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Surface functionalization of discrete metal-chalcogenide supertetrahedral clusters and the photocatalytic application†

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Atomically precise metal-chalcogenide supertetrahedral clusters (MCSCs) are supposed to be more attractive for functionalization than conventional metal-sulfide quantum dots owing to their potential ability to establish precise structure—composition—property relationships. However, the accurate surface functionalization of such cluster-based species remains difficult. In this paper, we present a facile method for synthesizing discrete MCSCs decorated with different functional groups *via* a one-step solvothermal reaction, which was demonstrated to have better solvent dispersibility compared with ligand-free ones. In addition, the composites were also prepared by combining ligand-free clusters (or ligand-partially protected or amino-modified ones) with two-dimensional MXene nanosheets. The composites derived from amino-modified clusters exhibited optimal performance of photocatalytic hydrogen evolution. Furthermore, the hydrogen bonding interactions between modified amino groups and MXene nanosheets were verified by ¹H-NMR spectroscopy. This work provides a facile approach for the surface functionalization of MCSCs, and facilitates the expansion of the functionality of atomically precise nano-species.

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Introduction

Discrete metal-chalcogenide supertetrahedral clusters (MCSCs), known as ultra-small "quantum dots", represent regularly fragmented units of zinc blende type materials. 1-6 Since their structures can be accurately identified at the atomic level, they have been widely studied in the fields of fluorescence, 7-13 photocatalysis, 14-20 and electrocatalysis 21-25 for establishing an accurate structure-composition-property relationship. However, such clusters usually exhibit poor dispersibility and conductivity during practical applications, and the weak binding forces between clusters and conductive substrates

limit their further development.^{26–32} Therefore, rational modification of clusters for improving the interactions between clusters and conductive substrates would be helpful for their applications in catalysis.

Owing to the advancement of organic template-guided synthesis, most of the discrete Tn and Pn clusters (two main types of MCSC structures, where n represents the number of metal layers in the basic cluster units, Scheme S1†) reported in recent years are predominantly ligand-free types.²⁹ The highdegree negative charges of these clusters are usually balanced by protonated organic amines (i.e., counterions), which results in poor dispersibility and instability. Alternatively, a group of Cn clusters (fully coated with organic ligands, Scheme S1†) has superior dispersibility. However, their monomeric composition and poor structural tunability make them a suboptimal choice for subsequent functional applications. Therefore, by combining the advantages of the above two types of structures, a series of ligand-partially protected Tn and Pn clusters has been developed (Scheme S2†). The few ligands at the cluster surface help to improve their contact with the solution molecules and reduce their negative charge density, thereby improving structural stability and dispersibility. This feature is well-suited for functional expansion, and makes them a promising choice.

Since MCSCs generally exhibit poor electrical conductivity, combining them with a suitable conductive substrate is desirable for promoting the separation of the photogenerated electrons and holes, which may effectively enhance photo-

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[†]Electronic supplementary information (ESI) available: Supplementary tables and figures, PXRD patterns, EDS and ¹H-NMR analysis. CCDC 2254140-2254148 for ISC-24, ISC-25, ISC-25-4'-NH₂, ISC-25-4'-CH₃, ISC-25-4'-OH, ISC-25-4'-F, ISC-25-4'-OCH₃, ISC-26-2'-NH₂ and ISC-26-4'-Cl. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3qi00983a

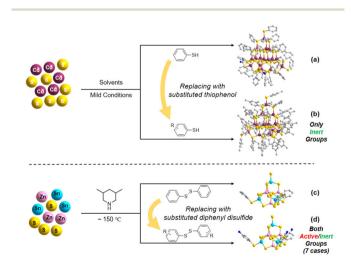
catalytic performance. In recent decades, MXenes, a layered transition metal carbide/carbonitride/nitride family, have attracted attention in many scientific fields, such as energy storage and conversion,³³ sensing,³⁴ and photocatalysis.^{35–38} In the domain of photocatalytic hydrogen evolution (PHE), Ti₃C₂T_r is one of the most studied MXenes for the following reasons: (1) the favorable hydrophilic ability supports its chemical reactions within aqueous solutions;³⁹ (2) the excellent electrical conductivity promotes the separation and transfer of the photoinduced charge carriers from semiconductors; 40 and (3) the appropriate work function allows it to form a Schottky heterojunction with most semiconductors. Therefore, the ultra-thin Ti₃C₂T_x substrate is regarded as a suitable and promising substrate, in which abundant surface O/F sites can also serve as potential hydrogen bonding receptors for anchoring discrete MCSCs.

