Ligand-triggered electrostatic self-assembly of CdS nanosheet/Au nanocrystal nanocomposites for versatile photocatalytic redox applications†

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A facile and efficient ligand-triggered electrostatic self-assembly strategy has been developed to fabricate a series of Au–CdS nanosheet (Ns) (Au–CdS Ns) nanocomposites with varied weight addition ratios of Au nanoparticles (NPs) by judiciously utilizing the intrinsic surface charge properties of assembly units, through which uniform dispersion and controllable deposition of Au NPs on the CdS Ns were achieved. Versatile probe reactions including photocatalytic oxidation of an organic dye pollutant, selective photocatalytic reduction of aromatic nitro compounds and photocatalytic hydrogen production reactions under visible light irradiation and ambient conditions were used to systematically evaluate the photoredox performances of the as-assembled well-defined Au–CdS Ns nanocomposites. It was unveiled that the photoactivities of Au–CdS Ns nanocomposites strongly depend on the weight addition ratio of Au NPs and the addition of an excess amount of Au NPs is detrimental to the separation of photogenerated charge carriers from CdS Ns. With the optimum addition amount of Au NPs (1 wt%), it was found that spontaneous assembly of Au NPs on the CdS Ns remarkably prolonged the lifetime of the photogenerated charge carriers from CdS Ns under visible light irradiation, thus resulting in significantly enhanced photocatalytic redox activities of Au–CdS Ns nanocomposites compared with those of CdS Ns. The crucial role of Au NPs in the photoredox reactions as efficient electron traps rather than plasmonic sensizers was determined. Moreover, predominant active species responsible for the photocatalytic process were unambiguously determined and a possible photocatalytic mechanism was elucidated. It is anticipated that our work could open up a new avenue to rationally prepare various 2D semiconductors–metal nanocomposites by utilizing such a simple and efficient self-assembly strategy for extensive photocatalytic applications in a myriad of fields.

1. Introduction

Semiconductor-based photocatalysis has been attracting a great deal of interest owing to its universal applications especially in the utilization of solar energy, environmental remediation and selective organic transformations to fine chemicals.1–4 Among a large variety of semiconductor materials, CdS, a well-known II–VI semiconductor, has attracted particular attention due to its suitable bandgap (2.4 eV) which corresponds well with the solar spectrum, and size-dependent electronic and optical properties, and thus recent years have witnessed their wide-ranging applications in a myriad of fields such as hydrogen production, environmental remediation, and solar cells.5–7 Nonetheless, utilization of CdS nanomaterials is limited by several issues, e.g., agglomeration is frequently observed in conventional CdS nanomaterials giving rise to a reduced specific surface area. Moreover, the high recombination rate of photogenerated electron–hole pairs and relatively poor photostability of CdS nanomaterials further restricts their wide-spread applications. In this regard, various strategies have been developed to surmount these obstacles, such as deposition of noble metal nanoparticles (NPs), integrating with the second semiconductor components or carbon materials, and forming p–n heterojunctions.8–13

It has been well-established that charge transport in CdS nanomaterials is substantially affected by the presence of...
surface defect states which can serve as charge traps leading to a fast recombination of photogenerated charge carriers.\textsuperscript{14,15} To solve this problem, coupling of Cds with metal nanocrystals (NCs) (e.g., Au, Ag, Pd, Pt, etc.) has been considered as an effective approach to suppress the recombination of photogenerated charge carriers by either utilizing the surface plasmon resonance (SPR) effect of metal NCs to enhance their light-harvesting efficiency in the visible region or constructing the Schottky barriers to facilitate the transfer of photogenerated charge carriers.\textsuperscript{8,16–23} More importantly, deposition of metal NCs on Cds could not only provide a heterojunction interface but also passivate Cds surface defects upon contact. Among plentiful metal NCs, Au NCs have been deemed as one of the most efficient metal NCs with fascinating catalytic activities.\textsuperscript{24–26} Thus far, a new class of Au–Cds nanocomposites has been prepared by combining the substantial light-harvesting properties of Cds with the catalytically active Au NCs for photocatalytic applications.\textsuperscript{27–30} It has been ascertained that monodispersion of Au NCs on the Cds surface in conjunction with their intimate interfacial interaction are two key factors affecting the photocatalytic performances of Au–Cds nanocomposites.\textsuperscript{15} To this end, various synthetic strategies have been developed to prepare Au–Cds nanocomposites but most of which are generally confined to conventional methods such as photo-reduction, deposition-precipitation, spray pyrolysis, sol-gel and electrochemical approaches.\textsuperscript{8,29–36} For example, Khon et al.\textsuperscript{36} reported the synthesis of Au/Cds nanocomposites with a tunable morphology through temperature-controlled reduction of gold-oleate complexes. Kumar et al.\textsuperscript{23} reported an in situ synthesis of Au–Cds hybrid nanoparticles using a simple continuous spray pyrolysis method.\textsuperscript{33} Most recently, Majeed et al.\textsuperscript{37} reported a novel iodide reduction method to prepare Au/Cds nanocomposites with the initial mean Au particle size between 2 nm to 5 nm.\textsuperscript{8} Despite the endeavors, rational construction of Au–Cds nanocomposites with a controllable deposition amount and monodispersivity of Au via a facile and green approach still constitutes a long-standing challenge by virtue of the large lattice mismatch between Au and Cds.\textsuperscript{37}

On the other hand, in recent years, 2D transition-metal compounds have received tremendous attention due to their unique electronic, geometric, and physical-chemical properties in comparison with the corresponding bulk materials.\textsuperscript{38–40} In particular, 2D semiconductors have been widely synthesized and utilized as photocatalysts for solar energy conversion and environmental remediation.\textsuperscript{41–43} Inspired by this and enlightened by the intrinsic structural merits of ultra-thin 2D Cds nanosheets (Cds Ns), it is thus highly desirable to judiciously integrate Cds Ns with Au NCs in a close integration manner which would take full advantage of the synergistic interaction between them giving rise to promising photocatalytic performances.

