Plasma-assisted doping of nitrogen into cobalt sulfide for loading cadmium sulfide: A direct Z-scheme heterojunction for efficiently photocatalytic Cr (VI) reduction under visible light

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\textbf{A B S T R A C T}

A direct Z-scheme heterojunction has been constructed by loading cadmium sulfide (\textit{CdS}) on cobalt sulfide doped with nitrogen (\textit{N-CoS}\textsubscript{2}) by \textit{N}\textsubscript{2} plasma treatment for efficient photocatalytic Cr\textsubscript{(VI)} reduction under visible light. It was discovered that the resulting \textit{CdS}/\textit{N-CoS}\textsubscript{2} nanocomposites could present different photocatalytic performances controllably depending on the plasma treatment time and \textit{CdS}/\textit{N-CoS}\textsubscript{2} ratios. Especially, the one with 5-min plasma treatment and 8/1 M ratio could exhibit the highest Cr(VI) photoreduction efficiency, which is over four and two folds higher than those of pristine \textit{N-CoS}\textsubscript{2} and \textit{CdS}, respectively. Herein, the plasma-assisted N doping could not only increase the surface wettability and conductivity of \textit{CoS}\textsubscript{2} but also decrease its Fermi level for improving the photocatalytic Cr(VI) reduction. More importantly, a direct Z-scheme heterojunction could be constructed by the combination of \textit{CdS} and \textit{N-CoS}\textsubscript{2} with suitable band structures, which could further booster the charge separation and transferring, without sacrificing the redox capacity of photogenerated carriers. The enhanced photocatalytic activity and stability of \textit{CdS}/\textit{N-CoS}\textsubscript{2} nanocomposites could thereby be expected for Cr\textsubscript{(VI)} reduction, with the efficiency up to 100\% within 25 min. Such a direct Z-scheme heterojunction created by the plasma treatment route may promise for the large-scale applications for the removal of various toxic pollutants in the environmental remediation field.

1. Introduction

Due to the rapid urbanization and industrialization, large volumes of wastewater that containing dyes [1–3], pharmaceuticals [4,5], micropollutants [6,7] and heavy metal ions [8] have been produced and flowed into the river, which seriously endangered the ecological safety. Among these pollutants, hexavalent chromium (Cr(VI)), a widely existed heavy metal ion in wastewater mainly from the dye production, petroleum refining, electroplating and leather processing industries, has gained global attention due to its highly toxic harm to human health and environment [9–11]. At present, a common solution is to convert Cr(VI) into Cr(III) of lower toxicity that can be removed by precipitation under neutral or alkaline conditions [12–14]. Although various treatment technologies including by zero valent iron nanoparticles reduction, ion exchange, electrochemical reduction, and biological treatment) have been widely applied for the reduction of Cr(VI), some limitations such as high cost, low efficiency, and secondary pollution risk may still prompt researchers to develop superior technologies [15–17].

Photocatalysis technology with the merits of environmental friendliness, low toxicity, and the one with direct use of solar energy have been preferably applied as the promising routes for the wastewater treatment, especially for the reduction of Cr\textsubscript{(VI)} [18–20]. In the typical photocatalysis process, Cr\textsubscript{(VI)} can be reduced to Cr\textsubscript{(III)} by accepting the photogenerated electrons migrating from the bulk to the surface of...
structure has been extensively applied as one of the most popular photocatalysts for water splitting and pollutant removals [20,23,24]. Unfortunately, some inherent shortcomings, such as the rapid recombination of photo-induced charges and photocorrosion under Z-scheme heterojunctions may not only efficiently accelerate the photocatalytic systems have been reported as the effective ways to avoid its drawbacks. The photo-induced charges and photocorrosion under Z-scheme heterojunctions not only efficiently accelerate the charge separation towards the enhanced photocatalytic activity [24–26]. Yet, the redox capacities of photogenerated electrons and holes are usually weakened in the type II heterojunction, which might not be beneficial for the required high Cr(VI) photoreduction activity. Alternatively, the Z-scheme heterojunctions may not only efficiently accelerate the photoinduced charge separation, but also maintain the strong redox abilities, thus rendering the heterostructures with reinforced performances for photocatalytic Cr(VI) removal [24–26].

Cadmium sulfide (CdS) with the narrow bandgap and favorable band structure has been extensively applied as one of the most popular photocatalysts for water splitting and pollutant removals [20,23,24]. Unfortunately, some inherent shortcomings, such as the rapid recombination of photo-induced charges and photocorrosion under Z-scheme heterojunctions may not only efficiently accelerate the photocatalytic systems have been reported as the effective ways to avoid its shortcomings. The photo-induced charges and photocorrosion under Z-scheme heterojunctions not only efficiently accelerate the charge separation towards the enhanced photocatalytic activity [24–26]. Yet, the redox capacities of photogenerated electrons and holes are usually weakened in the type II heterojunction, which might not be beneficial for the required high Cr(VI) photoreduction activity. Alternatively, the Z-scheme heterojunctions may not only efficiently accelerate the photoinduced charge separation, but also maintain the strong redox abilities, thus rendering the heterostructures with reinforced performances for photocatalytic Cr(VI) removal [24–26].