This work aims to improve the interactions between a cluster and a conductive substrate by manipulating the cluster surface environment, and eventually, improve the performance of photocatalytic hydrogen evolution (PHE). On the basis of the synthetic route of *Pn*-type clusters that are partially protected by ligands, ³² we changed the types of diphenyl disulfides to modify the cluster surface with different functional groups (Scheme 1). By taking advantage of the large number of O/F sites on the surface of MXene, which can easily form hydrogen bonds with amino-modified clusters, the PHE performance of amino-modified MCSCs (and ligand-free clusters) combined with MXene nanosheets was investigated.

Experimental

Materials

All chemicals were purchased from commercial sources and used without further purification. Deionized water was used in all synthetic procedures.



Scheme 1 Schematics of the surface functionalization of discrete MCSCs: (a and b) using the modified thiophenol and (c and d) using modified diphenyl disulfide.

Synthetic procedures

Synthesis of ISC-24, $10(3,5\text{-DMPH}^+)\cdot[(Zn_4Sn_4S_{17})^{10^-}]\cdot 4H_2O$. The synthetic procedure for ISC-24 followed our previous work, ³² except that the manganese source was replaced by a zinc source. A mixture of zinc acetate tetrahydrate (Zn $(OAc)_2\cdot 4H_2O$, 120 mg), tin dichloride (SnCl₂, 60 mg), sulfur powder (S, 120 mg), 3,5-dimethylpiperidine (3,5-DMP, 3.0 mL), and deionized water (H₂O, 1.0 mL) was added to a 25 mL Teflon-lined stainless steel autoclave and stirred for 30 min, then was heated to 125 °C for 7 days. After cooling down to room temperature, transparent colorless block crystals were obtained with a yield of 19.4% based on zinc acetate dihydrate.

Synthesis of ISC-25, $7(3,5\text{-DMPH}^+)\cdot[Zn_4Sn_4S_{14}(SPh)_3^{7-}]\cdot H_2O$. The synthetic procedure for ISC-25 followed our previous work, ³² except that the manganese source was replaced by a zinc source. Zinc acetate tetrahydrate $(Zn(OAc)_2\cdot 4H_2O, 120 \text{ mg})$, tin dichloride $(SnCl_2, 60 \text{ mg})$, sulfur powder (S, 120 mg), diphenyl disulfide $(Ph_2S_2, 160 \text{ mg})$, 3,5-dimethylpiperidine (3,5-DMP, 3.0 mL), and deionized water $(H_2O, 1.0 \text{ mL})$ were mixed in a 25 mL Teflon-lined stainless steel autoclave and stirred for 30 min, then heated to 125 °C for 14 days. After cooling down to room temperature, transparent colorless rhombohedral crystals were obtained with a yield of 16.8% based on zinc acetate dihydrate.

Synthesis of ISC-25-4'-NH₂, 7(3,5-DMPH⁺)-{[Zn₄Sn₄S₁₄(SPhNH₂)₃]⁷⁻}-H₂O. A mixture of zinc acetate tetrahydrate (Zn(OAc)₂·4H₂O, 120 mg), tin dichloride (SnCl₂, 60 mg), sulfur powder (S, 120 mg), di-(4,4'-amino)-diphenyl disulfide (S₂(NH₂Ph)₂, 160 mg), and deionized water (H₂O, 1.0 mL) was added to a 25 mL Teflon-lined stainless steel autoclave and stirred for 30 min, then heated to 125 °C for 14 days. After cooling down to room temperature, oblique octahedral or hexagonal transparent crystals were obtained with a yield of 12.6% based on zinc acetate dihydrate.

Synthesis of other ISC-25 and ISC-26 series samples with different decorated functional groups. Similar to the synthetic processes described above, the ligand of Ph_2S_2 was replaced by substituted Ph_2S_2 (e.g. $(ClPh)_2S_2$, the categories are summarized in Table S2†) in the same molar ratio with the other components unchanged.