Herein, a facile and efficient electrostatic self-assembly method has been developed to rationally fabricate well-defined Au–Cds Ns nanocomposites by directly harnessing the intrinsic surface charge properties of assembly units (i.e., Cds Ns@[L-cysteine and Au@[4-dimethylaminopyridine]), based on which positively charged Au@4-dimethylaminopyridine (Au@DMAP) NPs were spontaneously and uniformly deposited on the negatively charged Cds Ns@[L-cysteine by the pronounced electrostatic attractive interaction. It was revealed that the thus-assembled Au–Cds Ns nanocomposites demonstrated versatile and significantly enhanced photoredox performances including photocatalytic oxidation of an organic dye pollutant, photocatalytic reduction of aromatic nitro compounds and photocatalytic hydrogen production under visible light irradiation in comparison with Cds Ns, owing predominantly to the synergistic interaction between Au and Cds Ns. The Au component in the nanocomposites played a crucial role as efficient electron traps rather than plasmonic photosensitizers in the photocatalytic reaction, thereby boosting the lifetime of the photogenerated electron–hole pairs from Cds Ns. Moreover, predominant active species responsible for the photocatalytic process were determined and a specific photocatalytic mechanism was elucidated. It is hoped that our work could open up a new and general synthetic concept to prepare various metal–semiconductor nanomaterials by such a facile and efficient ligand-triggered self-assembly approach for extensive photocatalytic applications.

2. Experimental section

2.1 Materials

Cadmium chloride (CdCl\(_2\)-2.5H\(_2\)O), L-cysteine, sodium hydroxide, toluene, sodium sulfate anhydrous, sodium sulfide nonahydrate, benzoquinone (BQ), tert-butyl alcohol (TBA) and sulfuric acid were purchased from Xilong Chemical Co., Ltd. Sulfur, N,N-dimethylformamide, potassium bromide, 4-nitroaniline (4-NA), 2-nitroaniline (2-NA), 4-nitrotoluene (4-NT), 4-nitrophenol (4-NP) and sodium borohydride were purchased from Sinopharm group Co., Ltd. Diethylenetriamine, 4-dimethylaminopyridine (DMAP), 3-nitroaniline (3-NA), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP) and chloroacetic acid were purchased from Aladdin. Tetraoctyl ammonium bromide (TOAB) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were purchased from Xiya Reagent and Sigma, respectively. Deionized water (DI H\(_2\)O, 18.2 M\(_\Omega\) cm) was produced by Millipore. All reagents were of AR grade and used without further purification.

2.2 Preparation of Cds Ns

In a typical synthetic process,\textsuperscript{5} 0.32 mmol CdCl\(_2\)-2.5H\(_2\)O, 2.0 mmol S powder and 12 mL of diethylenetriamine (DETA) were mixed and vigorously stirred for 30 min to form a homogeneous suspension. The mixture was transferred to a Teflon-lined autoclave (20 mL) and heated at 80 °C for 48 h. After being cooled down to room temperature naturally, a light yellow precipitate was collected by centrifugation and washed with ethanol/H\(_2\)O (V : V = 1 : 1) three times. The obtained light yellow powder (Cds-DETA) was dried in an oven at 60 °C for 24 h. After that, 20 mg CdS-DETA, 10 mg L-cysteine, 0.1 mL of DETA and 40 mL of DI H\(_2\)O were added into a beaker (100 mL)
and ultra-sonicated continuously for 2 h under ambient conditions. The resultant yellow suspension was centrifuged at 800 rpm for 10 min to remove the large aggregates and the supernatant (top four-fifth of the centrifuged suspension) was collected to obtain the ultrathin CdS Ns suspension. Subsequently, the ultrathin CdS Ns suspension was centrifuged at 10,000 rpm for 10 min and washed with DI H2O 3 times to remove free l-cysteine and DETA. Finally, the sample was re-dispersed in DI H2O and the concentration of the thus-obtained CdS Ns was ca. 1.8 mg mL−1.

2.3 Preparation of Au NPs

30 mL of 30 mM HAuCl4 aqueous solution was added to 80 mL of 25 mM TOAB toluene solution. Afterwards, 25 mL of freshly prepared 0.4 M NaBH4 aqueous solution was rapidly added to the mixture under vigorous stirring. After 30 min the toluene phase was washed with 0.1 M H2SO4, 0.1 M NaOH and DI H2O three times, respectively, and dried with anhydrous Na2SO4. 1 mL of 0.1 M 4-dimethylaminopyridine (DMAP) aqueous solution was gradually added into 1 mL of the Au NP mixtures, by which direct phase transfer across the organic/aqueous boundary was completed within 1 h without stirring or agitation to obtain Au NP aqueous suspension.49

2.4 Self-assembly of Au–CdS Ns nanocomposites

10 mL of CdS Ns aqueous suspension and different weight addition ratios of Au@DMAP NPs (Au/CdS Ns = 0.5, 1.0 and 2.0 wt%) were mixed and stirred for 3 h to trigger the self-assembly process under ambient conditions. Subsequently, the mixture was filtered and washed with DI H2O 3 times to remove the free organic molecules and the yellow precipitate obtained was dried in an oven at 80 °C for 12 h. Finally, CdS Ns and Au–CdS Ns nanocomposites were sintered in a furnace at a heating rate of 5 °C min−1 and kept at 300 °C for 30 min. Au–CdS Ns nanocomposites with different Au/CdS Ns weight addition ratios of 0, 0.5, 1.0 and 2.0 wt% were labeled as CdS Ns, 0.5Au–CdS Ns, 1Au–CdS Ns and 2Au–CdS Ns, respectively.