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The research methodology is schematically illustrated by a flowchart in Fig. S1. Herein, CoSx was first fabricated from ZIF-67 template, and then treated by the N2 plasma treatment for doping N for the modification of CoSx via the one-pot solvothermal route. Unexpectedly, the as-fabricated CdS/N-CoSx could display the controllable photocatalytic activities depending on the plasma treatment time and CdS-to-N-CoSx molar ratios used, showing the highest one at the 5-min treatment and 8/1 M ratio. A photocatalytic efficiency of 100% within 30 min could be expected for CoSx for loading CdS, achieving the efficient photocatalytic activity for the reduction of Cr(VI) so far.

Inspired by the pioneering work mentioned above, in this work, a direct Z-scheme heterojunction has been initially constructed by loading CdS on CoSx, doped with nitrogen (N-CoSx) by plasma treatment for efficient photocatalytic reduction of Cr(VI) under visible illumination. The research methodology is schematically illustrated by a flowchart in Fig. S1. Herein, CoSx was first fabricated from ZIF-67 template, and then treated by the N2 plasma treatment for doping N for the modification of CoSx via the one-pot solvothermal route. Unexpectedly, the as-fabricated CdS/N-CoSx could display the controllable photocatalytic activities depending on the plasma treatment time and CdS-to-N-CoSx molar ratios used, showing the highest one at the 5-min treatment and 8/1 M ratio. A photocatalytic efficiency of 100% within 30 min could be expected for CdS/N-CoSx, which is over four and two folds larger than those of N-CoSx and CdS, respectively. Also, the N2 plasma treatment can enable the covalent doping of N elements into CoSx to yield Co-N bonds, as validated by the X-ray photoelectron spectroscopy (XPS) analysis results. In summary, the data of contact angle measurements and calculations of density functional theory (DFT) indicate that the plasma-assisted N doping can not only increase the surface wettability and conductivity of CoSx, but also decrease its Fermi level for improving the photocatalytic Cr(VI) reduction. Moreover, the possible photocatalytic mechanism for Cr(VI) photoreduction has been explored to follow the direct Z-scheme of electron pathway, as evidenced by the hydroxyl radical fluorescence measurements, electron spin resonance (ESR) tests, and reactive species capture experiments. To the best of our knowledge, this is the first report on the plasma-assisted N doping of CoSx for loading CdS to construct a direct Z-scheme heterojunction with efficient photocatalytic activity for the reduction of Cr(VI).

2. Experimental section

2.1. Materials

The chemicals and reagents like potassium bromate (KBrO3), cobaltous nitrate (Co(NO3)2·6H2O), citric acid (C6H8O7), cadmium nitrate (Cd(NO3)2·4H2O), and absolute ethanol were received from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The other chemicals like thiaoacetamide (TAA), 2-methylimidazolone (C4H6N2), and methanol were purchased from Aladdin Co. Ltd. (Shanghai, China). All materials were analytical grade and utilized as received without further purification.

2.2. Characterization

The plasma reaction system (PDC-002, Harrick, U.S.), consisting of a plasma cleaner, a gas flow mixer, a vacuum pump, and a digital vacuum gauge was employed for the nitrogen doping of CoSx sample. Moreover, the samples were characterized by X-ray powder diffraction (XRD), N2 adsorption–desorption isotherms, scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectra (DRS), Mott–Schottky (M–S) plots, photoluminescence (PL), electrochemical impedance spectroscopy (EIS), and transient photocurrents analysis. Also, the band structures, density of states, and work functions of the prepared composites were explored by density-functional-theory (DFT) calculations with CASTEP module [27,35]. More details about the characterization and DFT calculation were provided in the Supporting Information.

2.3. Fabrication of N-doped CoSx polyhedrons

N-doped CoSx (N-CoSx) polyhedrons were obtained by the N2 plasma treatment for CoSx polyhedrons. Herein, CoSx polyhedrons were synthesized via the one-step ZIF-67-templated solvothermal route according to our previous work [30]. An aliquot of obtained CoSx polyhedrons spread on the quartz plate was placed into the plasma chamber (RF 13.56 MHz, 45 W), which was backfilled with N2 (99.9999%) atmosphere at a pressure of 100 Pa, to be treated for different time (1.0, 3.0, 5.0, 7.0, and 9.0 min). The so-obtained N-CoSx polyhedrons were stored for further usage.

2.4. Preparation of CdS/N-CoSx photocatalysts

CdS/N-CoSx photocatalysts were synthesized by solvothermal methods [27,30]. Typically, an aliquot of 0.050 mmol N-CoSx and 0.40 mmol cadmium nitrate were added into 25 mL ethanol containing 0.53 mmol thiaoacetamide. Then, the resultant mixture was placed into the plasma chamber (RF 13.56 MHz, 45 W), which was backfilled with N2 (99.9999%) atmosphere at a pressure of 100 Pa, to be treated for different time (1.0, 3.0, 5.0, 7.0, and 9.0 min). The reaction mixtures were allowed to cool to room temperature and the precipitates were centrifuged and washed with distilled water three times. After cooling to room temperature, the precipitates were centrifuged and washed with water/ethanol mixture, and dried in vacuum at 40 °C overnight. The obtained nanocomposites were named as CdS/N-CoSx (8/1), of which 8/1 refers to the CdS-to-N-CoSx theoretical molar ratio acquired from the molar ratio of reactants. Accordingly, other nanocomposites were synthesized with different CdS-to-N-CoSx molar ratios via the same procedure, separately designated as CdS/N-CoSx (32/1), CdS/N-CoSx (16/1), CdS/N-CoSx (8/1), and CdS/N-CoSx (2/1). In addition, pristine CdS and CdS/N-CoSx (8/1) were synthesized for comparison by following the same method except for the introduction of N-CoSx and N2 plasma treatment.
2.5. Measurements of photocatalytic performances