Preparation of Ti₃C₂T_x **nanosheets.** Ti₃C₂T_x nanosheets (here T represents the oxygen terminus generated by HF etching) were synthesized according to the reported method (Schemes S2 and S3†). Ti₃AlC₂ powders (>98 wt% purity; particle size <75 μ m, *i.e.*, 200 mesh) were immersed in HF (10 wt%) solution at 300 K by stirring for 24 h. Then the resulting suspension was washed several times with deionized water and centrifuged to remove the remaining impurities and HF until the pH value of the solution reached 5–6. The wet sediment was washed twice with ethanol and transferred to a widenecked jar to air-dry for 3–4 days. The finally obtained sample was named Ti₃C₂T_x. The multilayered Ti₃C₂T_x was then stirred with dimethyl sulfoxide (DMSO) at 310 K for 24 h. The colloidal suspension was centrifuged to obtain the intercalated

powders. The powders were then washed several times with deionized water to remove the residual DMSO. Next, the residue was dispersed in deionized water in a weight ratio of Ti₃C₂T_x to water of 1:100. Afterward, ultrasonication treatment was carried out for 4 h to exfoliate the Ti₃C₂T_x powder into 2-D sheets under argon. The suspension was centrifuged at 3500 rpm for 10 min to remove the unexfoliated MXenes. Finally, the Ti₃C₂T_r nanosheets were obtained by filtration and dried in a vacuum for further experiments.

Preparation of P1-CNPs (CNPs: cluster-derived nanoparticles). P1-CNPs were prepared in the mixed solution of formamide and water (1:1 in volume). The corresponding crystals of 10 mg of ISC-24, ISC-25, and ISC-25-4'-NH2 were ground into powder and dispersed in 10 mL of 1:1 formamide/water. After 30 min of ultrasonication treatment, the formamide/ water solution of P1-CNPs with a concentration of 1 mg mL⁻¹ was prepared by mechanical stirring for 4 h.

Preparation of CMn samples. CMn samples were prepared by mixing 1 mg mL⁻¹ of the corresponding **P1-CNP** formamide aqueous solution with the one containing the ultra-thin $Ti_3C_2T_x$ nanosheets according to the mass percentage (CM0 is **P1-CNPs** without $Ti_3C_2T_x$ nanosheets).

Results and discussion

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Synthetic procedure and crystal structure description

The title compounds constructed from supertetrahedral P1-ZnSnS clusters were obtained by a facile one-step solvothermal reaction (see the Experimental section and the ESI† for details). To directly realize the functionalization of the partially protected P1-ZnSnS, various diphenyl disulfides decorated with different functional groups were selected, and the synthetic routine and molecular structure of the relevant compounds are shown in Fig. 1.

The obtained clusters mentioned in this work are all composed of the $[Zn_4Sn_4S_{17}]^{10-}$ core, so the functionalized samples are represented in a simplified form (e.g., ISC-25-ZnSnS-SPh is simplified to ISC-25, and the functionalized ISC-25 are represented as the site of the substituent on their benzene ligand, e.g., ISC-25-4'-NH₂). The derivatives of ISC-26 are also showcased in a similar pattern. The structural difference between ISC-25 and ISC-26 is the number of protecting ligands (three-corner protected in ISC-25 and four-corner protected in ISC-26, Fig. 1).

Interestingly, ISC-26-2'-NH2 was obtained using 2,2'-dinitrodiphenyl disulfide, instead of 2,2'-diaminodiphenyl disulfide. This may be attributed to excess sulfur powder in the reaction system, which reduces the nitro group to the amino group. A similar situation also occurs in ISC-25-4'-NH2, while ISC-25-4'-NH₂ can also be obtained by directly using 4,4-diaminodiphenyl disulfide. This process is also shown in detail in Table S2.†

A series of functionalized crystalline ISC-25 and ISC-26 samples was obtained in the transparent rhombohedral form, but ISC-26-4'-Cl appeared in the form of a transparent decagonal octahedron. Single crystal X-ray structural analysis revealed that the ISC-24 sample crystallized in P43n (No. 218), all ISC-25 series samples and ISC-26-2'-NH₂ crystallized in the $R\bar{3}$ space group (No. 148), and the ISC-26-4'-Cl sample crystallized in the C2/c space group (No. 15). These functionalized clusters are

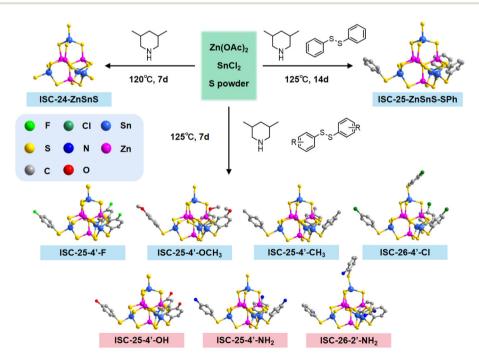


Fig. 1 Synthetic processes and molecular structures of ISC-24, ISC-25, and ISC-25&26 with different functional groups. The products with functional groups have been distinguished by different colored backgrounds in comment boxes (light blue: inert functional groups, e.g., -CH₃, -OCH₃, -Cl, -F; pink: active functional groups: e.g., -OH, -NH₂).

