum of these composite photocatalysts showed a red shift gradually with the change of the material structure. ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs had the highest light absorption ability in the visible region (curve f), a significant red shift of 50-70 nm is observed, indicating that the loading of several different semiconductor NPs of narrow band significantly improves the visible light absorption. Fig. 3B indicates a decrease in PL intensity (curve f). PL spectra have been widely used to investigate the electron-hole separation of the as-prepared photocatalysts [16]. The photogenerated electron-hole pairs are recombined at the oxygen vacancies of the TiO₂ NTAs surface resulting in PL. As displayed in Fig. 3B, the modified and unmodified TiO₂ NTAs are with the essentially same peak position, whereas the photoluminescence intensity decreases in the order of pure TiO₂ NTAs, CdTe/TiO₂, MoS₂/CdTe/TiO₂, CdS-Mn/MoS₂/CdTe/TiO₂, ZnS/MoS₂/CdTe/TiO₂ and ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs. The lower PL intensity implies a lower density of recombination centers (surface states), and consequently longer lifetime of photogenerated carriers leading to higher photocatalytic activity eventually.

1

Fig. 3: (A) Diffuse reflectance absorption spectra of (a) TiO_2 NTAs; (b) CdTe/TiO_2 NTAs; (c) $\text{MoS}_2/\text{CdTe/TiO}_2$ NTAs; (d) $\text{CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ NTAs; (e) $\text{ZnS/MoS}_2/\text{CdTe/TiO}_2$ NTAs; (f) $\text{ZnS/CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ NTAs. (B) PL spectra of these electrodes.

3.2. Photoelectrochemical measurements

The photocurrent density also demonstrates a strong dependence on the structure. As shown in Fig. 4A, under 79 mW/cm^2 of white light illumination and 0 V bias versus SCE, the unmodified TiO_2 NTAs display a weak response, while the $\text{ZnS/CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ NTAs electrode shows the best performances. The photocurrent density is 0.43 and 3.41 mA/cm^2 for pure TiO_2 NTAs and $\text{ZnS/CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ NTAs, respectively. Nyquist diagram of the electrochemical impedance spectroscopy (EIS) is an effective way to measure the electron transfer resistance (R_{et}). The size of arc radius on the Nyquist plot is related to the resistance of electron transfer and the separation efficiency of photogenerated electrons and holes on the electrode surface. It also reflects the energy barrier of electrode reaction [29]. Fig. 4B exhibits the EIS response of pure TiO_2 , CdTe/TiO_2 , $\text{MoS}_2/\text{CdTe/TiO}_2$, $\text{CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$, $\text{ZnS/MoS}_2/\text{CdTe/TiO}_2$ and

1 ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs electrodes in 0.2 mol L⁻¹ Na₂S electrolyte
 2 under illumination. R_{et} obtained on the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ decreases
 3 remarkably, which represents the fact that electron transfer is much easier and the
 4 redox reaction proceeds faster than that on the other electrodes. It is attributed to the
 5 good interaction of the CdTe, MoS₂, CdS-Mn and TiO₂. Namely, the stepwise level
 6 structure of semiconductor complex material reduces the interface resistance, thus
 7 improves the charge mobility [30].

8 The photoelectric performance of the hybrid electrode is further investigated by
 9 linear sweep photovoltammetry (LSV). As shown in Fig. 4C, the photocurrent
 10 response increases significantly on the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂, even at a
 11 potential of 0 V. Fig. 4D displays the corresponding photoconversion efficiency
 12 calculated using the following equation (1) [30] :

$$13 \quad \eta(\%) = j_p [E_{rev}^q - |E_{app}|] \times 100 / (I_0) \quad (1)$$

14 where j_p is the photocurrent density (mA/cm²), $j_p E_{rev}^q$ is the total power output,
 15 $j_p |E_{app}|$ is the electrical power input, and I_0 is the power density of incident light (79
 16 mW/cm²). E_{rev}^q equals 1.23 V, which is the standard potential for the water splitting
 17 reaction. The applied potential is $E_{app} = E_{meas} - E_{aoc}$, where E_{meas} is the electrode
 18 potential (vs. SCE) of the working electrode at which the photocurrent is measured
 19 under irradiation and E_{aoc} is the electrode potential (vs. SCE) of the same working
 20 electrode under open-circuit condition. As expected, ZnS/CdS-Mn/MoS₂/CdTe/TiO₂
 21 NTAs photoelectrode achieves the highest efficiency of 1.89% at -0.82 V vs. SCE
 22 which is about 50 times the efficiency of pure nanotubes as shown in Fig. 4D.