The photocatalytic performances of the photocatalysts were tested by the photoreduction of Cr(VI) under visible-light irradiation of a 300 W xenon lamp (PLS-SXE300D, Beijing PerfectLight). Typically, an aliquot of 5.0 mg photocatalyst was dispersed into 25 mL Cr(VI) (K₂Cr₂O₇) solution (10 mg/L, pH 3.0) with the solution temperature controlled at ambient temperature (20 ± 0.3 °C). Prior to the irradiation, the suspension was magnetically stirred in dark for 30 min to establish the adsorption/desorption equilibrium. Afterwards, 500 µL suspension was taken out every 5.0 min, and then centrifuged for the removal of photocatalysts. Subsequently, the Cr(VI) concentration was analyzed by the spectrophotometric method using diphenylcarbazide as the color reagent, in which the reaction product of diphenylcarbazide and Cr(VI) could exhibit a maximum absorption wavelength at 540 nm, and the relationship between the absorbance of reaction products and the Cr(VI) concentration could obey the Beer’s law [19-21].

Furthermore, the photocatalytic stability of so-obtained CdS/N-CoS₃ photocatalyst was evaluated by the photocatalytic reactions each run for five cycles. After each recycling run, the recycled photocatalyst was separated by centrifugation to be washed with HNO₃ for five cycles. After each recycling run, the recycled photocatalysts were reused in next reaction cycle according to the same procedure. Of note, for the photocatalytic reduction of Cr(VI), each set of data was recorded for at least three repeated experiments under the same condition to ensure the reliability of the experimental results.

3. Results and discussion

3.1. Fabrication and characterisation of photocatalysts

The CdS/N-CoS₃ photocatalysts were fabricated by loading CdS on N-CoS₃ via the solvothermal route [27,30]. Herein, CoS₃ polyhedrons were prepared from ZIF-67 templates and further treated by the N₂ plasma treatment for N doping to yield N-CoS₃. Afterwards, the CdS was grown on the resulted N-CoS₃ surface via the solvothermal route, resulting in CdS/N-CoS₃ nanocomposites. Of note, the obtained CdS/N-CoS₃ could display the controllable photocatalytic activities depending on the plasma treatment time and CdS-to-N-CoS₃ molar ratios used, and the one with 5-min plasma treatment and 8/1 M ratio can exhibit the highest photocatalytic activity for Cr(VI) reduction as demonstrated afterwards. Fig. S2 manifests the comparison of phase composition and crystal structures among different photocatalytic samples like CoS₃ and CdS, which are detected by the X-ray powder diffractometer (XRD) [36-38]. One can note that pristine CoS₃ only exhibited a broad peak at 2θ = 26°, which can be well indexed to the amorphous structure of CoS₃ [39]. After the N₂ plasma treatment for 5.0 min, the XRD pattern of pristine N-CoS₃ could present the similar diffraction peaks of amorphous CoS₃, whereas no diffraction peaks of cobalt nitride could be found in N-CoS₃, presumably due to that the amount of cobalt nitride produced onto the resulting nanocomposites might be too low to be recorded by the XRD. The reasons for the low production of cobalt nitride during this process were attributed to the experimental conditions of plasma treatment mainly including the plasma treatment temperature and plasma intensity and power, which has been reported by other previous works [32,33]. Moreover, after the modification of CdS onto N-CoS₃, three diffraction peaks at 2θ of 26.5°, 43.9°, and 52.0°, which should separately belong to the (1 1 1), (2 2 0) and (3 1 1) crystal plane of CdS (ICPDS 65-2887), could be registered for CdS/N-CoS₃ nanocomposites, indicating the coexistence of CdS and N-CoS₃ components in the nanocomposites [30]. Besides, the Brunauer-Emmett-Teller (BET) surface area of the as-prepared CdS/N-CoS₃ nanocomposites was firstly measured on the N₂ adsorption–desorption isotherms by taking pristine N-CoS₃ and CdS as the controls. It was found that the BET surface areas of N-CoS₃ and CdS were 76 and 32 m²/g, respectively. After the modification of CdS onto N-CoS₃, the as-prepared CdS/N-CoS₃ could display a BET surface area of 41 m²/g.