basically isomorphic to the structures previously reported.³² Combined with the results of C, H, and N elemental analysis of ISC-24, ISC-25, and ISC-25-4'-NH2 (Table S3†) and their SCXRD data (Table S1†), the formulas of the above three compounds were determined as follows: ISC-24: 10(3,5- $DMPH^{+})\cdot[(Zn_{4}Sn_{4}S_{17})^{10-}]\cdot H_{2}O;$ 7(3,5- $DMPH^{+}$)·{[$Zn_{4}Sn_{4}S_{14}(SPh)_{3}$]⁷⁻}· $H_{2}O$ and ISC-25-4'- NH_{2} : 7(3,5- $DMPH^{+}$)·{ $[Zn_{4}Sn_{4}S_{14}(SPhNH_{2})_{3}]^{7-}$ }· $H_{2}O$. Compared to the P1 cluster reported previously, the cluster reported here retained the pristine atomic arrangement of the divalent and tetravalent metal ions, i.e., each P1-ZnSnS contained one (M₄^{II}S)⁶⁺ and four $(M^{IV}S_4)^{4-}$ units to meet Pauling's electrostatic valence rule.

Morphology of Ti₃C₂T_r nanosheets and dispersed P1-CNPs

Layered Ti₃C₂T_x nanosheets were prepared by exfoliating bulk Ti₃AlC₂ powders in HF aqueous solution. The corresponding structure information for Ti₃AlC₂ and the preparation process are shown in Schemes S3 and S4.† After immersing them in HF solution for 24 h, the Ti₃AlC₂ powders (200 mesh) were successfully expanded and converted to the layered Ti₃C₂T_x structure (Fig. 2a). The emergence of layers was caused by the fact that the Al layers in Ti₃AlC₂ nanoparticles were etched away, and the interlayer space was increased by released H2. After intercalation by dimethyl sulfoxide (DMSO), the layered structures were further delaminated into 2D Ti₃C₂T_x nanosheets by ultrasonication (Fig. 2b). The AFM image in Fig. 2c shows that the thickness of Ti₃C₂T_x nanosheets is about 4 nm. In addition, PXRD characterization was performed on the Ti₃AlC₂ MAX phase and Ti₃C₂T_x nanosheets to distinguish the outcome of Al etching. As shown in Fig. 2d, there are a number of characteristic peaks at $2\theta = 9.95^{\circ}$, 19.50° , 34.38° , 37.49°, 39.21°, 42.13°, 48.72°, and 56.66°, which correspond to the (002), (004), (101), (103), (104), (105), (107), and (109) planes of the Ti₃AlC₂ MAX phase. This result is in agreement with the one in the published literature. 42,43 The degree of the

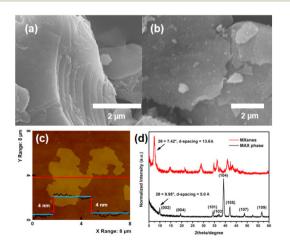


Fig. 2 SEM images of layered (a) and exfoliated $Ti_3C_2T_x$ nanosheets (b) obtained by HF treatment of Ti₃AlC₂ powder; (c) AFM images of dispersed single-layered Ti₃C₂T_x nanosheets; and (d) PXRD results of Ti₃AlC₂ powder and exfoliated Ti₃C₂T_x nanosheets.

(002) plane in PXRD is generally used to calculate the interlayer spacing of the layered material by applying Bragg's law, and the d-spacing of the Ti₃AlC₂ MAX phase is calculated to be approximately 5.0 Å. $Ti_3C_2T_x$ MXene nanosheets show a (002) peak at $2\theta = 7.42^{\circ}$, referring to a *d*-spacing of 13.6 Å (Fig. 2d). It is clearly demonstrated that the Al layer in the Ti₃AlC₂ MAX phase has been well etched, which allows water molecules to further exfoliate the Al layer for preparing single-layered Ti₃C₂T_x MXene nanosheets.⁴⁵