2.5 Characterization

X-ray diffraction (XRD) analysis was carried out by using a Philips Panalytical X’pert PRO with Cu-Kα radiation at λ = 0.1542 nm. XRD patterns were recorded with a scan step of 1° min−1 (2θ) in the range from 20° to 80°. Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed on a Nicolet 6700 equipped with a MCT/A detector. X-ray photoelectron spectroscopy (XPS) measurements were collected on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4 × 10−10 mbar using a monochromatic Al Kα X-ray beam (1486.60 eV). The binding energy was calibrated with respect to C (1s) at 284.6 eV. UV-Vis diffuse reflectance spectra (DRS) were obtained using a UV-Visible spectrophotometer (Macylab UV-1800A). Photoluminescence (PL) measurements were carried out on a F97 (Lengguang Tech.) fluorescence photometer with an exciting wavelength of 375 nm. Zeta potential was determined by electrophoretic light scattering (ELS) with Zetaplus (Brookhaven Instruments Corporation, Holtsville, NY, USA). Transmission electron microscopy (TEM) images were taken by using a JEOL JEM-1400 and Higher-Resolution TEM (HRTEM) images were taken by using JEM 2100 and F30. The morphology and elemental mapping of the samples were determined by scanning electron microscopy (SEM, Sigma HD). Specific surface areas were determined by a Brunauer–Emmett–Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micromeritics Instrument Corporation sorption analyzer (TriStar II3020). Photoelectrochemical (PEC) measurements were performed on an electrochemical workstation (CHI 660D). The electrochemical setup was composed of a conventional three-electrode system, a quartz cell containing 20 mL of Na2SO4 (0.2 M) aqueous solution, and a potentiostat. A platinum plate (8 × 18 mm) was used as a counter electrode and Ag/AgCl/KCl as a reference electrode. The sample films with active area (0.2 cm²) were vertically dipped into the electrolyte and irradiated with a 300 W Xenon arc lamp with a UV cutoff filter (λ ≥ 420 nm).

2.6 Photocatalytic activity measurements

Photocatalytic activities of different samples were evaluated by photocatalytic degradation of methylene blue (MB) under visible light irradiation (λ ≥ 420 nm) and ambient conditions. A 300 W Xe lamp (CEL-HXF300, 15A) equipped with a 420 nm cut-off filter was used as the light source and held 25.0 cm away from the glass reactor. 5 mg of the photocatalyst was dispersed in 50 mL of 10 ppm MB aqueous solution and the concentration of the photocatalyst was 0.1 mg mL−1. Before light irradiation, the suspension was stirred and kept in the dark for 6 h to achieve the adsorption–desorption equilibrium between the photocatalyst and MB. After that, the suspension was irradiated with visible light (λ ≥ 420 nm) and 2.5 mL of the sample solution was collected and centrifuged every 0.5 h for analysis. The concentration of MB was determined using a UV-Vis spectrophotometer by monitoring the variation of peak absorbance at 664 nm. To obtain the appearance quantum efficiency (AQE), photocatalytic activities of different samples were also measured under the same experimental conditions except for using the monochromatic light with different wavelengths (i.e., 380, 420, 450, 500, 550, 600 and 700 nm) as the light source.

2.7 Determination of the active species in the photocatalytic process

2.7.1 Detection of active species by quenching experiments.50,51 Quenching experiments were conducted under the same experimental conditions as that of the photodegradation reactions except for adding 1.0 mM scavengers in the reaction system. Different scavengers such as benzoquinone, tert-butyl alcohol, ammonium oxalate and K2S2O8 were utilized as the scavengers for quenching superoxide radicals (O2−), hydroxyl radicals (OH·), holes (h+) and electrons (e−), respectively.

2.7.2 Detection of hydroxyl radicals (OH·).52 In a typical process, 5 mg different samples was dispersed in 50 mL of a mixed solution of terephthalic acid (0.8 mM) and NaOH...
(0.4 mM) and then the suspension was irradiated with visible light ($\lambda \geq 420$ nm). At different time intervals (0, 30, 60, 90, 120, 150 and 180 min), 3 mL of the sample suspension was centrifuged (8000 rpm, 10 min) and finally 2.5 mL of the transparent solution was collected for PL measurement. The concentration of hydroxyl terephthalate anion was determined by using a F97 (Lengguang Tech.) fluorescence photometer with an excitation wavelength of 320 nm.

2.7.3 Detection of superoxide radicals (O$_2^{-}$) using electron paramagnetic resonance (EPR). Electron paramagnetic resonance spectra of spin-trapped radicals with 5,5-diemthyl-1-pyrroline N-oxide (DMPO) were recorded by using a BrukerEMX-10/12 spectrometer. Briefly, 5 mg of the sample was dispersed in 0.5 mL of methanol for the detection of superoxide radicals, into which 20 µL DMPO–methanol mixed solution (V : V = 1 : 10) was added. A 300 W Xe lamp (15 A, Microsolar 300, Perfect light, Beijing) equipped with a 420 nm-cut-off optical filter ($\lambda \geq 420$ nm) was used as the light source. The settings for the EPR spectrometer were as follows: center field = 3370 G, microwave frequency = 9.450343 GHz and power = 20.21 mW.