The morphologies of CdS/N-CoS₃ nanocomposites fabrication with the optimal 8/1 of CdS-to-N-CoS₃ molar ratio were investigated by the scanning electron microscopy (SEM) by using N-CoS₃ and CdS as the controls (Fig. 1). It can be seen that CoS₃ could exhibit a uniform polyhedral shape (Fig. 1A), of which the morphology could be well maintained in N-CoS₃ derived from CoS₃ after the N₂ plasma-assisted N doping (Fig. 1B). Furthermore, the hollow structure of the so-obtained polyhedrons could be demonstrated with the visual cracked polyhedrons (red dotted circles, Fig. 1A-B). More importantly, Fig. 1C shows the SEM image of CdS/N-CoS₃ nanocomposites. One can find that the as-prepared photocatalysts could be formed with good dispersion, in which N-CoS₃ polyhedrons were totally coated with CdS. In contrast, pristine CdS should be yielded in blocky and irregular agglomeration as a result of the random accumulation and Ostwald ripening (Fig. 1D) [40]. The elemental mappings of CdS/N-CoS₃ indicated that the Cd, Co, S, and N elements could be distributed throughout the SEM image of nanocomposites, confirming the formation of CdS/N-CoS₃ nanocomposites (Fig. S3). Moreover, to make a further insight into the microstructure, the so-obtained CdS/N-CoS₃ nanocomposites were explored by the transmission electron microscopy (TEM) (Fig. 2) [41]. One can see from Fig. 2A that CdS NPs were closely coated on N-CoS₃ polyhedrons. Furthermore, the N-CoS₃ parts in nanocomposites (red circular parts in Fig. 2A) were amplified by the high-magnified TEM imaging, showing no obvious lattice fringe (Fig. 2B), presumably due to the amorphous feature of N-CoS₃ as further confirmed by the fast Fourier transform (FFT) and reduced FFT images (inset of Fig. 2B). In contrast, the high-magnified TEM image of CdS in the nanocomposites (the blue circular parts in Fig. 2A) reveals that an obvious lattice fringe of 0.34 nm could be observed to be ascribed to the (111) plane of CdS, which are further supported by the diffraction ring of FFT image and the corresponding lattice spacing of reduced FFT image (inset of Fig. 2C). Herein, the (111) plane of CdS should be consistent with those of pristine CdS (Fig. 2D), showing two different lattice fringes of 0.34 and 0.21 nm separately corresponding to the (111) and (220) planes of CdS [30]. The above morphological data confirm the formation of CdS/N-CoS₃ photocatalysts.

The chemical and valence states of the so-obtained CdS/N-CoS₃ samples were comparably investigated by the X-ray photoelectron spectroscopy (XPS) (Fig. 3). It was found from Fig. 3A that Co 2p could consist of two spin–orbit doublets with two satellite peaks. Herein, the first doublet peaks at 793.93 and 778.88 eV and the second ones at 797.46 and 781.19 eV should be ascribed to the Co 2p³/₂ and Co 2p½ of Co⁰ and Co⁵⁺, respectively. The peaks at 802.62 and 784.55 eV should be attributed to the satellite peaks of Co 2p. Moreover, one can note that the binding energies of Co 2p in N-CoS₃ could shift to lower binding energies in comparison with that of pristine CoS₃, indicating the occurrence of charge transfer for N-CoS₃, which might be caused by the change of Fermi level associated with the p-type doping of nitrogen [32,33]. Moreover, in the XPS spectra of Cd 3d (Fig. 3B), two peaks at 411.93 and 405.18 eV belonged to the Cd 3d₅/₂ and Cd 3d₃/₂ in CdS could be observed whereas the peaks ascribed to the Cd 3d₅/₂ and Cd 3d₃/₂ in CdS/N-CoS₃ could shift negatively and located at 404.99 and 416.69 eV, which might be ascribed to the charge transfer between CdS and N-CoS₃ [24,30]. Furthermore, Fig. 3C reveals the high-resolution XPS spectra of N 1 s. Herein, two strong peaks at about 399.23 and 401.34 eV should be separately ascribed to the pyridinic-N and graphitic-N [42,43]. Also, a low intensity peak located at around 399.82 eV ascribed to the Co-N bond was detected [42,43], indicating the successful doping of N in CoS₃. What’s more, one can see from the XPS spectra of S 2p (Fig. 3D), the S 2p spectra of CoS₃ could consist of two spin–orbit doublets, of which the first doublet peaks at 162.11 and 169.01 eV and the second ones at 163.34 and 170.16 eV should be separately assigned to the S 2p½ and S 2p½. Particularly, after the N₂ plasma treatment for CoS₃ for 5.0 min, the binding energies of S 2p in the
resulted N-CoS might have shifted negatively in comparison with CoS, presumably due to the doped nitrogen might serve as the p-type dopant \[32,33\]. In addition, after the coating of CdS onto N-CoS, the peak ascribed to the S 2p of N-CoS in the resulted CdS/N-CoS (8/1) could shift positively as compared to that of N-CoS. In contrast, the one ascribed to the S 2p of CdS could shift to lower binding energies compared to that of CdS, suggesting that the electron transferring between CdS and N-CoS might have occurred at the interfaces of CdS/N-CoS nanocomposites with different Fermi levels \[30,32,33\].

In order to make an in-depth investigation of the charge transferring between CdS and N-CoS in CdS/N-CoS nanocomposites, the work function (Φ) values of CoS, N-CoS, and CdS were calculated by using the density functional theory (DFT) computational software \[39\] (Fig. 4). As aforementioned by the XPS results above, the main component of amorphous CoS in both N-CoS and CdS/N-CoS should be CoS. Hence, the CoS phase (JCPDS 65–3418) has been utilized to

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**Fig. 1.** SEM images of (A) CoS polyhedrons, (B) N-CoS polyhedrons, (C) CdS/N-CoS (8/1) nanocomposites, and (D) CdS.