The nanoparticles generated from the cluster dispersion are denoted as P1-CNPs (CNPs: cluster-derived nanoparticles) in this work. Three examples of clusters were selected for comparison to test their dispersibility: ISC-24 without ligand protection, ISC-25 with a partially protected ligand, and ISC-25-4'-NH₂ with a partially protected ligand modified with amino (-NH₂) groups. The corresponding P1-CNP solutions were prepared by adding the ground crystals of the above three compounds to the formamide/water solution (1:1), followed by stirring for 4 h and sonicating for 1 h. The particle sizes of P1-CNPs formed from ISC-24 were found to be 25-55 nm (Fig. 3a, mean size ~40 nm), which far exceeded the size of individual clusters (~1.6 nm). This suggests that the dispersed particles existed in the aggregated form of multi-clusters. In contrast, the mean particle sizes of P1-CNPs formed by ligand-partially protected ISC-25 and amino-modified ISC-25-4'-NH2 were found to be 4-7 nm and 1-4 nm, respectively (Fig. 3b and c). The latter two were significantly more accessible to solution. This can be explained by the low negative charge of the clusters and the improved solubility.

In addition, no effective lattice striations were observed in the HRTEM images of the P1-CNPs formed by the dispersed clusters. This suggests that P1-CNPs have adopted an amorphous state, which is probably due to the small size of the individual clusters (~1.6 nm).

Fabrication and morphology of P1-CNPs/Ti₃C₂T_x nanocomposites (CMn)

The nanocomposites consisting of P1-CNPs and exfoliated $Ti_3C_2T_x$ are denoted as CMn (n indicates the weight percentage of the added $Ti_3C_2T_x$, n = 0 indicates that no $Ti_3C_2T_x$ was added). The fabrication process for the composite is shown in Scheme S4.† The results of PXRD characterization of CM1 (composed of ISC-25-4'-NH₂ derived CM0 and $Ti_3C_2T_x$) are shown in Fig. S11.†

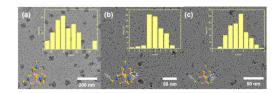


Fig. 3 TEM images of P1-CNPs formed by (a) ISC-24; (b) ISC-25, and (c) ISC-25-4'-NH2, and the insets show the size distribution and the molecular structures of the corresponding clusters.

Due to the low loading amount and low crystallinity, only the diffraction peaks of MXene nanosheets were observed. In order to characterize the morphology and structure of CMn, we performed HRTEM tests on the corresponding samples. Firstly, the morphology of Ti₃C₂T_x was characterized, and clear lattice stripes were observed as shown in Fig. 4a and b. However, for CM1, the lattice stripes were not detected in the HRTEM images (Fig. 4c and d). This was also confirmed by the selected area electron diffraction (SAED) characterization. As shown in Fig. S3a,† single-crystal diffraction patterns of Ti₃C₂T_x were observed when selected electron diffraction was performed on the regions shown in Fig. 4a and b, while the CM1 composites exhibited a polycrystalline form (Fig. S3b†), consistent with the states shown in Fig. 4c and d. In addition, we also performed HAADF-STEM characterization on CM1 prepared with ISC-25-4'-NH2 as the precursor, and performed EDS mapping tests (Fig. 4e-j). The constituents of Zn, Sn, S, and N in the clusters were uniformly distributed on the Ti₃C₂T_x nanosheets, demonstrating the successful preparation of the composites.

PHE performance of CMn

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The photocatalytic performance of the above composites was tested by conducting PHE reactions under full-spectrum irradiation using the Na₂S/Na₂SO₃ reagent as the sacrificial reagent. Firstly, ISC-25-4'-NH2 derived CM0 was selected for the PHE reaction, and the H₂ production rate was calculated to be 17.51 μ mol g⁻¹ h⁻¹ according to the data shown in Fig. 5a. This poor PHE performance could be attributed to the low separation efficiency of the photogenerated electron-hole pairs of CM0. Enhanced photocatalytic activities were obtained for the ISC-25-4'-NH₂ derived samples containing a certain percentage of Ti₃C₂T_x (1%, 2.5%, 5%, and 10%, i.e., CM1, CM2.5, CM5, and CM10, respectively). The PHE rate from CM1 was calculated to be 158.32 µmol g⁻¹ h⁻¹ (Fig. 5a and b). This result indicates that the Ti₃C₂T_x nanosheets play an important role in separating the photogenerated electron-hole pairs for P1-CNPs. The PHE activity of CM2.5, CM5 and CM10 decreased to 113.37, 121.07, and 89.43 μ mol g⁻¹ h⁻¹, respectively. These results were caused by the aggregation of Ti₃C₂T_x and P1-CNPs, which was verified by its TEM images (Fig. S4†). Under such situation, the Ti₃C₂T_x nanosheets partially mask the active sites of P1-CNPs, thereby leading to a reduced photocatalytic efficiency.

