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Article

CdS-modified one-dimensional g-C₃N₄ porous nanotubes for efficient visible-light photocatalytic conversion

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ABSTRACT

A heterojunction photocatalyst based on porous tubular g-C₃N₄ decorated with CdS nanoparticles was fabricated by a facile hydrothermal co-deposition method. The one-dimensional porous structure of g-C₃N₄ provides a higher specific surface area, enhanced light absorption, and better separation and transport performance of charge carriers along the longitudinal direction, all of which synergistically contribute to the superior photocatalytic activity observed. The significantly enhanced catalytic efficiency is also a benefit originating from the fast transfer of photogenerated electrons and holes between g-C₃N₄ and CdS through a built-in electric field, which was confirmed by investigating the morphology, structure, optical properties, electrochemical properties, and photocatalytic activities. Photocatalytic degradation of rhodamine B (RhB) and photocatalytic hydrogen evolution reaction were also carried out to investigate its photocatalytic performance. RhB can be degraded completely within 60 min, and the optimum H₂ evolution rate of tubular g-C₃N₄/CdS composite is as high as 71.6 μmol h⁻¹, which is about 16.3 times higher than that of pure bulk g-C₃N₄. The as-prepared nanostructure would be suitable for treating environmental pollutants as well as for water splitting.

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1. Introduction

Metal-free graphitic carbon nitride (g-C₃N₄) has attracted great interest in photocatalytic degradation and H₂ production owing to its low cost, nontoxicity, good thermal and chemical stability, visible-light response, and proper electronic band structure. However, fast carrier recombination, low optical

absorption in the visible region, and small surface area dramatically impact its overall performance [1,2].

Over the past few years, many approaches have been investigated to improve the photocatalytic activity of g-C₃N₄ [2–4]. Doping metallic or nonmetallic elements is an efficient strategy to modify the surface properties and electronic structures [5–8]. Reducing the particle size or forming a hierarchical

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structure is also an effective method for addressing the drawbacks of g-C₃N₄ by enlarging the specific surface area, shortening the diffusion pathway of charge carriers, and further promoting the separation and transfer of electron-hole pairs [4]. Besides, constructing a heterojunction is another way of improving the photocatalytic performance of g-C₃N₄. Various semiconductors have been reported to form heterostructures with g-C₃N₄, such as TiO₂, MoS₂, Bi₂WO₆, Ag₃PO₄, NiS₂, and carbon quantum dots [9–15], which can suppress the recombination of photoinduced electrons and holes.

CdS is a fascinating visible-light photocatalyst for H₂ evolution owing to the narrow bandgap (2.42 eV) and suitable band edge positions [16,17]. However, CdS is unstable owing to the photocorrosion effect of the photogenerated holes, fast recombination of the photoexcited charge carriers, and aggregation of CdS nanoparticles, which limit its application as a photocatalyst to a great extent. These problems can be solved by coupling CdS with various semiconductors (TiO₂, BiVO₄, ZnO, Fe₂O₃, etc.) [18–21]. These heterostructures show enhanced photocatalytic activities. The band edge offsets between g-C₃N₄ and CdS are suitable for charge transfer, and therefore, the coupling of CdS with g-C₃N₄ can effectively accelerate the separation of photoinduced charge carriers and alleviate the photocorrosion occurring in CdS due to photogenerated holes [16,17,22–24]. However, as Ge et al. [25] reported that the H₂ evolution efficiency was not as high as expected, being only ~9 times that of pure g-C₃N₄. More efforts are therefore required to further improve the photocatalytic activity of g-C₃N₄ and CdS hybrid.

The porous one-dimensional nanostructure offers a great advantage in terms of improving both the specific surface area and charge carrier mobility [26–28]. Herein, we designed a porous tubular g-C₃N₄ by using ethylene glycol as a template, which could be removed easily. The porous structures provide higher specific surface areas than pure g-C₃N₄, which make it an ideal substrate for loading CdS nanoparticles. The g-C₃N₄ nanotube can inhibit the photocorrosion of CdS and promote the separation of the photogenerated electrons and holes. The photocatalytic activities of porous g-C₃N₄/CdS nanotubes for the degradation of RhB and the photocatalytic hydrogen evolution reaction (HER) under visible light irradiation were determined. This study may provide a new insight into the design of photocatalysts with high visible light activities.