**Fig. 2.** TEM image of (A) CdS/N-CoS with the amplified views for displaying (B) N-CoS and (C) CdS; (D) high-magnified TEM image of CdS.
build the crystal model. Obviously, the calculated Φ value of CoS(100) and CdS(111) surface are almost consistent with our previous works \cite{27,30}. One can find that the Φ values of CoS(100) and N-CoS(100) surfaces were obtained to be 3.78 and 3.927 eV, respectively, indicating a lower Fermi level of N-CoS(1 0 0) could be obtained for improving the charge transferring of CoS after nitrogen doping, which should be consistent with the data of XPS analysis above. Moreover, it was observed that the Φ value of CdS(1 1 1) surface (4.92 eV) is higher than that of N-CoS(1 0 0) surface. Therefore, at the interfaces of CdS and N-CoS in CdS/N-CoS, the electrons might have transferred from N-CoS to CdS until the Fermi level equilibrium, resulting in the electron concentrations increased in CdS and decreased in N-CoS, so as to form an interfacial electric field between CdS and N-CoS, with the orientation from N-CoS to CdS \cite{30,44}. Therefore, a direct Z-scheme heterojunction can be created for CdS/N-CoS nanocomposites.

The optical absorption properties of the so-obtained CdS/N-CoS samples were comparably probed by using UV–vis diffuse reflectance spectra (DRS) \cite{Fig. 5}. It can be seen from Fig. 5A that pristine CoS \(_x\) can exhibit a long-wavelength absorption edge due to its narrow bandgap value. After the N\(_x\) plasma treatment for 5.0 min, the resulted N-CoS \(_x\) could display similar absorption edges to pristine CoS \(_x\) without obvious shifts, indicating that the band gap (E\(_g\)) of N-CoS \(_x\) could remain the same as that of CoS \(_x\) \cite{32,33}. Moreover, after loading CdS onto N-CoS \(_x\), the resulted CdS/N-CoS \(_x\) nanocomposites could display obviously a red shift in the absorption edges (Fig. 5A), which might be resulted from the heterojunction created by amorphous N-CoS \(_x\) and CdS. Furthermore, according to the Tauc plot shown in Fig. 5B, the E\(_g\) values of CdS and N-CoS \(_x\) were obtained to be 2.54 and 1.51 eV, respectively. More importantly, the conduction band (CB) levels of these semiconductors were estimated by the Mott-Schottky (M–S) plots, with the results shown in Fig. 5C-D. Obviously, the derived CB potential of N-CoS \(_x\) was about -0.63 eV, which is than that of CdS (-0.51 eV) at a higher potential. Notably, the valence band (VB) of CdS and N-CoS \(_x\) were calculated by the subtraction between the E\(_g\) value and the CB value \cite{29}. Accordingly, the VB values of CdS and N-CoS \(_x\) were 2.03 and 0.88 eV, respectively. Based on the results, the position of CB for N-CoS \(_x\) was more negative than that of CdS, while the position of VB for CdS was more positive than that of N-CoS \(_x\), therefore, the CdS/N-CoS \(_x\) nanocomposites have met the requirement for the construction of a direct Z-scheme system, which could achieve the quick spatial separation of interfacial charges and simultaneously possess the strong redox abilities, rendering the heterostructures with reinforced performances for the following photocatalytic Cr(VI) removal.

To explore the changing surface wettability and conductivity properties of the so-obtained CoS \(_x\) before and after N\(_x\) plasma treatment (N-CoS \(_x\)), the contact angle and cyclic voltammetry measurement were separately performed \cite{33,45}. Obviously, the contact angle of N-CoS \(_x\) was much lower than that of pristine CoS \(_x\) (Fig. 54), indicating that the heteroatom N doping by plasma treatment should aid to dramatically increase the surface wettability of N-CoS \(_x\). Besides, one can note from Fig. 55 that the plasma-assisted N doping could improve the conductivity of CoS \(_x\). Therefore, the so enhanced surface wettability and conductivity of N-CoS \(_x\) should aid to increase the photocatalysis of CdS/N-CoS \(_x\) for photocatalytic Cr(VI) reduction \cite{46}. Moreover, the wetting and conduction properties as functions of plasma-treatment time have been further explored with the results shown in Fig. 56. One can note from Fig. 56A that the contact angle (CA) value could decrease as increasing the plasma-treatment time until 5.0 min. Furthermore, the conductivity of resulted N-CoS \(_x\) was observed to increase with increasing plasma-treatment time until 5.0 min, over which the conductivity would be almost unchanged (Fig. 56B). Therefore, the plasma-treatment time of 5.0 min might be chosen as the optimal plasma-treatment time in the following photocatalytic reduction experiments.
3.2. Evaluation of photocatalytic performances