The photocatalytic stability of ISC-24, ISC-25, and ISC-25-4'-NH₂ derived CM1 composites was also investigated (Fig. 5d-f). The activity of the ISC-24 derived CM1 decreased by 52.9% for the second round of photocatalysis, and further decreased by 25.4% to 8.71 μ mol g⁻¹ h⁻¹ in the third round of testing (Fig. 5d). This can be attributed to the poor stability of the ISC-24 derived sample. For the CM1 composites prepared with ISC-25 and ISC-25-4'-NH2 as precursors, the photocatalytic activity of the second and third rounds decreased by 83.2%, 75.4% and 96.3%, 91.3%, respectively, compared to the first round. The results show that the composites containing P1-CNPs with the amino-modified clusters have good stability.

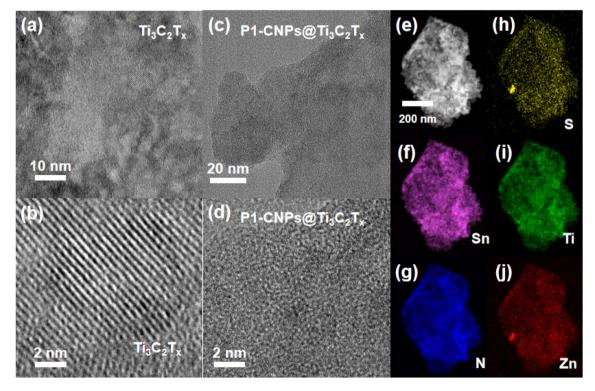


Fig. 4 HRTEM images of MXene nanosheets (a and b) and ISC-25-4'-NH₂ derived CM1 (c and d). HAADF-STEM image of P1-CNPs/Ti₃C₂T_x nanocomposites (e), and EDS elemental mapping images of (f) Sn, (g) N, (h) S, (i) Ti, and (j) Zn, respectively.

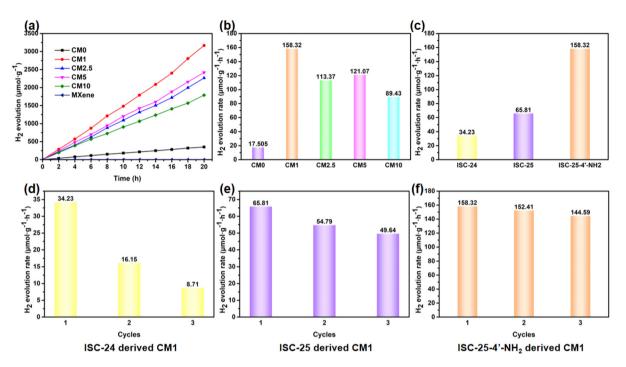


Fig. 5 Investigation of photocatalytic properties of CMn. (a and b) Comparison of PHE performance of CM0, CM1, CM2.5, CM5, and CM10 nanocomposites under irradiation using ISC-25-4'-NH2 derived CMn. (c) Comparison of PHE performance of CM1 composite materials using ISC-24, ISC-25, and ISC-25-4'-NH₂ derived CMn. (d-f) Test results of multiple cycles on CM1 composite materials using ISC-24, ISC-25, and ISC-25-4'-NH₂ derived CMn.

¹H-NMR test for P1-CNPs and CMn

Considering that the CM1 derived from ISC-25-4'-NH2 has good PHE performance and high stability, we assume that the amino groups in the modified P1 cluster play an important role. Therefore, the ¹H-NMR test was conducted to verify the above conjecture (Fig. 6). The formation of hydrogen bonds between the amino groups and the oxygen terminus of Ti₃C₂T_x nanosheets caused the chemical shift values of hydrogen atoms to be shifted towards the lower field due to this effect. Similar situations have been reported in the case of an S···H-N hydrogen bond.44 In addition, protonated 3,5-dimethylpiperidine, which acts as counterion during cluster dispersion, also interacts electrostatically with the oxygen terminus on the Ti₃C₂T_x nanosheets to form hydrogen bonds, as evidenced by the result of the H_d signal moving from 7.1 ppm to 8.0 ppm in Fig. 6. This interaction also provides a theoretical basis for the enhanced photocatalytic performance of ISC-24 and ISC-25 based CM1 (Fig. 5c).

