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nanosheets and their photocatalytic performance

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Ultra-low-temperature growth of CdS quantum dots on g-C<sub>3</sub>N<sub>4</sub>

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CdS quantum dots deposited on carbon nitride  $(g\text{-}C_3N_4)$  nanosheets have been synthesized by ultra-low temperature(-60  $^\circ\text{C}$ ) liquid phase precipitation reactions. The obtained CdS quantum dots were uniformly distributed on the surface of the g-C\_3N\_4 nanosheets with average diameter of 5 nm. Correspondingly, the CdS/g-C\_3N\_4 exhibits highly enhanced photocatalytic performance.

The preparation of high-quality semiconductor nanocrystals, particularly in quantum size (quantum dots, QDs), has become a dominating research field, due to the unique size-dependent properties and well-defined electronic and optical properties.<sup>1-3</sup> This has attracted great attention in controlling the crystal structure of semiconductor materials in both growth and nucleation.<sup>4</sup> Hot injection method and non-injection organic synthesis method are the most common synthesis methods for semiconductor nanocrystal production.<sup>5</sup> These methods usually require a heating process at specific reaction temperatures for semiconductor nanocrystal growth. The heating process could stimulate reactive precursors to nucleate nanoparticles and result in a coinstantaneous nucleation and growth.<sup>6</sup>

Usually, the QD formations contain the nucleation and growth process. According to the classical nucleation, the necessary Gibbs free energy of activation for nuclei formation ( $\Delta G^*$ ) in a typical solution synthesis can be described as follow: <sup>7-9</sup>

$$\Delta G^* = \frac{16\pi \gamma^3 v^2}{3k_B^2 T^2 \left( \ln \frac{C \cdot C_0}{C_0} \right)^2}$$
(1)

Where  $\gamma$  is the increase in the free energy per unit surface area of the nucleus,  $\nu$  is the molar volume of the nucleus, T is the

temperature,  $k_B$  is the Boltzmann constant,  $C_0$  is the saturation concentration of the solution, and C is the actual concentration of the reactants. In addition to the time dependence of the rate of conversion, the rate constant k is temperature dependent, usually assumed to follow an Arrhenius relation of the form:

$$k = Ae^{-Ea/RT}$$
(2)

Where T is the thermodynamic temperature, A is the preexponential function and Ea is supposed to represent the activation energy for the reaction. According to the equations (1) and (2), at the certain concentration of the reactants, the nucleation of the reaction products can be effectively suppressed by reducing the temperature of the reactants.<sup>10-12</sup>

In this work, we focus our attentions toward producing cadmium sulfide (CdS) QD nanocrystals through controlling the reaction temperature. CdS QDs have unique properties and adjustable band gaps, making it widely applied to water pollution treatment and H<sub>2</sub> production.<sup>13-16</sup> However, shape control of high quality homogeneous and stable semiconductor QDs from traditional solution chemistry is extremely difficult, mainly because of the difficulty in controlling the diffusion, aggregation and nucleation of the product molecule in the liquid phase. <sup>17-20</sup> One of the most efficient routes to solve these problems is to load cadmium sulfide QDs onto graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) nanosheets to form stable 0D/2D nanocomposites.  $^{21, 22}$  g-C<sub>3</sub>N<sub>4</sub> is a metal-free semiconductor, the photocatalyst activity of  $g-C_3N_4$  can be greatly enhanced via different methods, such as supporting various materials as co-catalysts, such as carbon or metals, and forming composites with other semiconductors.<sup>23-25</sup> Interactions between two moieties can make QDs more dispersive and stable, meanwhile the accelerated charge facilitated can efficiently quench the photoluminescence of QDs, thereby suppressing the recombination of photoexcited charge.<sup>26, 27</sup>.

Herein, a CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposite photocatalyst was fabricated by an ultra-low temperature liquid phase precipitation reaction. CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites were employed for visible-light-driven photocatalytic hydrogen evolution and degradation for the organic dye, Rhodamine B. The photostability of obtained photocatalysis was significantly enhanced. A series of characterizations reveals that CdS QDs with average diameter of 5 nm are uniformly scattered on

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 $g-C_3N_4$  nanosheets. The obtained CdS content of 4.5wt% the  $g-C_3N_4$  nanocomposites could greatly improve the photocatalytic activity of  $g-C_3N_4$  nanosheets for hydrogen generation and degradation for organic dye Rhodamine B.