2.8 Photocatalytic reduction of aromatic nitro compounds

For anaerobic photocatalytic reduction of 4-nitroaniline (4-NA) under an inert atmosphere ($\text{N}_2$), a 300 W Xe lamp (CEL-HXF300, 15A) equipped with a 420 nm-cut-off filter ($\lambda \geq 420$ nm) was used as the light source and was kept 25.0 cm away from the glass reactor. 10 mg photocatalyst and 40 mg NH$_4$HCO$_3$ were mixed with 30 mL of 4-NA aqueous solution (20 mg L$^{-1}$) in a glass reactor under N$_2$ bubbling. Before light irradiation, the suspension was stirred and kept in the dark for 1 h to achieve the adsorption–desorption equilibrium between the photocatalyst and 4-NA. After that, the suspension was irradiated with visible light ($\lambda \geq 420$ nm). At different time intervals (0, 5, 10, 15, 20, 25, 30 and 35 min), 3 mL of the sample solution was collected, centrifuged (12 000 rpm) and analyzed on a UV-Vis spectrophotometer (Maqylab UV-1800A). Alternatively, photo reduction of other aromatic nitro compounds, including 3-NA, 2-NA, 4-NP, 3-NP, 2-NP and 4-NT were also carried out and their photoreduction activities were measured under the same experimental conditions.

2.9 Photocatalytic hydrogen production

Photocatalytic H$_2$ production reactions were carried out on an online photocatalytic hydrogen production system (Lab Solar-IIAG, Perfect Light, Beijing). 50 mg of the sample was dispersed by ultrasonication in 100 mL of aqueous solution containing 0.25 M Na$_2$S and 0.25 M Na$_2$SO$_3$ as sacrificial reagents in a reaction cell. The suspension solution was degassed for 30 min to remove air completely before light irradiation. Then, the solution was irradiated by using a 300 W Xe lamp (15 A, Micro solar 300, Perfect light, Beijing) equipped with a 420 nm-cut-off optical filter ($\lambda \geq 420$ nm). The H$_2$ evolution amount was determined using an online gas chromatograph (GC-2018, TCD).

3. Results and discussion

Scheme 1 illustrates the spontaneous ligand-triggered self-assembly process for fabricating Au–CdS Ns nanocomposites by mediating the intrinsic surface charge properties of CdS Ns and Au NP assembly units. It should be emphasized that the CdS Ns are capped by a large amount of L-cysteine molecules which afford plentiful carboxyl functional groups on the surface and thus the deprotonation of these carboxyl groups endows CdS Ns with a pronounced negatively charged surface. This can be corroborated by the zeta potential ($\zeta$ = −15.4 mV, Fig. S1†) and Fourier Transform Infrared Spectroscopy (FTIR) results (Fig. S2†) of CdS Ns. On the other hand, with regard to Au NPs which are protected by DMAP molecules, partial protonation of exocyclic nitrogen atoms in the DMAP linker give rise to a positively charged surface of Au@DMAP, which can also be mirrored by the zeta potential ($\zeta$ = +14.2 mV, Fig. S1†) and FTIR results (Fig. S2†). Hence, when these two assembly units are mixed together, positively charged Au@DMAP NPs are able...
to be spontaneously and rapidly attracted onto the negatively charged CdS Ns@α-cysteine surface by substantial electrostatic interaction resulting in Au–CdS Ns nanocomposites. With a view to reinforce the interfacial contact between Au and CdS Ns and removing the organic moieties capped on their surfaces, Au@DMAP/CdS Ns nanocomposites were finally calcined at low temperature yielding the well-defined Au–CdS Ns nanocomposites.

3.1 Characterization of Au–CdS Ns nanocomposites

Crystalline phases of different samples are determined by the X-ray diffraction (XRD) technique. As shown in Fig. 1, the peaks at 2θ values of 24.8, 26.6, 28.2, 43.7, 47.9 and 51.8° can be accurately indexed to the (100), (002), (101), (110), (103) and (112) crystallographic planes of the hexagonal structure of CdS (JCPDS 77-2306), respectively.31 It is worth noting that no obvious Au diffraction peaks are observed in the XRD pattern of 0.5Au–CdS Ns nanocomposites, which is probably due to the low weight addition percentage of Au NPs in the nanocomposites.36 When the weight addition percentage of Au NPs was increased to 2 wt% an obvious distinctive peak at 38.1° is clearly observed and it can be attributed to the (111) crystal plane of cubic-phase Au (JCPDS 089-3697). Therefore, XRD results indicate that Au NPs have been successfully assembled on the CdS Ns frameworks via the electrostatic self-assembly approach.

The microstructure and morphology of Au NPs, CdS Ns and 1Au–CdS Ns nanocomposites were explored by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Fig. 2a shows the TEM image of Au@DMAP NPs, from which it is clear to see that Au@DMAP NPs demonstrate good monodispersity and uniform particle size of ca. 4.0 nm (Fig. S3†). TEM (Fig. 2b) and panoramic scanning electron microscopy (SEM) images (Fig. S4†) of CdS Ns reveal the typical ultrathin nanosheet-like structure with several hundred nanometers.49 Additionally, AFM results reveal that the CdS Ns possess a thickness of ca. 4 nm (Fig. S5†), which is consistent with previous result. As shown in the TEM image of the 1Au–CdS Ns nanocomposite (Fig. 2b and c), Au NPs are uniformly attached on the CdS Ns substrate without agglomeration, suggesting that the self-assembly strategy developed is efficient in fabricating Au–CdS Ns nanocomposites. Notably, the Au NPs’ size on the CdS Ns is retained after calcination, revealing the substantial interfacial integration between Au NPs and CdS Ns, which prevents the agglomeration of Au NPs. This speculation can be confirmed by the HRTEM image, as displayed in Fig. 2d, wherein the lattice fringe spacings of 0.235 and 0.34 nm are attributed to the (111) and (100) crystal planes of Au NCs and hexagonal CdS nanocomposites, respectively. The monodispersed dispersion of Au NPs on the CdS Ns can also be evidenced by the HAADF-STEM result of the 1Au–CdS Ns nanocomposite. As manifested by the elemental mapping results in Fig. 3(b–d), Cd, S, and especially Au elements are uniformly distributed on the surface of 1Au–CdS nanocomposites, suggesting that Au NPs are evenly distributed on the whole CdS Ns substrate. Therefore, TEM, HAADF-STEM and elemental mapping results concurrently certify the monodispersion of Au NPs on the CdS Ns through electrostatic self-assembly buildup.