Optical and electrochemical properties of CMn

To further understand the enhanced photocatalytic performance of CMn composites compared to P1-CNPs, a series of optical and electrochemical properties were characterized. Firstly, UV-vis absorption spectra were obtained to characterize the light absorption capability of the samples. As shown in Fig. 7a, the light absorption of CM1 was significantly increased compared to CM0 in the whole range of 260-460 nm due to the dispersed Ti₃C₂T_x nanosheets, and similar phenomena

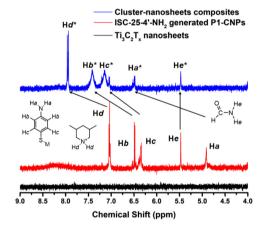
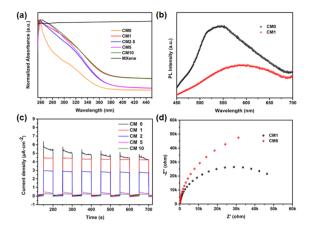


Fig. 6 ¹H-NMR spectra of Ti₃C₂T_x nanosheets, P1-CNPs formed by ISC-25-4'-NH₂, and their composite materials with a chemical shift value of 4.0-9.0 ppm (see Fig. S5-S7† for original data).

were observed for CM2.5, CM5 and CM10. Subsequently, steady-state photoluminescence (PL) spectra were recorded for the ISC-25-4'-NH₂ derived CM0 and CM1, as shown in Fig. 7b. The emission intensity of CM1 was significantly weakened compared to that of CMO, suggesting that the electron-hole recombination in CM1 composites is well-suppressed because of the effective charge transfer between P1-CNPs and Ti₃C₂T_r.

In addition, the photoelectric response and electrochemical impedance spectra (EIS) were recorded to detect the separation of photogenerated electron-hole pairs and the interfacial



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Fig. 7 (a) UV-vis absorption spectra of MXene nanosheets and CMn; (b) PL spectra of ISC-25-4'-NH2 derived P1-CNPs and CM1 (Ex = 380 nm); (c and d) photoelectric response curves (c) and electrochemical impedance spectra (d) of ISC-25-4'-NH2 derived CMn.

charge transfer. As shown in Fig. 7c, CM0 showed the highest transient photocurrent densities, but were less stable compared to the prepared CMn decorated electrodes. According to this situation, CM0 should have a higher PHE efficiency. However, considering the feature of sharp reduction of the photocurrent (Fig. 7c), we also compared the EIS curves of CM0 and CM1, as shown in Fig. 7d. The fitted EIS spectra of CM1 showed a smaller semicircle and a lower interfacial resistance, revealing the more efficient electron-hole pair separation and transfer efficiency of the CM1 heterostructure. We therefore attribute the low photocatalytic efficiency of CM0 to poor stability and weak conductivity. CM1 exhibited the highest photocurrent density in the CMn series, corresponding to its highest PHE performance and stability, while CM2.5, CM5, and CM10 exhibited lower photocurrent densities due to the formation of a sandwich-like structure, as shown in Fig. S4,† where the multilayered $Ti_3C_2T_x$ nanosheets may cover the active sites of P1-CNPs.

X-ray photoelectron spectroscopy (XPS) tests were also carried out on ISC-25-4'-NH2 derived P1-CNPs, Ti₃C₂T_x nanosheets, and CM1 composites to further verify the formation of composites between the two substances, and the results are shown in Fig. S8-S10.† The Zn, Sn and S signals of ISC-25-4'-NH₂ are consistent with those of P1-CNPs, and the high-resolution XPS spectra of Ti 2p showed four deconvoluted peaks (Fig. S10†) with binding energies of 464.8 eV and 459.0 eV corresponding to Ti-O 2p1/2 and Ti-O 2p3/2 and 461.2 eV and 455.3 eV corresponding to Ti-C 2p^{1/2} and Ti-C 2p^{3/2}, respectively. This result is in agreement with the HRTEM ones described above.

Photocatalytic mechanism and the band structure

To further understand the enhanced photocatalytic performance of the CMn series composites compared to CM0, we conducted a series of characterization studies. The Mott-Schottky analysis was first performed to evaluate the flat-band potential

and Fermi levels of CM0 and CM1 prepared from ISC-25-4'-NH₂. 45-47 As shown in Fig. 8a, the flat-band potentials of CM0 and CM1 were calculated to be -0.87 V and -0.26 V (versus NHE, pH = 7), which were directly treated as Fermi levels since the surface Fermi levels are very close to the flat-band potential. 48,49 To further determine the valence band (VB) and E_{σ}^{50} of CM0 and CM1, XPS valence band spectroscopy (VB-XPS) and solid-state UV-vis diffuse reflectance spectroscopy were also carried out. From the VB-XPS results (Fig. 8c and d), the VB positions of CM0 and CM1 were determined to be 1.44 eV and 0.96 eV relative to the Fermi level, 51 which indicates that the VB positions of CM0 and CM1 are 0.57 V and 0.70 V (versus NHE, pH = 7), respectively. The band gaps of CM0 and CM1 were found to be 3.27 eV and 3.26 eV, respectively, according to Fig. 8b. The corresponding conduction bands (CB) edges of CM0 and CM1 were calculated to be -2.70 V and -2.56 V (versus NHE, pH = 7), respectively, by combining the CB = E_g – VB equation.⁵²