The photocatalytic performances of developed CdS/N-CoS\(_x\) nanocomposites were evaluated comparably by the photoreduction of Cr(VI) under the illumination of xenon lamp (equipped with a cut-off filter of 420 nm), where the changed concentrations of Cr(VI) were recorded with UV–vis absorption spectroscopy by using the standard diphenylcarbazide method [47]. Herein, the photographs and the corresponding spectra of the utilized xenon lamp (equipped with a cut-off filter of 420 nm) were provided in Fig. S7. One can note that the utilized Xenon lamp could exhibit the visible spectra with the wavelength ranging from 420 to 800 nm, which could be utilized to simulate the visible light pretty well. Besides, the calibration curve of the UV–vis absorption intensities versus Cr(VI) concentrations could exhibit a correlation coefficient of 0.9998, indicating a good linear dependence relation between Cr(VI) concentrations and absorbance values (Fig. S8). Prior to the irradiation, of note, the as-prepared photocatalysts should be dispersed in the Cr(VI) solutions in dark for 30 min to establish the adsorption/desorption equilibrium. The dark adsorption and photocatalytic performances for the so-obtained samples are summarized in Table S1. It was found that the so-obtained samples could possess the favorable adsorption capacity for Cr(VI). Especially, the resulted N-CoS\(_x\) (5 min) could exhibit higher adsorption efficiency for Cr(VI) than the CdS/N-CoS\(_x\), which might be ascribed to its larger specific area or the excellent surface wettability as reported elsewhere [20,48,49]. Of note, all the CdS/N-CoS\(_x\) nanocomposites could exhibit the considerably high adsorption properties for Cr(VI). Initially, the Cr(VI) photoreduction performances of N-CoS\(_x\) fabricated by the plasma treatment for pristine CoS\(_x\) with different time were investigated (Fig. 6A). One can note that the pristine CoS\(_x\) displayed only 18% of Cr(VI) photoreduction efficiency. After the N\(_2\) plasma treatment for different time, the so improved surface wettability and conductivity could be beneficial for the access of Cr(VI) to photocatalysts to realize the acceleration of the reactions of photocatalytic Cr(VI) reduction, therefore all of the resulted N-CoS\(_x\) could exhibit much enhanced Cr(VI) photoreduction efficiencies [46,48,49]. And the one with 5-min plasma treatment could present the...
Thus selected as the optimal one in the whole experiments. Moreover, as summarized in Table S2. Apparently, the developed CdS/N-CoS-based heterojunction photocatalysts reported previously are summarized in Table S2. One can see that the comparison results of photocatalytic Cr(VI) reductions over various CdS-based heterostructures reported previously. It should be noted that though the CdS/N-CoS (8/1) could display the best photocatalytic Cr(VI) reduction but its adsorption performance was lower than those molar ratios of 2/1 and 4/1, indicating that the adsorption property might not be the main factor affecting the photocatalytic performance of photocatalysts, which is consistent with previous works reported elsewhere [13,16].

To deeply understand the effects of heterostructure formed between N-CoSx and CdS on the photocatalytic activity of CdS/N-CoSx composites, control experiments about the photocatalytic Cr(VI) reduction were carried out for the physically mixed N-CoSx and CdS with the same molar ratio and CdS/N-CoSx without N2 plasma treatment (Fig. 7A). As expected, the physically mixed composites displayed much lower photocatalytic activity than the developed nanocomposites, confirming that the formed heterojunctions should play the vital role in enhancing the photocatalytic performances of the developed CdS/N-CoSx photocatalysts. Moreover, one can note that the photocatalytic Cr(VI) reduction efficiency of developed CdS/N-CoSx photocatalysts is nearly 1.2-fold higher than that of the ones without N2 plasma treatment (CdS/CoSx), indicating that the heterojunction so constructed by the plasma treatment-assisted doping of N into CoSx for loading CdS could achieve much better photocatalytic activity.

To explore the roles of different reactive species in the reactions of Cr(VI) photoreduction, a series of free radical scavengers were introduced into the reaction solutions (Fig. 8A–S9A). Herein, KBrO3, citric acid, isopropanol (IPA), and p-benzoquinone (PBQ) were separately added into the reaction solutions to capture photo-induced electrons (e−), holes (h+), hydroxyl radicals (•OH), and superoxide radical (•O2) [20,50]. One can note from Fig. 7A that introducing KBrO3 into the reaction solution could remarkably inhibit the rate of photocatalytic Cr(VI) reduction. In contrast, an enhanced rate for Cr(VI) photoreduction could be observed after the introduction of C6H5O2−, which might be
resulted from the depletion of holes by citric acid leading to the suppressed recombination between holes and electrons [20]. Moreover, the photocatalytic reduction efficiency decreased slightly in the presence of PBQ, whereas almost no change could be observed after the addition of IPA. Notably, the role of the free radicals participating in the photocatalytic process was clearly depicted by the changed absorption spectra of Cr(VI) for the tested samples in the presence of different free radical scavengers shown in Fig. S10 B–E. One can find that the addition of KBrO₃ and PBQ could slow down the absorbance intensity of Cr(VI) for the tested samples, while the addition of IPA and citric acid exerted almost no effect, demonstrating that both e⁻ and •O₂ might be responsible for the enhanced Cr(VI) photocatalytic reduction with CdS/N-CoSₓ, where the e⁻ might play the major role. To further ascertain the generation of •O₂ produced in CdS/N-CoSₓ–photocatalytic reactions under visible light illumination, the electron spin resonance (ESR) analysis was conducted with the results shown in Fig. 7B. As expected, with the irradiation time increasing, the gradually increasing signals of •O₂ radicals could be observed for the CdS/N-CoSₓ–photocatalytic reactions under visible light illumination, whereas no signal could be detected in dark, indicating the formation of •O₂ radicals in the process of photocatalytic reactions.