2. Experimental

2.1. Materials

All the reagents used were purchased from Aladdin Chemical Reagent Co., Ltd and Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout this study. All the chemicals were analytical grade and used as-received without any further purification.

2.2. Synthesis of melamine nanofibers (MNFs)

Briefly, 1 g of melamine was dissolved in 30 mL ethylene glycol at 60 °C with continuous magnetic stirring to form a

transparent solution. Afterwards, 60 mL of 0.15 mol/L aqueous nitric acid was added drop by drop. After cooling to room temperature, the generated white precipitate was collected and washed with ethanol three times and dried in a vacuum oven at 60 °C overnight.

2.3. Synthesis of tubular g-C₃N₄ (T-CN)

The as-prepared MNFs were sealed in a quartz boat and enfolded by a tin foil with a few pinpricks. Then the sample was heated to 550 °C for 2 h at the ramp rate of 10 °C/min. The obtained product was washed with deionized water three times and dried in the vacuum oven at 60 °C overnight. For comparison, bulk g-C₃N₄ (B-CN) was prepared by direct calcination of melamine at 550 °C for 2 h by employing the same heating rate.

2.4. Synthesis of tubular g-C₃N₄/CdS (T-CN/CdS)

Typically, 0.1 g of T-CN was sonicated and dispersed in 80 mL deionized water. Afterwards, 1 mmol (5, 10, and 20 mmol) of cadmium chloride and thioacetamide with cadmium/sulfur stoichiometric ratio of 1:1 were added into the above solution. Then, the solution was heated and stirred at 60 °C for 30 min, and the resulting yellow precipitate washed with ethanol and deionized water several times and dried at 60 °C overnight. The prepared samples were named T-CN/CdS-x (x = 1, 5, 10, and 20), where x represents the molar weight of CdS. The entire synthesis process is illustrated in Scheme 1.

2.5. Characterization

The Fourier transform infrared spectroscopy (FT-IR) patterns of the photocatalysts were obtained in a transmission mode between 4000 and 400 cm⁻¹. The crystalline phases were characterized by using an X-ray diffractometer (Bruker D8 Advance with Cu K_{α1} radiation at 40 kV and 30 mA). The morphology and sample size were determined by scanning electron microscopy (SEM; HITACHI S-4800) and transmission electron microscopy (TEM; JEM2100), respectively. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB 220i-XL system. The Brunauer-Emmett-Teller (BET) surface area was measured by an ASAP 2010 V5.02H analyzer. The UV-vis diffuse reflectance spectra (DRS) of the samples

Scheme 1. Synthetic process of T-CN/CdS.

were obtained by using a UV-vis spectrophotometer (UV-3600, Shimadzu, Japan). The photoluminescence (PL) spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

2.6. Electrochemical tests

Electrochemical tests were performed by using a three-electrode system with an electrochemical workstation (CHI660C Instruments, China). Fluorine-doped tin oxide conductive glass, platinum wire, and saturated Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. Here, 0.5 mol/L aqueous Na₂SO₄ solution acted as the electrolyte. A 300 W xenon lamp with a UV-cutoff filter ($\lambda \geq 420$ nm) was used as the visible light source. The photocurrent responses were obtained by using a photochopper to simulate the light/dark conditions at 25 s intervals. The electrochemical impedance spectra (EIS) were recorded over the frequency range 1–10⁵ Hz with an amplitude of 10 mV at the same bias voltages. The Mott-Schottky plots were recorded by using the impedance-potential mode in the dark.

2.7. Photoassisted degradation tests

For all the photocatalytic experiments, the distance between the xenon lamp (300 W with a 420 nm UV-cutoff filter) and the surface of the reacting solution was maintained at 10 cm. A mass of 0.04 g of the catalyst was added to 100 mL of RhB solution (10 mg/L). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium. At specific time intervals (15 min), 3 mL of the suspension was collected and centrifuged (8000 rpm, 10 min) to remove the photocatalyst particles thoroughly. The absorbance of RhB was determined by the UV-vis spectro-

photometer at the maximum absorption wavelength of 554 nm.

According to Lambert-Beer theory $A = \varepsilon \times b \times c$, where A refers to the absorbance of the sample, ε is the molar absorption coefficient, b is the width of the sample cell, and c is the molar concentration of RhB, we know that the absorbance of RhB is directly proportional to its concentration, and the degradation efficiency (X) can be expressed as $X = (C_0 - C_t)/C_0 \times 100\%$, where C_0 is the initial adsorption equilibrium concentration and C_t is the molar concentration of RhB at different times.