This result is consistent with the light absorption and emission performance of these electrodes mentioned earlier. To sum up, A stepwise band edge level, type II-like model is proposed to elucidate the possible charge transfer mechanism in ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs photoelectrode system (as described in Scheme 1) [31, 32]. In an ideal type II QDs, the spatially separated electron and hole wave functions reduce their coulomb interaction, increasing the lifetimes of single and multiple exciton states [33].

Meanwhile, in order to give a reasonable interpretation of the superior performance of the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs photoelectrode, charge transport and recombination behavior was well investigated. The open-circuit voltage-decay measurements were conducted by monitoring the Voc transient during relaxation from an illuminated quasi-equilibrium state to the dark equilibrium, see Fig. 4E. When the AM-1.5 illumination on the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs photoelectrode at open circuit is interrupted, the excess electrons are removed due to recombination with holes trapped in the composite and dissolved oxygen in the electrolyte which scavenges electrons. The photo-voltage decay rate directly relate to the electron lifetime by the following expression (2) [34]:

$$\tau_n = \left[\frac{-k_B T}{e} \right] \left[\frac{dV_{oc}}{dt} \right]^{-1} \quad (2)$$

where $k_B T$ is the thermal energy, e is the positive elementary charge, and dV_{oc}/dt is the derivative of the open-circuit voltage transient. Fig. 4F is the plot of the response time obtained by applying eq (2) to the data in Fig. 4E. At the same V_{oc} value, the

1 response time of the photoelectrodes follows an order of
2 $\text{ZnS/CdS-Mn/MoS}_2\text{/CdTe/TiO}_2$ NTAs > $\text{ZnS/MoS}_2\text{/CdTe/TiO}_2$ NTAs >
3 $\text{CdS-Mn/MoS}_2\text{/CdTe/TiO}_2$ NTAs > $\text{MoS}_2\text{/CdTe/TiO}_2$ NTAs > CdTe/TiO_2 NTAs >
4 TiO_2 NTAs. Based on above analyses, the $\text{ZnS/CdS-Mn/MoS}_2\text{/CdTe/TiO}_2$ NTAs
5 photoelectrode exhibits superior recombination characteristics, with the longer
6 lifetimes indicating enhanced separation of the photogenerated charges in the novel
7 structure. The ZnS layer with a large bandgap at the electrode/electrolyte solution
8 interfaces acted as a potential barrier, which was similar to an insulating layer
9 employed in the conventional metal–insulator–semiconductor solar cells. The ZnS
10 layer allows the adjustment of the electric field and potential distribution in the
11 interface between the electrodes and the electrolyte, thus suppresses the dark current
12 and back recombination of the injected electrons [35, 36].

Fig. 4: (A) Photocurrent responses of pure TiO₂ NTAs (a); CdTe/TiO₂ NTAs (b); MoS₂/CdTe/TiO₂ NTAs (c); CdS-Mn/MoS₂/CdTe/TiO₂ NTAs (d); ZnS/MoS₂/CdTe/TiO₂ NTAs (e) and ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs electrodes (f). (B) and (C) The corresponding EIS analysis and I-V curves respectively. (D) and (E) The photoconversion efficiency and open-circuit photovoltage responses of these electrodes. (F) Response time determined by open-circuit potential decay for corresponding photoelectrodes shown in (E).

3.3. Photocatalytic degradation of p-Nitrophenol (PNP) and rhodamine B chloride (RhB)

The photocatalytic degradation activities of the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂

1 NTAs heterostructures are shown in Fig. 5A and Fig. 5B. Prior to the light irradiation,
2 the solution was magnetically stirred in dark to ensure the establishment of an
3 adsorption-desorption equilibrium of the PNP or RhB molecules on the photocatalyst.

4 As reported, in addition to the large specific surface area, the 2D nanomaterials
5 (MoS_2 nanosheets) may provide a better anchoring surface for adsorbing molecules
6 compared to 1D or 0D nanostructures [9]. It is believed that this kind of attractive
7 nanomaterials with a high adsorption capacity will have important applications in the
8 water treatment. For example, remove organic pollutants and even some toxic heavy
9 metal ions [28]. After the adsorption process, the photocatalytic degradation activities
10 of $\text{ZnS/CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ NTAs heterostructures were investigated. It only
11 takes about 40 min for the $\text{ZnS/CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ heterostructure to
12 completely degrade PNP, and about 80 min to degrade RhB. Such a catalytic
13 efficiency is satisfactory compared with the previous researches [25, 37, 38]. As
14 illustrated in Fig. 5(C, D), it is clearly seen that under identical conditions, the
15 $\text{ZnS/CdS-Mn/MoS}_2/\text{CdTe/TiO}_2$ NTAs exhibit much higher activity than that of TiO_2
16 NTAs with other modifications. The degradation rates of PNP and RhB for the above
17 photocatalysts are 1.23%、29.5%、41.7%、60.5%、67.7%、84.8% and 96.6%
18 or 0.9%、21.1%、35.5%、46.4%、48.1%、57.9% and 70.8% under 20 min
19 light irradiation, respectively (Fig. 5C and Fig. 5D). We believe that the enhanced