The synthesis mechanism of CdS/g-C<sub>3</sub>N<sub>4</sub> is illustrated in Fig. 1. g-C<sub>3</sub>N<sub>4</sub> nanosheets were dispersed into CdCl<sub>2</sub> precursor solutions. In conventional precipitation synthesys methods, Na<sub>2</sub>S solution is slowly dropped into the CdCl<sub>2</sub> precursor solutions. CdS nanoparticles loading on g-C<sub>3</sub>N<sub>4</sub> is then prepared by the spontaneous nucleation and agglomeration of CdS nanocrystals, the obtained material is room temperature (RT) CdS/g-C<sub>3</sub>N<sub>4</sub>. In contrast, we slowly dropped the Na<sub>2</sub>S solution into CdCl<sub>2</sub> precursors at -60 °C, CdS quantum dots supported on g-C<sub>3</sub>N<sub>4</sub> were obtained, and the grown progress of CdS nanocrystals were suppressed at ultra-low-temperature reaction progress.

The morphology of heterojunctions was investigated by transmission electron microscopy analysis. As shown in TEM image (Fig. 2a), it was clearly seen that the CdS QDs with an average size of 5 nm (Fig. S1) were homogeneously dispersed on the lamellar surface of g-C<sub>3</sub>N<sub>4</sub>. The HRTEM image further revealed that the characteristic interplanar spacing of 0.336 nm matches the (111) lattice planes of hawleyite CdS (Fig. 2b and Fig. 2d). As for the control sample, CdS nanoparticles synthesized at  $25^{\circ}$ C were randomly accumulated on the surface of the g-C<sub>3</sub>N<sub>4</sub> nanosheets (Fig. 2c). Furthermore, CdS nanoparticles showed larger size and a wider size distribution compared with CdS QDs (Fig. 2d). Most of the CdS nanoparticles had diameters from 20 to 50 nm (Fig. S2). The amount of CdS QDs loading on g-C<sub>3</sub>N<sub>4</sub> nanosheets was 4.5% as measured by inductively coupled plasma ion emission spectroscopy (ICP/IES). Clearly, the mentioned results strongly attested that the CdS QDs had been homogeneously modified on the  $g-C_3N_4$  surface to compose CdS/g-C<sub>3</sub>N<sub>4</sub> via the ultra-low temperature precipitation approach.

The phase structure and composition of the samples were further revealed by XRD, UV-vis spectra, and XPS, respectively. The XRD patterns of the CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub> and pure g-C<sub>3</sub>N<sub>4</sub> were shown in Fig. 3a. Two obvious diffraction peaks were displayed at 27.4° and 13.1° corresponding to pure g-C<sub>3</sub>N<sub>4</sub>, belonging to the typical graphitic interlayer (002) peak and the in-plane structural packing motif (110). <sup>;/</sup> The pure CdS displays three distinct diffraction peaks at 26.7°, 44.1°and 52.2°respectively corresponding to (111), (220), and (311) crystal planes of CdS (JCPDS No. 75-0581). The XRD pattern of CdS/g-C<sub>3</sub>N<sub>4</sub> and RT CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites



Fig. 1. The schematic outline for the CdS nanoparticles deposited on

g-C<sub>3</sub>N<sub>4</sub> nanosheets.



Fig. 2. (a) TEM and (b) HRTEM images of CdS/g-C<sub>3</sub>N<sub>4</sub>. (c) TEM and (d) HRTEM images of RT CdS/g-C<sub>3</sub>N<sub>4</sub>.

show diffraction peaks of both CdS and g-C<sub>3</sub>N<sub>4</sub>, while the characteristic peaks of CdS (26.7°) and g-C<sub>3</sub>N<sub>4</sub> (27.4°) were very close and overlap with each other. The peak width of the CdS/g-C<sub>3</sub>N<sub>4</sub> at 44.1° and 52.2°, were smaller than that of RT CdS/g-C<sub>3</sub>N<sub>4</sub>, which indicated the crystalline size of CdS prepared at ultralow temperature is smaller than that prepared at 25°C.

The optical properties of CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub>, pure g-C<sub>3</sub>N<sub>4</sub>, and CdS were further characterized by ultraviolet visible absorption spectroscopy (UV-vis). The adhering of CdS to the g-C<sub>3</sub>N<sub>4</sub> lead to an improvement in the whole investigated wavelength range (Fig. S3 and Fig. 3b). As shown in Figure S3 and Figure 3b, the pure CdS exhibited an absorption edge at 521 nm with band gap of 2.38 eV, the pure g-C<sub>3</sub>N<sub>4</sub> exhibits an absorption edge at 444 nm with band gap of 2.79eV. The samples of CdS/g-C<sub>3</sub>N<sub>4</sub> and RT CdS/g-C<sub>3</sub>N<sub>4</sub> have absorption edges at 455 nm and 471 nm, which corresponded to the band gaps of 2.72 eV and 2.63 eV. Thus, the CdS/g-C<sub>3</sub>N<sub>4</sub> and CdS, which contribute to efficiently produce photogenerated electrons-holes.