2.8. Photocatalytic H₂ evolution tests

The photocatalytic H₂ evolution tests were conducted in a 250 mL sealed quartz flask at a constant temperature and negative pressure. A 300 W xenon lamp was used as the light source with a cutoff filter ($\lambda \geq 420$) nm to trigger the photocatalytic reaction. In a typical experiment, 0.1 g of the photocatalyst with 3 wt% platinum loading was dispersed in 100 mL of an aqueous solution containing 10 vol% triethanolamine (TEOA). Before irradiation, the system was bubbled with N₂ to remove air completely. The H₂ was analyzed by a gas chromatograph (Agilent, 7820A) equipped with a thermally conductive detector (TCD) and a 5 Å molecular sieve column, with high-purity N₂ serving as the carrier gas. In the cyclic tests, the system was bubbled with N₂ to completely remove the residual H₂ before the next cycle.

3. Results and discussion

3.1. Morphology and structure

The morphological images of the as-prepared samples were collected by SEM and TEM. It can be observed from the SEM image (Fig. 1a) that vimineous and uniform MNFs exhibit high aspect ratios, with the sectional width being less than 2 μ m.

Fig. 1. SEM images of (a) melamine nanofibers and (b) T-CN; (c) TEM image and a magnified image (inset) of T-CN/CdS-10; (d) HRTEM image of T-CN/CdS-10; (e) Elemental mapping images of carbon, nitrogen, cadmium, and sulfur; (f) EDX pattern.

T-CN with numerous porous structures can be confirmed through SEM in Fig. 1b. Owing to the high reactivity of the amine of the melamine molecule, it can be easily protonated by treating with dilute aqueous HNO_3 . Thus, it can be deduced that the fibrous crystal is a class of salt that is composed of protonated melamine and nitric ions. The existence of both H^+ and NO_3^- is prerequisites for fibrous self-assembly, which can be maintained by electrostatic attraction, p-p stacking interactions, and H bonding. After the thermal treatment, a porous structure can be formed with the release of NH_3 molecules [29]. It can be seen from Fig. 1c and the inset of Fig. 1c that CdS nanoparticles with an average size of around 20 nm disperse uniformly on the surface of T-CN/CdS-10 composite. HRTEM (Fig. 1d) shows that lattice spacings are 0.332 and 0.302 nm, corresponding to the (002) lattice planes of g- C_3N_4 and (111) lattice planes of CdS, respectively, which indicate the coexistence of g- C_3N_4 and CdS. The elemental mapping images (Fig. 1e) verify the uniform distribution of carbon, nitrogen, cadmium, and sulfur elements. The weight rate of CdS is about 11.0%, as shown in Fig. 1f.

The crystal structure and phases of the samples were investigated through X-ray diffraction (XRD) analysis, and the results are shown in Fig. 2a. There are two similar diffraction peaks for bulk and tubular g- C_3N_4 . The former peak located at 13.1° corresponds to the in-plane structural packing of tri-s-triazine units ((100) crystal planes), while the peak at 27.5° can be ascribed to the interplanar stacking of conjugated aromatic system ((002) crystal planes) [30,31]. It is remarkable that, because of the less ordered stacking of the tri-s-triazine motifs, the peak corresponding to the (100) crystal plane of tubular g- C_3N_4 is much weaker than that of bulk g- C_3N_4 . The XRD data of pure CdS reveal characteristic 2θ peaks at 24.9° , 27.1° , 36.8° , 44.3° , 48.2° , and 52.4° , which correspond to the hexagonal wurtzite structure (JCPDS no. 65-3414). Besides, the main characteristic diffraction peaks of T-CN/CdS composites gradually shift from T-CN to CdS with the increase in the proportion of the CdS hybridized to T-CN.