The composition and elemental chemical states of 1Au–CdS Ns nanocomposites were analyzed by X-ray photoelectron spectroscopy (XPS). Fig. 4a shows the survey XPS spectrum of 1Au–CdS Ns nanocomposites which is mainly composed of Cd, S and Au core-elements. The relatively weak peak intensity of the Au signal is mainly due to the relatively low weight addition ratio of Au NPs on the CdS Ns. More specifically, Fig. 4b demonstrates the high-resolution spectrum of Au 4f which discloses doublet peaks at 83.9 and 87.6 eV originating from the spin orbital splitting of Au 4f7/2 and Au 4f5/2 states,8,54 thereby revealing that the Au element in the 1Au–CdS Ns nanocomposite exists in the form of metallic.

Fig. 2 TEM images of (a) Au NPs, (b) CdS Ns, (c) 1Au–CdS Ns nanocomposite, and (d) HRTEM image of the 1Au–CdS Ns nanocomposite.
Au (Au\(^0\)). Moreover, as shown in Fig. 4c, two substantial peaks at 405.8 and 412.5 eV corresponding to Cd 3d\(^{5/2}\) and Cd 3d\(^{3/2}\) are observed in the high-resolution spectrum of Cd 3d for 1Au–CdS Ns nanocomposites, both of which correspond to the Cd element in the oxidation state of +2 (Cd\(^{2+}\)).\(^{55,56}\) Consistently, the peak at 161.6 eV corresponding to the S 2p\(^{3/2}\) spin–orbit in the high-resolution spectrum of S 2p (Fig. 4d) manifests that the S element is in the valence state of −2 (S\(^{2-}\)).\(^{56–58}\) Besides, successful removal of organic moieties in the interfacial domain of nanocomposites can be reflected by the high-resolution spectra of C 1s and O 1s (Fig. S6†). As a result, XPS results indicate that elemental chemical states of the elements in Au–CdS Ns nanocomposites are retained after self-assembly and they are in faithful agreement with the chemical states of individual components.

The optical properties of CdS Ns and Au–CdS Ns nanocomposites with different weight addition ratios were probed by UV-Vis diffuse reflectance spectra (DRS). As shown in Fig. 5, both CdS Ns and Au–CdS Ns nanocomposites exhibit a pronounced characteristic absorption peak at ca. 475 nm in the visible region owing predominantly to the band-gap photoexcitation of CdS. Moreover, it is apparent that the absorption intensity of the peak (475 nm) in Au–CdS Ns nanocomposites gradually increases with the increasing weight addition ratio of Au NPs in the visible region ranging from 400 to 800 nm, which may be caused by the attachment of Au NPs for achieving enhanced light-harvesting efficiency.\(^{34}\) Noteworthily, no obvious SPR peak but rather a weak and relatively broad peak was observed in the DRS results of Au–CdS Ns nanocomposites, which may be ascribed to the ultra-small size of Au NPs (Fig. S7†).\(^{34,59}\)

The specific surface area and porous structure of CdS Ns and 1Au–CdS Ns nanocomposites were investigated by BET measurements (Fig. S8†). The specific surface areas of CdS Ns and 1Au–CdS Ns nanocomposites are determined to be 54.6 and 36.9 m\(^2\) g\(^{-1}\), respectively. The reduction in specific surface area might be attributed to the occupation of active sites in the pores of CdS Ns by Au NPs, which is consistent with pore size distribution results in Fig. S8b.†

### 3.2 Photocatalytic oxidation performances

Photocatalytic performances of different samples were evaluated by degradation of methylene blue (MB), a frequently seen organic dye pollutant, under ambient conditions and visible light irradiation (\(\lambda \geq 420\) nm). As displayed in Fig. 6a, photocatalytic performances of Au–CdS Ns nanocomposites increase with the increasing weight addition ratios of Au NPs. However, when the weight addition percentage of Au NPs is increased to 2 wt%, photocatalytic activity decreases, which can probably be...
attributed to the increased surface defects formed at the interfacial region of Au–CdS Ns nanocomposites acting as electron–hole recombination centres. Nonetheless, note that all Au–CdS Ns nanocomposites demonstrate remarkably enhanced photocatalytic activities as compared with blank CdS Ns under the same experimental conditions. Among the Au–CdS Ns nanocomposites with varied weight addition ratios of Au NPs, the 1Au–CdS Ns nanocomposite exhibits the optimal photocatalytic activity, indicating that the photoactivities of Au–CdS Ns nanocomposites are heavily dependent on the loading amount of Au NPs. The reaction rate constants calculated based on the first-order-kinetic model ($\ln(C_0/C) = kt$) are determined to be 0.0058, 0.0079, 0.0088 and 0.0076 min$^{-1}$ for CdS Ns, 0.5Au–CdS Ns, 1Au–CdS Ns and 2Au–CdS Ns nanocomposites, respectively. It is worth noting that the reaction rate constant of 1Au–CdS Ns is around 51.7% higher than that of CdS Ns, highlighting the pivotal role of Au NPs in improving the photocatalytic performances of Au–CdS Ns nanocomposites. The dominant active species responsible for the photocatalytic performances of 1Au–CdS Ns nanocomposites were determined by quenching experiments by adding different scavengers, PL and electron paramagnetic resonance (EPR) measurements. Fig. 6d shows the photocatalytic activities of 1Au–CdS Ns nanocomposites with the addition of benzoquinone (BQ), tert-butyl alcohol (TBA), ammonium oxalate (AO), and potassium persulfate ($K_2S_2O_8$) as scavengers for quenching superoxide radicals ($O_2^{•−}$), hydroxyl radicals ($OH^{•}$), holes ($h^+$) and electrons ($e^{−}$), respectively. It is clearly seen that no obvious decrease in the photoactivities of 1Au–CdS Ns nanocomposites was observed by adding AO and $K_2S_2O_8$ as the scavengers as compared with its pristine photocatalytic activity without adding any scavengers, indicating that holes and electrons are not the direct active species involved in the photodegradation of MB but rather transform into other various active species. However, photoactivities of 1Au–CdS Ns nanocomposites significantly decrease with the addition of 12.5% vs. 28.6%, respectively. The results strongly indicate that monodisperse deposition of Au NPs on the CdS Ns via the ligand-triggered electrostatic self-assembly approach is beneficial for boosting the photostability of CdS Ns. It is possible that the photoexcited holes in situ formed in the valence band (VB) of CdS Ns in the nanocomposite can be more efficiently transferred to other reaction sites and meanwhile be transformed into other active species instead of directly oxidizing CdS Ns, thus resulting in improved photostability of 1Au–CdS Ns nanocomposites.