Fig. 5: (A) UV-vis determination of photocatalytic degradation of PNP (100 mL, 20 mg/L) and RhB (B) using ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs as the catalyst under AM 1.5G illumination. (C, D) corresponding photocatalytic performances and degradation kinetics analyses (E, F) of different photoelectrodes (a: TiO₂ NTAs; b: CdTe/TiO₂ NTAs; c: MoS₂/CdTe/TiO₂ NTAs; d: CdS-Mn/MoS₂/CdTe/TiO₂ NTAs; e: ZnS/MoS₂/CdTe/TiO₂ NTAs and f: ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs). Letter “k” indicates rate constant, which is determined from the slope of the line (E, F).

photocatalytic activity of the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ heterostructure is attributed to not only the strong adsorption capacity of MoS₂ nanosheets [9], but also the formed heterostructure with matched energy bands among MoS₂ nanosheet,

CdTe, CdS-Mn and TiO₂ nanotube. A schematic illustration of the energy band matching within such semiconductor heterostructures (ZnS/CdS-Mn/MoS₂/CdTe/TiO₂) is depicted in Scheme 1.

Scheme 1: Scheme diagram of the composite material construction and ideal stepwise band edge structures for efficient transport of the excited electrons and holes in ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ NTAs electrode.

The degradation mechanism was elucidated based on the reported ones [36] and displayed in scheme 1 with the following equations:

Under illumination, the photo-excited electrons from the VB of CdTe NPs are directly transferred to CB of CdTe, then transmitted to CB of MoS₂ nanosheets, CdS-Mn and TiO₂ step by step driven by the built-in potential in the heterojunction, and eventually to accumulate on the surface of TiO₂ NTAs. These electrons can be scavenged by dissolved oxygen molecules to yield superoxide radical anion $\cdot\text{O}_2^-$. Then, $\cdot\text{O}_2^-$ reacts with H^+ to produce hydroxyl radical ($\cdot\text{OH}$). On the contrary, the holes in the VB of TiO₂ are transferred to VB of CdS-Mn, MoS₂ and CdTe stage by stage and can be consumed by the sacrificial agents (S^{2-} , SO_3^{2-}) or organic contaminant (PNP or RhB). Meanwhile, the holes in CdTe/MoS₂/CdS-Mn QDs can potentially react with water or OH^- adhering to the surface of the photoelectrode to form highly reactive $\cdot\text{OH}$, a strong oxidizing agent to decompose the organic pollutants. As a result, the heterostructure can improve the separation, retard the recombination and prolong the lifetime of photogenerated electron-hole, leading to the superior photocatalytic activity.

In addition, the ZnS/CdS-Mn/MoS₂/CdTe/TiO₂ heterostructure exhibits the stable performance, i.e. there is no obvious decrease in photocatalytic degradation activity even after five cycles (Fig. 6 A and Fig. 6 B).

Fig. 6: Photocatalytic stability of $\text{TiO}_2/\text{CdTe}/\text{MoS}_2/\text{CdS-Mn}/\text{ZnS}$ NTAs on degradation of 20 mg/L PNP solution (A) and RhB solution (B), and the experiment was repeated five times.

4. Conclusions

The $\text{ZnS}/\text{CdS-Mn}/\text{MoS}_2/\text{CdTe}/\text{TiO}_2$ heterostructure with stepwise level structure was prepared for the first time via the hydrothermal reaction and pulse electrodeposition coupled with successive ionic layer adsorption and reaction (SILAR) processes. The $\text{TiO}_2/\text{CdTe}/\text{MoS}_2/\text{CdS-Mn}/\text{ZnS}$ heterostructure showed an excellent photocatalytic activity for removal of PNP and RhB, giving the highest degradation kinetics rate constant ($k=0.1187 \text{ min}^{-1}$ and $k=0.2829 \text{ min}^{-1}$, respectively). It is believed that the matched energy band of $\text{TiO}_2/\text{CdTe}/\text{MoS}_2/\text{CdS-Mn}/\text{ZnS}$ heterostructure favors the charge transfer and suppresses the photo-induced carriers recombination, leading to the enhanced photocatalytic activity for degradation of organic contaminant. Moreover, the multi-semiconductor co-sensitized TiO_2 NTAs exhibited good stability. We believe that the development of novel photocatalyst constructed by combination of 1D, 2D and 3D nanostructures, with a broad visible light absorption window, is promising towards the high-performance photocatalysis applications.

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Graphical Abstract