The chemical structures were analyzed by using FT-IR. As shown in Fig. 2b, the sharp peak centered at $\sim 810\text{ cm}^{-1}$ corresponds to a breathing mode of the s-triazine units of g- C_3N_4 . On

the other hand, the absorption bands in the range $1200\text{--}1750\text{ cm}^{-1}$ can be attributed to the aromatic C–N stretching vibration mode. The broad band located at $\sim 3150\text{ cm}^{-1}$ corresponds to the stretching mode of the N–H bond [32–34]. Meanwhile, the typical absorption peaks of CdS emerge in all the composites, which indicate that CdS was successfully deposited with T-CN by the present synthetic route without any structural changes. As for the pure CdS sample, the bands at 1400, 1290, 1106, 963, and 701 cm^{-1} are attributed to the Cd–S bond. The broad band centered at 3420 cm^{-1} and the band observed at 1617 cm^{-1} originate from the water molecules absorbed on the surface of the sample [35,36]. However, no characteristic peaks related to the Cd–S bond appear in the patterns of the T-CN/CdS-x composites owing to the low contents of CdS.

XPS was carried out to analyze the surface elementary compositions and chemical states. The C 1s spectrum of T-CN/CdS-10 (Fig. 3a) could be deconvoluted into three peaks centered at 288.6, 286.4, and 284.8 eV; the first two peaks correspond to the binding energy of the carbon atom in the C–(N)₃ and N–C=N bonds of g- C_3N_4 , whereas the third peak could be attributed to the adventitious hydrocarbon of the instrument [37]. There are three main peaks in the high-resolution N 1s spectra (Fig. 3b): the characteristic peak at 400.2 eV can be assigned to the delocalized π -electron of the C–N heterocycle, the peak at 398.5 eV can be assigned to the binding energy of the sp^3 -hybridized nitrogen atom in the N–(C₃N₃)₃ bond, and the peak at 397.8 eV can be assigned to the binding energy of the sp^3 -hybridized nitrogen atom in the C=N–C bond. It can also be observed from the high-resolution C 1s and N 1s spectra that the peaks of T-CN/CdS-10 slightly shift to higher binding energies when compared with those of pure T-CN, indicating the presence of strong interfacial interactions between g- C_3N_4 and CdS. Additionally, in the Cd 3d orbital scan spectrum (Fig. 3c), the peaks located at 412.3 and 404.9 eV could be attributed to the Cd^{2+} of CdS. In the S 2p orbital scan spectrum (Fig. 3d), the peaks located at 162.4 and 161.2 eV could be attributed to the S^{2-} of CdS [35]. Based on the above analysis, it can be confirmed that the graphic phases C_3N_4 and CdS coexist in T-CN/CdS-10 sample with a strong interfacial force.

Low-temperature N_2 adsorption-desorption experiments

Fig. 2. (A) XRD patterns and (B) FT-IR spectra of the as-prepared samples (a) B-CN; (b) T-CN; (c) T-CN/CdS-1; (d) T-CN/CdS-5; (e) T-CN/CdS-10; (f) T-CN/CdS-20; and (g) CdS.

Fig. 3. High-resolution (a) C 1s and (b) N 1s spectra of T-CN and T-CN/CdS-10; high-resolution (c) Cd 3d and (d) S 2p spectra of T-CN/CdS.

were carried out to analyze the specific surface area and pore size distribution of the photocatalyst because these two factors play essential roles in determining the properties of photocatalysts. The N_2 adsorption-desorption isotherms of B-CN and T-CN displayed in Fig. 4 confirm that both these samples exhibit type IV isotherms, which indicate the presence of mesoporous and macroporous structures. The small hysteresis loop of B-CN at high P/P_0 is caused by the aggregation of the B-CN particles. In contrast, T-CN exhibits an obvious hysteresis loop at high P/P_0 , indicating the presence of slit-shaped mesopores and macropores. It can be seen from the BJH pore size distribution diagram (inset of Fig. 4) that B-CN reveals a small peak centered at 4 nm. As for T-CN, a wide peak at approximately 20 nm can be ascribed to the abundant small mesopores. Additionally, the pore volumes of B-CN and T-CN are 0.032 and 0.214 cm^3/g (Table 1), respectively, and a higher pore volume is more beneficial for the absorption of more substrates. The

Fig. 4. N_2 adsorption-desorption isotherms and BJH pore size distributions (inset) of the as-prepared samples.

BET specific surface area of T-CN was calculated to be 38.8 m^2/g , which is 6.2 times higher than that of B-CN (6.3 m^2/g). The enlarged specific surface area can offer more active sites for the reaction, thus further increasing the photocatalytic activity. In addition, the porous structure can effectively reduce the migration distances of the electrons and holes, thereby reducing the recombination probability of the carriers as well as facilitating their migration to the surface of the material for the occurrence of the corresponding reactions. The specific surface area of the CdS-modified $g-C_3N_4$ nanotube was determined to be 38.2 m^2/g , which is close to that of bare T-CN. The slight decrease in the specific surface area could be attributed to the blockage of the porous channel in the $g-C_3N_4$ nanotube by the CdS nanoparticles.