The influences of solution pH values on the photocatalytic reduction tests were explored with the results shown in Fig. S11. One can note that the so-obtained photocatalysts could display much higher performances...
for photocatalytic Cr(VI) reduction at lower pH values, suggesting that the Cr(VI) in solutions might be readily reduced if surrounded with abundant protons, which are consistent with the previously reported works [25,27]. Besides, the photocatalytic stability of the developed CdS/N-CoSₙ photocatalysts was examined by the photocatalytic reduction of Cr(VI) for five cycles (Fig. 8A). One can see that CdS/N-CoSₙ nanocomposites might have no significant loss of photocatalytic performance after the five-recycle tests, suggesting the photocatalysts can present the high photocatalytic stability. Furthermore, the tests for Cd ion leaching were carried out with the results displayed in Table S3. Accordingly, the leaching Cd ion concentrations are much lower in CdS/N-CoSₙ-photocatalyzed reactions than the pristine CdS-photocatalyzed ones, indicating that the photostability of CdS in CdS/N-CoSₙ nanocomposites should be greatly enhanced after the coupling with N-CoSₙ [23]. Furthermore, the crystal structure and surface elements of the recycled CdS/N-CoSₙ photocatalysts were investigated by XRD and XPS spectroscopies by taking the fresh one as the control (Fig. 8B-C). Accordingly, no obvious difference could be detected in the crystal structure and elementary composition for the photocatalysts recycled for five times. Remarkably, Fig. 8D reveals that the binding energy of Cr 2p₃/2 in the recycled photocatalysts was located at around 576.9 eV, which is consistent with that of Cr(III) in Cr(OH)₃ reported previously [51]. Furthermore, the morphology and element distribution of the recycled CdS/N-CoSₙ photocatalysts were further explored by the SEM imaging (Figs. S12 and 13). It can be found from Fig. S12 that the morphology of the recycled CdS/N-CoSₙ photocatalyst is basically the same as that of the fresh one in Fig. 1C. Moreover, the elemental mappings of the recycled CdS/N-CoSₙ photocatalyst (Fig. S13) observed the distributions of Cd, Co, S, and N elements throughout the images of nanocomposite, indicating that the as-prepared CdS/N-CoSₙ photocatalysts can enjoy the desirably high photocatalytic stability.

3.3. Possible photocatalytic mechanism

To investigate the interfacial separation efficiencies of photo-generated electron-hole pairs, some common photo/electrochemical characterizations were first performed for the developed CdS/N-CoSₙ nanocomposites, with the data shown in Fig. 9. One can see from Fig. 9A that the photocurrents of CdS/N-CoSₙ were much higher than those of pristine CdS and N-CoSₙ, indicating that low photogenerated carrier’s recombination efficiency might be expected for CdS/N-CoSₙ, which is consistent with the data of photocatalytic performances in Fig. 6B. Moreover, the charge-transfer resistances of CdS/N-CoSₙ nanocomposites fabricated with different CdS-to-N-CoSₙ molar ratios were comparably characterized by the electrochemical impedance spectroscopy (EIS) measurements (Fig. 9B). Obviously, CdS/N-CoSₙ nanocomposite can possess a smaller high-frequency semicircle than those of pristine CdS and N-CoSₙ, suggesting a lower charge-transfer resistance registered for CdS/N-CoSₙ nanocomposite with the faster electron transfer. Simultaneously, the photoluminescence (PL) spectra of prepared nanocomposites with various CdS-to-N-CoSₙ molar ratios were comparably explored (Fig. 9C). It is noted that the PL intensity of CdS/N-CoSₙ was reduced drastically in comparison with that of pristine CdS, confirming that the recombinination rate of photo-induced carriers might have been suppressed after being loaded onto N-CoSₙ, which may help to boost the photocatalytic performance of CdS/N-CoSₙ photocatalysts. The band edges of CdS in different alkaline electrolytes were investigated (Fig. 9D), where the Cd²⁺ lattice reduction peak potential may approximate the CB value of CdS [52,53]. One can note that the slope was measured to be only −29 mV/pH, suggesting that the CB value of CdS might not follow the Nernstian dependence on pH values (−59 mV/
pH), which is also consistent with the earlier reports [52-54]. Due to the water redox potentials (H$_2$/H$^+$ and OH/$\cdot$OH) may follow the steeper Nernstian dependence [53], there should be a crossover with the VB value of CdS at high pH values as illustrated in Fig. 10. Of note, the CB potential of CdS is 0.94 V (vs. NHE) at the pH of 14.7. Accordingly, the VB value was estimated to be 1.60 V (vs. NHE) by considering the $E_g$ value of 2.54 eV for CdS (Fig. 5B), which is lower than the potential $E(\cdot$OH/$\cdot$OH) = 1.51 V (vs. NHE) at pH 14.7 [55]. Therefore, the holes in the VB of CdS should enable the oxidization of hydroxyl anions at high pH values, as described in the works elsewhere [53,56]. It is worthy to mention that the VB potential of N-CoS$_x$ (0.89 V vs. NHE) is much larger than the standard redox potential of $\cdot$OH/OH (2.69 V vs. NHE), which may be unable to produce $\cdot$OH radicals under visible light illumination [30]. Therefore, the production of $\cdot$OH radicals should be employed to probe the proposed e$^-$/h$^+$ transfer mechanism for the CdS/N-CoS$_x$-based photocatalysis by following the direct Z-scheme pathway, where the e$^-$ in lower CB of CdS might have been directly recombined with the h$^+$ in larger VB of CoS in the CdS/N-CoS$_x$ photocatalytic process.