The CdS/g-C<sub>3</sub>N<sub>4</sub> samples were further investigated by XPS. The XPS peaks of Cd 3d and S 2p (Fig. S4) indicated the formation of CdS. The energies of the main peaks of Cd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> are found at 404.8 eV and 411.5 eV, respectively, which are consistent with those of Cd 3d in CdS. <sup>28</sup> The minor peak of S 2p at 161.6 eV and 162.8 eV is closed to that of CdS, which is most possible from the elemental sulfur, which was adsorbed on surface of g-C<sub>3</sub>N<sub>4</sub>. <sup>29</sup>

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Fig. 3. (a) XRD pattern of g-C<sub>3</sub>N<sub>4</sub>, CdS/g-C<sub>3</sub>N<sub>4</sub> and RT CdS/g-C<sub>3</sub>N<sub>4</sub>. The dark cyan line is the standard pattern of the CdS (JCPDS No. 75-0581). (b)  $(ahu)^2$  versus hu curve of CdS, g-C<sub>3</sub>N<sub>4</sub>, CdS/g-C<sub>3</sub>N<sub>4</sub> and RT CdS/g-C<sub>3</sub>N<sub>4</sub>. The dashed lines are tangents of the curves. The intersection value is the band gap.

The recombination of the photo-generated electrons and holes were investigated by photoluminescence (PL) spectra with an excitation of 325 nm. The spectra of different samples had similar shape emission peaks (Fig. S5). The pure  $g-C_3N_4$  sample exhibited an intense emission peak at 455 nm, at the same time, the intensity of this emission band dropped significantly for the composite samples with CdS, which indicates a valid transfer of electron-hole pairs from  $g-C_3N_4$  to CdS.<sup>30</sup>

Photocatalytic H<sub>2</sub> evolution activity of the synthesized CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites was measured under visible light irradiation, and 0.5wt% Pt was added as co-catalyst to cut dowm the overpotential of H<sub>2</sub> evolution. As shown in Fig. 4a and Fig. S6, the CdS QDs grown at ultralow temperature on g-C<sub>3</sub>N<sub>4</sub> nanosheets noticeably improved the photocatalytic  $H_2$  evolution activity compared to pure g-C<sub>3</sub>N<sub>4</sub>. More specifically, the  $CdS/g-C_3N_4$  nanocomposites exhibited a  $H_2$ evolution rate of 4.967 mmol  $h^{-1}g^{-1}$ , which was more than 59 times higher than pure  $g-C_3N_4$  (0.083 mmol  $h^{-1}g^{-1}$ ). Compared with the CdS (0.997 mmol  $h^{-1}g^{-1}$ ) and RT CdS/g-C<sub>3</sub>N<sub>4</sub> (1.72 mmol  $h^{-1}g^{-1}$ ), CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites displayed excellent photocatalytic for hydrogen evolution. The stability test results of CdS/g-C<sub>3</sub>N<sub>4</sub> were shown in Fig. 4b, no distinct decrease of H<sub>2</sub> evolution was observed after a five-run test of photocatalytic H<sub>2</sub> evolution. The XPS (Fig.S8) and XRD (Fig.S9) of CdS/g-C<sub>2</sub>N<sub>4</sub> after the H<sub>2</sub> evolution stability test were measured. No obvious changes in materials properties were exhibited.

The photocatalytic activities of samples were also measured by RhB photodegradation under visible light ( $\lambda > 420$  nm). From Fig. 4c and Fig. S7, the CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites showed much higher photodegradation efficiency (Dp =89.5%) than pure g-C<sub>3</sub>N<sub>4</sub> (Dp =12.7%), CdS (Dp =40.6%) and RT CdS/g-C<sub>3</sub>N<sub>4</sub> (Dp =50.2%). This demonstrates that the recombination of CdS QDs and g-C<sub>3</sub>N<sub>4</sub> can tremendously improve the photodegradation efficiency. The cycling test of photocatalytic degradation of RhB with CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposite was repeated five times (Figure 4d), displaying that it possesses great stability and repeatability. The XPS (Fig.S10) and XRD (Fig.S11) of CdS/g-C<sub>3</sub>N<sub>4</sub> after the RhB degradation stability test were measured. No obvious changes in materials properties were exhibited.