3.2. Optional properties

UV-vis diffuse reflectance spectroscopy was used to analyze the photoabsorption properties of the samples. As shown in Fig. 5a, the characteristic absorption edge of T-CN is located at 460 nm, and T-CN presents a wider absorption edge at 525 nm. It is noteworthy that the photoabsorption abilities of T-CN and T-CN/CdS- x composites are stronger than that of the CdS sample in the visible region. This phenomenon may originate from the multiple reflections of incident light within the hierarchical nanotube structure.

The bandgap energies of T-CN and CdS can be estimated by

Table 1

N_2 adsorption test results of B-CN and T-CN.

Sample	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
B-CN	6.3	~4	0.032
T-CN	38.8	~20	0.214

Fig. 5. (a) UV-vis DRS; (b) Band energy analysis plots; (c) PL spectra of the as-prepared samples.

using Kubelka-Munk theory according to the formula $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α represents the absorption coefficient, h is Planck's constant, ν is the light frequency, A is a constant of the conductor, n is a constant dependent on the transition type of the semiconductor (for direct transition, the value is 1; for indirect transition, the value is 4), and E_g is the bandgap energy. Thus, the bandgaps estimated from the intercepts of the tangents to the plots of $(\alpha h\nu)^{n/2}$ vs. photon energy ($h\nu$) are 2.70 and 2.36 eV (Fig. 5b) for T-CN and CdS, respectively. The band energy shows an obvious blue shift with the increase in T-CN content, compared to that of CdS, due to the enhanced photon absorption of T-CN.

PL emission spectra can be obtained when the photogenerated electron-hole pairs combine together. Hence, the intensity of the PL emission peak can directly reflect the separation rate of photoexcited carriers. As observed in Fig. 5c, the PL spectra of the samples show different luminescence intensities at the excitation wavelength of 320 nm. The pristine B-CN and CdS

show stronger PL emission peaks, which suggest that the electrons and holes of B-CN and CdS undergo facile recombination. However, because of the structural effect, the PL intensity of T-CN is much lower than those of B-CN and CdS, which can decrease the diffusion distance of the electrons and holes to the surface of the photocatalyst. More importantly, the T-CN/CdS-10 composite exhibits the lowest fluorescence intensity, which indicates that the recombination of electron-hole pairs can be further inhibited by constructing a T-CN/CdS heterojunction by coupling with CdS nanoparticles.

3.3. Electrochemical properties

Fig. 6a shows the photocurrent responses for five on-off cycles under visible light irradiation. When the light is turned on, reproducible and steady photocurrents are recorded when using T-CN, CdS, and T-CN/CdS-10 as the working electrodes. It is noticeable that the T-CN/CdS-10 composite exhibits a much

Fig. 6. (a) I - t curves; (b) EIS Nyquist plots; (c) and (d) Mott-Schottky plots of the as-prepared samples.

higher photocurrent density compared with the other samples, which suggests that effective separation of the photogenerated electron-hole pairs can be achieved between T-CN and CdS. When the light is turned off, the photocurrent responses of the samples can be negligible. Fig. 6b shows the EIS of T-CN, CdS, and T-CN/CdS composite. Under the same conditions, the radius of the T-CN/CdS-10 heterojunction is smaller than that of pristine T-CN and CdS, indicating that the interfacial resistance between T-CN and CdS is weak. These results are consistent with the photocurrent response results. To deduce the conduction band (CB) position as well as to verify that the synthesized T-CN/CdS samples are suitable for H_2 production, the flat band positions of T-CN and CdS were investigated through Mott-Schottky experiments in the dark. As shown in Fig. 6c and 6d, both T-CN and CdS exhibit positive slopes, which indicate that both are typical n-type semiconductors. Moreover, the flat band potential of CdS (-0.69 eV vs. Ag/AgCl at pH = 6.6) is more positive than that of T-CN (-1.31 eV vs. Ag/AgCl at pH = 6.6), but more negative than that of water reduction (H^+/H_2 : -0.59 eV vs. Ag/AgCl at pH = 6.6), indicating that photogenerated electrons can transfer from T-CN to CdS to further reduce H^+ into H_2 . The valence band (VB) positions of T-CN and CdS can thus be calculated based on the CB positions and bandgap energies, and are 1.39 and 1.67 eV vs. Ag/AgCl at pH = 6.6, respectively.