attributed to the increased surface defects formed at the interfacial region of Au–CdS Ns nanocomposites acting as electron–hole recombination centres. Nonetheless, note that all Au–CdS Ns nanocomposites demonstrate remarkably enhanced photocatalytic activities as compared with blank CdS Ns under the same experimental conditions. Among the Au–CdS Ns nanocomposites with varied weight addition ratios of Au NPs, the 1Au–CdS Ns nanocomposite exhibits the optimal photocatalytic activity, indicating that the photoactivities of Au–CdS Ns nanocomposites are heavily dependent on the loading amount of Au NPs. The reaction rate constants calculated based on the first-order-kinetic model ($\ln(C_0/C) = kt$) are determined to be 0.0058, 0.0079, 0.0088 and 0.0076 min$^{-1}$ for CdS Ns, 0.5Au–CdS Ns, 1Au–CdS Ns and 2Au–CdS Ns nanocomposites, respectively. It is worth noting that the reaction rate constant of 1Au–CdS Ns is around 51.7% higher than that of CdS Ns, highlighting the pivotal role of Au NPs in improving the photocatalytic performances of Au–CdS Ns nanocomposites. The dominant active species responsible for the photocatalytic performances of 1Au–CdS Ns nanocomposites were determined by quenching experiments by adding different scavengers, PL and electron paramagnetic resonance (EPR) measurements. Fig. 6d shows the photocatalytic activities of 1Au–CdS Ns nanocomposites with the addition of benzoquinone (BQ), tert-butyl alcohol (TBA), ammonium oxalate (AO), and potassium persulfate ($K_2S_2O_8$) as scavengers for quenching superoxide radicals ($O_2^{•−}$), hydroxyl radicals ($OH^{•}$), holes ($h^+$) and electrons ($e^{−}$), respectively. It is clearly seen that no obvious decrease in the photoactivities of 1Au–CdS Ns nanocomposites was observed by adding AO and $K_2S_2O_8$ as the scavengers as compared with its pristine photocatalytic activity without adding any scavengers, indicating that holes and electrons are not the direct active species involved in the photodegradation of MB but rather transform into other various active species. However, photoactivities of 1Au–CdS Ns nanocomposites significantly decrease with the addition of
BQ and TBA as the scavengers, which indicates that $\text{O}_2^{2-}$ and $\text{OH}^-$ radicals are the predominant active species responsible for the photodegradation process. Among which, $\text{O}_2^{2-}$ radicals mainly originate from the trapping of photogenerated electrons by molecular oxygen dissolved in the reaction system. There are generally two pathways to produce OH$^-$ radicals: one involves the direct oxidation of $\text{H}_2\text{O}$/or –OH with holes and the other involves the transformation of $\text{O}_2^{2-}$ radicals via a series of intermediate reactions into OH$^-$ radicals.57

The formation of OH$^-$ radicals during the photocatalytic process for 1Au–CdS Ns nanocomposites can be further verified by photoluminescence (PL) spectra using terephalic acid (TA) as the probing molecule. As shown in Fig. 7a, the characteristic PL peak intensity of TA at ca. 440 nm gradually increases with the increasing irradiation time and the peak intensity is proportional to the irradiation time (Fig. 7a, inset), which strongly confirms the formation of OH$^-$ radicals over 1Au–CdS Ns nanocomposites in the photocatalytic reaction system.60 Furthermore, the EPR result of 1Au–CdS Ns nanocomposites (Fig. 7b) also corroborates the presence of the $\text{O}_2^{2-}$ signal ($g_{zx} = 2.025$, $g_{yy} = 2.009$, $g_{xx} = 2.003$) in the reaction system acting as the primary active species.61