Based on the above analysis, we proposed a photocatalytic mechanism for illustrating the higher PHE performance of the CMn series composites, as shown in Fig. 9. After P1-CNPs combined with the $Ti_3C_2T_x$ nanosheets to form a binary complex, the Fermi level of CM1 shifted upwards relative to CM0. The Mott-Schottky curve in Fig. 8a shows that P1-CNPs are n-type semiconductors and their flat-band potential is much more negative than that of the $Ti_3C_2T_x$ nanosheets, so the close contact between the two components in CM1 results in the transfer of electrons from the P1-CNPs to the Ti₃C₂T_x nanosheets. This is evidenced by the flat-band potential correction (-0.10 V vs. NHE) in CM1 compared to CM0, suggesting that the Fermi level of P1-CNPs in CM1 decreases upon their binding to $Ti_3C_2T_x$. A similar situation was reported in the studies of Jakob53 and Ran.46 Furthermore, the immobilized positive charges in the P1-CNPs are near the P1-CNPs/

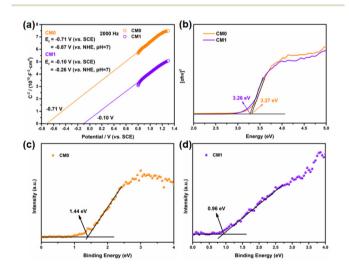


Fig. 8 (a) Mott-Schottky plots of ISC-25-4'-NH2 derived P1-CNPs (i.e. CM0) and CM1 composites: (b) solid-state UV-vis diffuse reflectance spectra of CMO and CM1; (c and d) valence band XPS spectra of CMO (c) and CM1 (d).

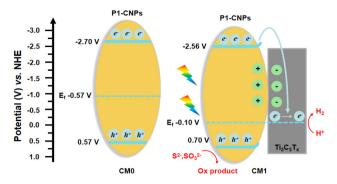


Fig. 9 Proposed schematic diagram of the photocatalytic mechanism for CM0 and CM1 under light irradiation.

Ti₃C₂T_x interface, where a space charge layer (or internal electric field) is formed and the CB and VB in the P1-CNPs are bent "upwards", thus forming a Schottky junction between them. Under full-spectrum solar irradiation, electrons are excited from the VB of the P1-CNPs to the CB, and due to the reduced thickness of the space charge layer in the P1-CNP particles, photogenerated electrons in the CB can still migrate through the "upward" bent CB to the Fermi level of Ti₃C₂T_x, leaving photogenerated holes in the VB of P1-CNPs. The previously mentioned formation of Schottky junctions can act as electron traps for trapping photogenerated electrons without blocking the transfer of electrons from P1-CNPs to $Ti_3C_2T_x$. Start the transfer of electrons to the $Ti_3C_2T_x$ nanosheets through the above pathway, the excellent electrical conductivity of Ti₃C₂T_x allows electrons to quickly shuttle to the surface. As a result, based on the excellent HER capabilities of Ti₃C₂T_x, the CMn series composites achieved more efficient PHE performance compared to pure P1-CNPs.

Conclusions

In summary, we proposed a strategy for disulfide bond cleavage to prepare discrete MCSCs with multiple active/inactive modified functional groups. Furthermore, three models with different structures were tested for their dispersibility, binding strength with MXene nanosheets, and photocatalytic hydrogen generation performance. The results showed that the aminomodified clusters had better performance than ligand-free type ones. This work provides insights for the subsequent design and synthesis of other types of discrete MCSCs with active functional groups, and is expected to have long-term implications for the functional expansion of metal chalcogenide cluster-based nanomaterials.

Author contributions

Jin Wu: Investigation, writing - original draft, and writing review & editing. Qiang Fu and Zixin Wu: TEM image testing. Peipei Sun: data curation. Xing Zhu and Ying Wang: HRTEM

and SAED testing. Ning Chen: funding acquisition. Tao Wu: Writing - review & editing, supervision, project administration, and funding acquisition.

Conflicts of interest

The authors declare no competing financial interests.

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