3.4. Photocatalytic activities and mechanism

The photocatalytic degradation efficiency of RhB was measured under visible light irradiation ($\lambda \geq 420$ nm). As presented in Fig. 7a, RhB can barely be degraded in the absence of a photocatalyst, indicating that RhB exhibits stable chemical properties and cannot be self-degraded under visible light irradiation. T-CN exhibits enhanced photocatalytic activity compared with

that of B-CN; approximately 59.2% of RhB can be degraded within 60 min of irradiation. CdS exhibits a higher photocatalytic performance; approximately 78.5% of RhB can be degraded over the same duration. It is noteworthy that when T-CN and CdS combined and formed binary composites, the T-CN/CdS- x composites, especially T-CN/CdS-10, showed enhanced photocatalytic degradation abilities, which can be ascribed to the establishment of a heterojunction between T-CN and CdS. Fig. 7b illustrates that all the samples obey apparent first-order reaction rate. Fig. 7c illustrates the variation in the absorbances at the excitation wavelength of 554 nm when using T-CN/CdS-10 as the photocatalyst. The absorbances obviously decrease with increasing irradiation time. No absorbance peak can be observed after irradiation for 60 min, which suggests that RhB dye decomposed completely.

The photocatalytic performance was also evaluated for water splitting to produce H_2 in a TEOA aqueous solution under visible light irradiation. As depicted in Fig. 7d, after 5 h of visible light irradiation, B-CN and T-CN show a relatively low H_2 production, with only 19.7 and 69.2 μmol of H_2 being generated, respectively. This can be ascribed to the poor charge transport ability. On the other hand, T-CN/CdS composites exhibit enhanced apparent water splitting activities, especially T-CN/CdS-10 composite with an average H_2 production of 362.7 μmol . It can also be observed in Fig. 7e that the H_2 production rate over T-CN/CdS-10 is up to 71.6 $\mu\text{mol/h}$, which is about 16.3 and 4.6 times higher than those of B-CN and T-CN, respectively. The enhanced photocatalytic activity can be primarily attributed to the synergistic effect between T-CN and CdS. Furthermore, as shown in Fig. 7f, the excellent H_2 production rate over T-CN/CdS-10 can be maintained over five cycles of photocatalytic reactions, which indicates its promise in practical applications.

On the basis of the above experimental results and discus-

Fig. 7. (a) Photocatalytic degradation of RhB; (b) Kinetic linear curves of the degradation rate; (c) UV-vis spectral changes over time for RhB; (d) Amounts of H_2 evolved after 5 h; (e) Kinetic linear curves of the H_2 evolution rate; (f) Results of H_2 production cyclic tests on T-CN/CdS-10 sample.

sion, the catalytic mechanism of T-CN and T-CN/CdS composites toward photocatalytic degradation and H_2 evolution was inferred, as illustrated in Scheme 2. According to previous research [26,27], a one-dimensional tube-like photocatalyst displays a higher charge carrier mobility along the longitudinal direction, which is beneficial for the separation and transfer of electrons and holes; this, together with the high specific surface area, accounts for the excellent photocatalytic performance of T-CN compared with that of B-CN. For the T-CN/CdS composites, because the CB position of T-CN is more negative than that of CdS and the VB position of CdS is more positive than that of T-CN, the photogenerated electrons are prone to transfer from T-CN to CdS while the holes are prone to transfer from CdS to T-CN; thus, electrons and holes are spatially separated. In the RhB photocatalytic degradation system, holes with strong oxidizing properties can oxidize H_2O to $\cdot OH$, which can further oxidize and degrade RhB; meanwhile, the holes can also directly oxidize and degrade RhB. In the photocatalytic H_2 evolution system, the electrons present in the CB of CdS are transferred to the surface of the platinum particles, where they reduce the H^+ absorbed on the surface of the catalyst and release H_2 ; meanwhile, holes are consumed by the TEOA added to the catalytic system.