3.3 Probing the separation efficiency of photogenerated electron–hole pairs

To evaluate the separation of photogenerated electron–hole charge carriers on the interfacial domain of CdS Ns and 1Au–CdS Ns nanocomposites, photoelectrochemical (PEC) measurements under visible light irradiation were conducted.62 Fig. 8a shows the on–off transient photocurrent responses of CdS Ns and 1Au–CdS Ns nanocomposites under visible light irradiation ($\lambda \geq 420 \text{ nm}$), from which it is obvious that 1Au–CdS Ns nanocomposites demonstrated significantly enhanced photocurrent density relative to CdS Ns, implying that the separation efficiency of photogenerated charge carriers over 1Au–CdS Ns nanocomposites is much higher than that of CdS Ns. Besides, 1Au–CdS Ns nanocomposites exhibited relatively high stability and only a slight decrease of photocurrent density was observed after 6 cycles. It is highly possible that photoelectrons produced on the conduction band (CB) of CdS Ns are able to transfer to the neighboring intimately contacted Au NPs component owing to the formation of Schottky barriers under visible light irradiation, thus enabling efficacious separation of photogenerated electron–hole pairs. In this case, Au NPs act as efficient electron collectors and traps to

![Fig. 7](a) Time-dependent PL spectra of TA aqueous solution containing 1Au–CdS Ns nanocomposites under visible light irradiation ($\lambda \geq 420 \text{ nm}$) with the inset showing the PL intensity of TA at 440 nm as a function of irradiation time and (b) EPR spectrum for detecting superoxide radicals ($\text{O}_2^{2-}$) in 1Au–CdS Ns nanocomposites under visible light irradiation ($\lambda \geq 420 \text{ nm}$).

![Fig. 8](a) On–off transient photocurrent responses and (b) electrochemical impedance spectroscopy Nyquist plots of CdS Ns and 1Au–CdS Ns nanocomposites under visible light irradiation ($\lambda \geq 420 \text{ nm}$) in a $\text{Na}_2\text{SO}_4$ (0.2 M) aqueous solution.
prolong the lifetime of electron–hole pairs.\textsuperscript{31} To assure this speculation, electrochemical impedance spectroscopy (EIS) measurements were further carried out under visible light irradiation.\textsuperscript{63} It has been well-established that the charge separation efficiency of the working electrode is closely associated with the semicircle radius of the Nyquist plot.\textsuperscript{57} Generally, a smaller semicircle radius indicates the more efficient separation of photogenerated charge carriers and vice versa.\textsuperscript{64} As reflected in Fig. 8b, the EIS Nyquist plots of 1Au–CdS Ns nanocomposites exhibits a smaller semicircle radius in the intermediate-frequency region as compared with that of CdS Ns, thus once again disclosing the much more efficient separation of the photogenerated electron–hole pairs over 1Au–CdS Ns nanocomposites.

Photoluminescence (PL) spectrum has been ascertained to be an effective tool to evaluate the separation of photogenerated charge carriers over semiconductors. In general, the lower PL intensity suggests a longer lifetime of photogenerated charge carriers and thus a reduced recombination rate.\textsuperscript{65} The PL emission spectra of CdS Ns and Au–CdS Ns nanocomposites are displayed in Fig. 9 and S11† which show that the PL intensity of 1Au–CdS Ns nanocomposites is remarkably lower than CdS Ns, indicative of the fact that the lifetime of the photogenerated charge carriers over CdS Ns is prolonged with the deposition of Au NPs.\textsuperscript{34,66,67} The substantial quenching of the PL peak of 1Au–CdS Ns nanocomposites is mainly due to the transfer of photoelectrons from the conduction band (CB) of CdS Ns to Au NPs, which is consistent with photocatalytic and PEC results.\textsuperscript{8,67,68}

To unveil the reasons accounting for the significantly enhanced photocatalytic performances of 1Au–CdS Ns nanocomposites, photocatalytic degradation of MB over CdS Ns and 1Au–CdS Ns nanocomposites under different monochromatic light irradiation (380, 420, 450, 500, 550, 600 and 650 nm) were performed. Apparent quantum efficiency (AQE) at each wavelength of monochromatic light, which was defined as the ratio of the number of decomposed MB molecules to the

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**Fig. 9** PL spectra of CdS Ns and 1Au–CdS Ns nanocomposites with an excitation wavelength of 375 nm.

**Fig. 10** AQE curve (right axis) with the corresponding UV-Vis diffuse reflectance spectrum (left axis) of 1Au–CdS Ns nanocomposites.

**Fig. 11** Photocatalytic performances of CdS Ns and 1Au–CdS Ns nanocomposites toward the reduction of aromatic nitro compounds including (a) 2-NA, (b) 3-NA, (c) 4-NA, (d) 2-NP, (e) 3-NP, (f) 4-NP, (g) 4-NT under visible light irradiation (λ ≥ 420 nm) with the addition of ammonium formate as a hole scavenger and nitrogen bubbling under ambient conditions, and (h) photocatalytic hydrogen evolution over CdS Ns and 1Au–CdS Ns nanocomposites under visible light irradiation (λ ≥ 420 nm).
number of incident photons, was used to describe the influence of wavelength on the photocatalytic activities of CdS Ns and 1Au–CdS Ns nanocomposites.69 As shown in Fig. 10, no obvious peak is observed in the AQE plot of 1Au–CdS Ns nanocomposites within the wavelength range of 500–600 nm and the result indicates that the SPR effect of Au NPs (Fig. S7†) does not contribute to the photocatalytic performance of 1Au–CdS Ns nanocomposites. Moreover, it is found that the AQE action spectrum of 1Au–CdS Ns is almost the same as that of CdS Ns (Fig. S12†), which highlights the crucial role of the photosensitization effect arising from CdS Ns in boosting the significantly enhanced photocatalytic performance of 1Au–CdS Ns nanocomposites.