To confirm this e$^-$/h$^+$ transfer mechanism for the CdS/N-CoS$_x$-photocatalyzed reactions, the fluorescence spectra of the reaction products of $\cdot$OH for CdS/N-CoS$_x$ were monitored by using CdS and N-CoS$_x$ as controls (Fig. 11A) [57]. Obviously, under visible light illumination, the intensities of $\cdot$OH reaction products might have the order: CdS/N-CoS$_x$(8/1) > CdS > N-CoS$_x$. Apparently, CdS/N-CoS$_x$ could produce much more $\cdot$OH radicals than the N-CoS$_x$ or CdS. Furthermore, the generated $\cdot$OH radicals were further explored by the electron spin resonance tests (Fig. 11B). As expected, the as-prepared CdS/N-CoS$_x$(8/1) nanocomposite displayed no $\cdot$OH radical signals in dark, but showing an obvious characteristic spectra belonged to the $\cdot$OH radical signals under the visible light irradiation, which were well consistent with the fluorescence analysis results aforementioned (Fig. 11A). Hence, the proposed direct Z-scheme electron-hole transfer mechanism can be described as illustrated in Scheme 1. Herein, under visible-light illumination, both N-CoS$_x$ and CdS in the CdS/N-CoS$_x$ nanocomposite could be first excited to generate e$^-$ and h$^+$. Furthermore, owing to the internal electric field at the interface formed by the N-CoS$_x$ and CdS with different Fermi levels, the e$^-$ in the CB of CdS would be directly combined with the h$^+$ in VB of N-CoS$_x$, leaving the e$^-$ and h$^+$ with enhanced redox abilities in the CB of N-CoS$_x$ and VB of CdS, respectively. These remaining e$^-$ should then reduce Cr(VI) into Cr(III), whereas the h$^+$ should oxidize H$_2$O to yield O$_2$ [13,58]. In addition, the O$_2$ adsorbed on

![Fig. 9.](image-url) (A) Transient photocurrent responses and (B) electrochemical impedance spectra of (a) N-CoS$_x$, (b) CdS, and (c-g) CdS/N-CoS$_x$ with different CdS-to-N-CoS$_x$ molar ratios (c-g: 32/1–2/1). (C) Photoluminescence spectra of CdS and CdS/N-CoS$_x$ with different CdS-to-N-CoS$_x$ molar ratios (32/1–2/1). (D) The conduction band edges of CdS assigned from lattice Cd$^{2+}$ reduction peak potentials under different pH conditions.

![Fig. 10.](image-url) The energy diagram for the pH-dependent $\cdot$OH formation. Herein, the redox potentials of OH$^-$/OH follow Nernstian behavior (slope $-59$ mV/pH), but the dependence of CdS conduction and valence bands on pH is only $-29$ mV/pH. The gray dots are the measured conduction band minima values from Fig. 9D.
CdS/N-CoS$_x$ might be reduced to 'O$_2$' radicals by the remaining e$^-$ in the CB of N-CoS$_x$, which might also aid to accelerate the photoreduction of Cr(VI) [50,59]. More importantly, the plasma-assisted N doping can greatly increase the surface wettability and conductivity of N-CoS$_x$ for efficiently loading CdS. A direct Z-scheme heterojunction could thus be created for promoting the charge separation and transferring of CdS/N-CoS$_x$, achieving the enhanced activities and stability for photocatalytic Cr(VI) reductions [49].

4. Conclusion

In summary, direct Z-scheme heterojunctions of CdS/N-CoS$_x$ nanocomposites have been constructed by loading CdS on CoS$_x$ with N doped by the plasma treatment for the efficiently Cr(VI) photocatalytic reduction under visible illumination. The N$_2$ plasma treatment can not only facilitate the N elements to be doped covalently into CoS$_x$ by forming Co-N bonds, but also regulate its surface wettability, conductivity and Fermi level. More importantly, the design of such a direct Z-scheme heterojunction by the plasma treatment route could display much better photocatalytic performances than these without N$_2$ plasma treatment. Particularly, the one with 5-min plasma treatment and 8/1 M ratio could present the highest photocatalysis performance with the efficiency of 100% within 25 min. In addition, the photocatalytic mechanism for Cr(VI) photoreduction has been explored to follow the direct Z-scheme electron transferring pathway, as evidenced by the hydroxyl radical fluorescence measurements, ESR tests, and reactive species capture experiments. Although the detailed photocatalysis mechanism should be further explored, this work may provide a new way for designing the direct Z-scheme heterojunctions via the plasma treatment-assisted N doping route, thus promising for the wide photocatalytic applications in the energy and environment fields.

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Fig. 11. (A) The 'OH formation amounts of N-CoS$_x$, CdS and CdS/N-CoS$_x$ (8/1) monitored by the fluorescence spectra of 2-hydroxypara-terephthalic acid (the product of 'OH radicals reacting with terephthalic acid) taken after 25 min of visible illumination. (B) The electron spin resonance spectra of 'OH radicals for CdS/N-CoS$_x$ (8/1) nanocomposite before and after the visible light illumination.

Scheme 1. The possible charge transfer mechanisms for photocatalytic Cr(VI) reduction over CdS/N-CoS$_x$ composites based on the Z-scheme heterojunction under visible illumination.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