4. Conclusions

A newly designed porous $g-C_3N_4$ tube with a reasonable loading capacity of CdS has been proved to be a promising photocatalyst for the degradation of contaminants and for H_2 evolution. The T-CN/CdS composites display obviously enhanced photocatalytic performance for the degradation of RhB and water splitting compared with those single-component photocatalysts. The highest RhB degradation efficiency was realized when using the T-CN/CdS-10 composite as the photocatalyst. The optimum H_2 evolution efficiency is up to $71.6 \mu\text{mol/h}$, which is about 16.3 times higher than that of B-CN. This study may broaden views on the design of new morphologies and structures of $g-C_3N_4$ -based semiconductor photocatalysts for better utilization of solar energy.

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Scheme 2. Illustration of the photocatalytic mechanism.

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Graphical Abstract

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CdS-modified one-dimensional g-C₃N₄ porous nanotubes for efficient visible-light photocatalytic conversion

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A porous g-C₃N₄ tube with a high specific surface area and reasonable loading capacity of CdS was fabricated and applied to the degradation of contaminants and to H₂ evolution. It exhibited a H₂ evolution efficiency that was enhanced 16.3 times.

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CdS修饰的一维g-C₃N₄多孔纳米管在光催化降解污染物和产氢中的应用种 奔^a, 陈 雷^a, 韩德志^b, 王 亮^a, 冯丽娟^a, 李 勤^{c,*}, 李春虎^a, 王文泰^{a,*}^a中国海洋大学海洋化学理论与技术教育部重点实验室, 化学化工学院, 山东青岛266100, 中国^b青岛科技大学化工学院, 山东青岛266042, 中国^c格里菲斯大学昆士兰微米纳米技术中心, 布里斯班, 澳大利亚

摘要: 利用太阳光在光催化材料作用下将低能量密度的太阳能转化成化学能储存在氢气和一氧化碳等清洁能源中, 有利于能量的存储、运输和使用, 具有广阔的前景. 光催化技术的关键在于催化剂, 以TiO₂为代表的传统半导体光催化剂存在着电子与空穴复合率高、禁带宽度过大和无法吸收可见光等缺点, 这些因素限制了其在光催化领域的进一步发展和应用. 因此, 寻找优秀的光催化材料是科研工作者的不懈追求.

石墨相氮化碳是一种仅由C和N两种元素组成的有机半导体材料, 具有良好的热稳定、耐腐蚀性和生物相容性, 这些优点使得石墨相氮化碳在多个领域都极具应用前景. 在光催化领域, 石墨相氮化碳独特的电子结构、稳定的物理化学性质, 以及其导带位置(约-1.12 eV)远小于氢离子的还原电势(0 eV), 使其能够很好地应用于光解降解污染物和光解水产氢.

目前, 石墨相氮化碳光催化技术的研究重点在于如何解决石墨相氮化碳比表面积过小和光量子效率低的问题. 针对这些问题, 我们对石墨相氮化碳光催化材料的结构进行了设计, 构建出CdS修饰的一维g-C₃N₄多孔纳米管. 以三聚氰胺为原料, 通过质子化处理, 得到表面光滑、质地均匀、拥有超高长径比的三聚氰胺纳米纤维(MNFs), 然后对其进行煅烧处理得到多孔纳米管状g-C₃N₄催化剂. 随后, 在纳米管的基础上通过水热法与CdS颗粒复合, 成功制备出多孔管状g-C₃N₄/CdS复合异质结型催化剂. 利用多种表征手段对所合成的新型光催化剂的形貌、结构、光学性质及光电性质进行了表征, 并评估了

其光催化降解罗丹明B和光解水产氢性能,考察了催化剂的循环利用及稳定性.

SEM和TEM结果表明,管状的石墨相氮化碳拥有丰富的孔道结构,其增大的比表面积有利于暴露更多的活性位点,从而提高了光催化性能.光催化降解罗丹明B实验表明,多孔管状g-C₃N₄的催化性能较体相g-C₃N₄有明显提高.当管状g-C₃N₄与适量CdS复合形成异质结型光催化剂时,光催化效果得到进一步提升,其中当CdS负载量为10 mol%时,复合物的催化效果最好,在60 min内可完全降解罗丹明B.在光催化分解水产氢实验中,5 h内管状g-C₃N₄/CdS复合物产氢量高达362.7 μmol,分别是体相g-C₃N₄的16.3倍和管状g-C₃N₄的4.6倍.

关键词: 管状石墨相氮化碳; 硫化镉; 可见光催化剂; 光催化产氢; 光催化降解染料

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