### 3.4 Photocatalytic reduction performances

Apart from the aforementioned photocatalytic oxidation reaction toward the degradation of an organic dye pollutant, photoreduction performances of 1Au–CdS Ns nanocomposites including anaerobic photoreduction of a series of aromatic nitro compounds and photocatalytic hydrogen production under visible light irradiation (λ ≥ 420 nm) were also probed. It should be emphasized that the photogenerated holes are completely quenched by the scavengers in these two reactions systems and only photoelectrons are involved in the reactions. Photocatalytic reduction of 4-nitroaniline (4-NA) to 4-phenylenediamine (4-PDA) over CdS Ns and 1Au–CdS Ns nanocomposites is presented as a typical example, which is monitored by the UV-vis light absorption spectra. Prior to light irradiation, only one absorption peak at 380 nm corresponding to 4-NA is observed, while two new peaks at ca. 300 nm and 240 nm gradually arise with the progress of reaction which are attributed to the formation of 4-PDA, indicating the successful reduction of 4-NA to 4-PDA. Fig. S13† shows the time-dependent variations of the absorbance spectra of 4-NA catalyzed by CdS Ns, 1Au–CdS Ns nanocomposites and P25 as a function of irradiation time, from which it is apparent that the 1Au–CdS Ns nanocomposite exhibits more rapid decrease in the absorption intensity of 4-NA as compared with CdS Ns and P25. Specifically, as shown in Fig. 11c, the photoreduction rate of 4-NA over 1Au–CdS Ns nanocomposites and CdS Ns are determined to be 100% and 55.4% after irradiation for 20 min, indicating that the 1Au–CdS Ns nanocomposite exhibits much more enhanced photoreduction activity toward the reduction of 4-NA in comparison with CdS Ns. Besides 4-NA, photocatalytic reduction of a series of other aromatic nitro compounds, including 2-NA, 3-NA, 2-NP, 3-NP, 4-NP and 4-NT over CdS Ns and 1Au–CdS Ns nanocomposites were also probed as shown in Fig. 11. Consistently, 1Au–CdS Ns nanocomposites also exhibits significantly enhanced photocatalytic performances toward the reduction of other aromatic nitro compounds relative to pure CdS Ns, implying the versatile photoreduction capability of 1Au–CdS Ns nanocomposites.

Photocatalytic hydrogen evolution of CdS Ns and 1Au–CdS Ns nanocomposites under visible light irradiation were evaluated and the results are shown in Fig. 11h. Apparently, blank CdS Ns exhibits a hydrogen evolution rate of 8.4 μmol h⁻¹ under visible light irradiation (λ ≥ 420 nm) for 5 h, while under the same conditions the 1Au–CdS Ns nanocomposite demonstrates a remarkably enhanced H₂ evolution rate of 23.5 μmol h⁻¹ which is 1.8 times higher than that of CdS Ns. The substantially improved photocatalytic hydrogen production of 1Au–CdS Ns nanocomposites is principally due to the vital role of Au NPs as electron reservoirs which remarkably reduces the recombination of photogenerated electron–hole carriers and thus increases the hydrogen production. Consequently, the results suggest that, apart from the photooxidation reaction, Au–CdS Ns nanocomposites also demonstrate significantly enhanced visible-light-responsive photoreduction performances as compared with CdS Ns.
3.5 Photocatalytic mechanism

The photocatalytic mechanism of Au–CdS Ns nanocomposites is vividly depicted in Scheme 2. Firstly, when Au–CdS Ns nanocomposites is irradiated by visible light, bandgap photoexcitation of CdS Ns occurs, for which electrons are excited from the VB to the CB, thereby leaving holes in the VB and producing electron–hole charge carriers. Regarding the photodegradation of an organic dye pollutant (MB), OH· and O₂⁻ radicals have been determined to be the primary active species based on a series of the aforementioned quenching experiments, PL and EPR techniques. Therefore, it is rationally speculated that the photogenerated holes on the VB of CdS Ns are able to oxidize H₂O/or −OH to generate OH· radicals. Simultaneously, owing to the intimate interfacial contact between CdS Ns and Au NPs afforded by the self-assembly approach as well as a lower Femi level of Au than the CB of CdS Ns, the photogenerated electrons on the CB of CdS Ns are easily trapped by the Au NPs which act as efficient electron reservoirs. Based on this, O₂⁻ radicals are generated through the reaction of the trapped electrons with O₂ molecules adsorbed on the Au NP surface. Alternatively, it is worth noting that some OH· radicals can be produced by the transformation of O₂⁻ via two-electron reduction reactions. Consequently, it is these two sources of active species (i.e., OH· and O₂⁻ radicals) that result in the mineralization of MB to carbon dioxide and water. On the other hand, with regard to the anaerobic photoreduction of 4-NA, since the whole experiments are performed under an inert atmosphere (N₂ bubbling) and photogenerated holes are completely quenched by the scavenger (ammonium oxalate), the escaped photogenerated electrons trapped by Au NPs are directly transferred to the aromatic nitro compound molecules fulfilling the reduction process under visible light irradiation. As for the photocatalytic hydrogen reaction, in a similar way, hydrogen is produced by the direct reaction of photoelectrons trapped by Au NPs with water.

4. Conclusions

In summary, a facile and efficient ligand-triggered self-assembly strategy based on a pronounced electrostatic interaction was developed to prepare well-defined Au–CdS Ns nanocomposites in which Au NPs and CdS Ns as assembly units were intimately integrated and, more importantly, deposition amount of Au NPs on the 2D CdS Ns framework could be finely tuned. It was found that the thus-assembled Au–CdS Ns nanocomposites demonstrated versatile and significantly enhanced photoredox performances including photo-oxidation of an organic dye pollutant, anaerobic photoreduction of aromatic nitro compounds, and photocatalytic hydrogen production, in comparison with CdS Ns under visible light irradiation. The reasons accounting for the significantly improved photoredox performances of Au–CdS Ns nanocomposites were predominantly ascribed to the pivotal role of Au NPs as electron reservoirs rather than the plasmonic photo-

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