According to the mentioned experimental results, we confirm that the improvement of photocatalytic activity for CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites are attributed to efficient interfacial transfer and separation of photogenerated carriers between the g-C<sub>3</sub>N<sub>4</sub>





Fig. 4. (a) Comparison of the visible light-driven photocatalytic evolution  $H_2$  activity of CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> and CdS. (b) Cycling tests of visible-light-driven photocatalytic evolution  $H_2$  activity of CdS/g-C<sub>3</sub>N<sub>4</sub>. (c) Comparison of the visible-light-driven photocatalytic degradation RhB activity of CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> and CdS. (d) Cycling tests of visible-light-driven photocatalytic degradation RhB activity of CdS/g-C<sub>3</sub>N<sub>4</sub>. (e) The transient photocurrent responses of CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> and CdS under visible-light irradiation. (f) Electrochemical impedance spectroscopy (EIS) of CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> and CdS under visible-light irradiation.

usually applied to research the excitation and transfer of photogenerated charge carriers. Fig. 4e showed the transient photocurrent response of CdS/g-C<sub>3</sub>N<sub>4</sub>, RT CdS/g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> and CdS. From the Fig. 4e, we can expressly figure out that the photocurrent response of g-C<sub>3</sub>N<sub>4</sub> is lower than other samples. The photocurrent response of CdS/g-C<sub>3</sub>N<sub>4</sub> was significantly higher than of the RT CdS/g-C<sub>3</sub>N<sub>4</sub> and CdS. The generation of the photocurrent is mainly the result of photoinduced electrons diffusing to the ITO. <sup>31</sup> The transient photocurrent responses showed that the separation efficiency of the photogenerated electrons and holes in the CdS/g-C<sub>3</sub>N<sub>4</sub> was markedly improved as a result of the synergistic effect between CdS and g-C<sub>3</sub>N<sub>4</sub>. The increasing of the photocurrent has linear relationship with photocatalytic activity. Electrochemical impedance spectroscopy (EIS) was also performed to characterize charge carrier transportation. Fig.4f displayed that the impedance

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radius of the CdS/g-C<sub>3</sub>N<sub>4</sub> was smaller than that of RT CdS/g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> and CdS. which indicates the higher efficiency of photoinduced electron-hole pairs through an interfacial interaction between g-C<sub>3</sub>N<sub>4</sub> and the CdS quantum dots<sup>32-34</sup>.

Fig. S12 showed the schematic illustration of the  $CdS/g-C_3N_4$ photocatalytic mechanism. Because of suitable match overlapping band structures and similarly contacted interfaces, photoexcited electrons in the CB of g-C<sub>3</sub>N<sub>4</sub> can immediately move to the CB of CdS. In the same time, photoexcited holes in the VB of CdS spontaneously move to the VB of g-C<sub>3</sub>N<sub>4</sub>. The mechanism of hydrogen evolution over the composite material was presented in Fig. S12a. As a consequence, L-ascrobic acid (H<sub>2</sub>A) adhering on the  $g-C_3N_4$  surface can be oxidized by photoinduced holes. On the surface of Pt nanoparticles, the separated electrons will have enough time to induce  $H^+$  to  $H_2$ . Fig S12b showed the process of degradation of RhB. The adsorbed dissolved oxygen could generate •O<sup>2-</sup> free radicals, due to the photogenerated electrons transferred to the surface of composite. Meanwhile, active •OH radicals were produced by H<sub>2</sub>O splitting. When  $h^{\dagger}$  moved from the VB of the g- $C_3N_4$  and CdS, both  $h^+$  and •OH free radicals can transform from RhB into products.

#### Conclusions

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In summary, a facile ultra-low-temperature reaction approach was developed to synthesize CdS quantum dots supported on g-C<sub>3</sub>N<sub>4</sub> nanosheets. The resulting CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites exhibited high photocatalytic performance for H<sub>2</sub> production and degradation of RhB. The synthesized nanocomposites with 4.5wt% CdS quantum dots displayed a H<sub>2</sub> evolution rate of 4.967 mmol h<sup>-1</sup>g<sup>-1</sup>, which was 59 times higher than pure g-C<sub>3</sub>N<sub>4</sub> and could retain over 90% activity after 4 cycles. Meanwhile, CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites displayed a degradation rate of 89.5% for RhB solution in 75 min and could retain over 95% activity after 5 cycles. This study may inspire the development an approach for the synthesis of CdS quantum dots and their potential for photocatalystic applications.

### **Conflicts of interest**

There are no conflicts to declare

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