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A Novel Method for Development of Carbon Quantum Dot/Carbon Nitride Hybrid Photocatalyst with Response for Infrared Light Irradiation

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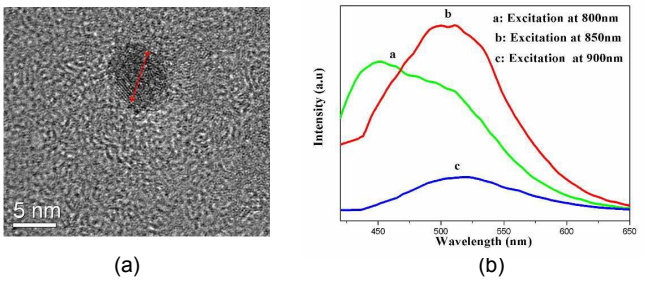
Abstract: A novel method has been developed to combine carbon quantum dot (CQD) with carbon nitride at 450 °C to synthesize an infrared-responsive photocatalyst. In the hybrid photocatalyst, CQD acts as the light source to upconvert infrared light to visible light, while carbon nitride utilize the light emitted by CQD to degrade pollutants.

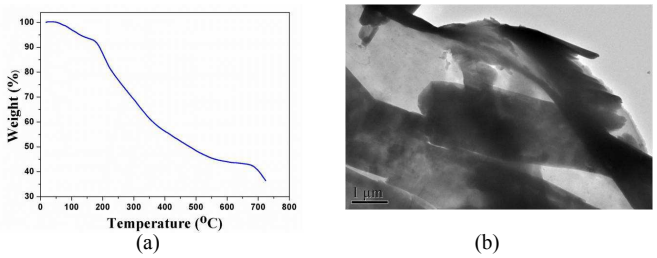
Carbon quantum dot (CQD) is a new type of carbon nanomaterial with discrete, quasi-spherical morphology.[1] The luminescence property of CQD is unique since it can not only absorb short wavelength light to emit long wavelength light (downconversion photoluminescence), but also absorb long wavelength light and emit short wavelength light (upconversion photoluminescence).[2] Given the low cost, fascinating luminescence property and low toxicity, CQD has drawn great attention for application in photovoltaic, sensor, bioimaging and photocatalytic fields.[1-4] Photocatalysis is a process utilizing solar energy to significantly promote the photochemical reactions, e.g., photodegradation of environmental pollutants.[5] So far, most of photocatalysts, such as TiO_2[6] and carbon nitride,[7] can only use the ultraviolet and visible light, which occupy 4% and 43% of solar energy, respectively. Even infrared light accounts for ~53% of solar energy, since its energy is low, the photocatalytic application of infrared light is still limited. Hence, how to use infrared light has been a challenge for scientists in photocatalytic field. The fascinating upconversion photoluminescence of CQD might provide a new strategy to utilize infrared light. Recently, CQD has been hybridized with TiO_2[8-9] and Cu_2O[10] at room temperature to develop catalysts that could harvest infrared light. In these composite, CQD acts as the light source to emit ultraviolet or visible light by absorbing near infrared light.[8-10] The interaction of CQD with TiO_2/Cu_2O could be explained by the complexation between the COOH, OH groups on CQD[1-2] and OH group on TiO_2 (or Cu_2O).[11-12] However, for some photocatalysts with hydrophobic surface, e.g., carbon nitride,[7,13-19] it is difficult to construct composite containing both CQD and hydrophobic carbon nitride at room temperature since the interaction between them is not strong enough. Carbon nitride is a new type of organic polymeric photocatalyst with excellent visible-light response and high chemical stability, which makes it suitable for environmental application, especially under harsh conditions[7, 13] In addition, this unique photocatalyst might represent an important step towards artificial photosynthesis since the reducing and oxidizing centers within photosynthetic organisms are biopolymer.[20] To the best of our knowledge, there is still no study to combine CQD and carbon nitride together for synthesis of a new generation of infrared-responsive photocatalyst. Herein, a facile method has been developed to synthesize CQD-carbon nitride composite at 450 °C and the resulted composite could effectively degrade methyl orange (MO) under infrared light irradiation (λ>800 nm).

CQD was prepared following the method of Li et al.,[10] and characterized by transmission electron microscopy (TEM), UV-visible (UV-Vis) and photoluminescence spectrophotometers. From Fig 1(a), the size of the synthesized carbon material is around 5 nm. More High-resolution TEM images are provided in Fig. S1. A UV peak at ~270 nm was observed (Fig S2), being due to the characteristic aromatic absorption of CQD.[21-22] As shown in Fig 1(b), visible light with wavelength between 440 and 540 nm could be emitted by CQD when it was excited at 800, 850 and 900 nm, respectively, which is consistent with the previous reports.[10]



(a) (b)

Fig 1. (a) TEM image of CQD at 5 nm scale; (b) Photoluminescence spectra of CQD at the excitation wavelength of 800, 850 and 900 nm, respectively.



(a) (b)

Fig 2. (a) Thermogravimetric analysis of CQD; (b) TEM image of CQD treated at 450 oC for 2 h.

Carbon nitride photocatalyst was synthesized using melamine as the precursor heated at 450 °C for 2 h, named as Mem450.[23] X-ray diffraction (XRD), UV-vis and TEM characterization results (Fig. S3) all agree well with the results in the literature,[23] indicating that the polymeric photocatalyst has been successfully synthesized. Mem450-CQD composite was prepared by adding Mem450 into CQD solution (total carbon content of 0.93 g/L), followed by stirring for 10 h; then, the mixture was centrifuged and the precipitant was washed by deionized water for three times. As shown in Fig. S4, the color of supernatant in Mem450-CQD suspension is nearly identical to that of CQD solution, and there is no obvious color difference between Mem450-CQD precipitant and Mem450. Furthermore, the photodegradation experiment showed that the composite could not effectively degrade MO under infrared irradiation (Fig. S5). This implies that the amount of CQD in Mem450-CQD composite prepared by simple mixing is not high enough and could not effectively harvest infrared light (λ>800 nm). This might be due to that the hydrophobic surface of Mem450 inhibits the strong interaction with the hydrophilic groups on CQD.

High temperature treatment is a common method to fuse different materials together. However, for CQD, as the temperature increases to 450 °C, nearly 50% weight lost was observed (Fig 2(a)), being due to the lost of the adsorbed water, dehydration and decarboxylation of the functional groups on CQD surface. TEM characterization also suggests that CQD treated at 450 °C for 2 h has aggregated together (Fig. 2(b)), which has lost the property of upconversion photoluminescence.

In our study, a novel strategy has been proposed to overcome this problem (Fig. 3). To prepare CQD/carbon nitride composite, 8 mL CQD solution (total carbon content of 0.93 g/L) was mixed with melamine solution (1 g melamine in 40 mL deionized water), followed by evaporation at 80 °C to form Mem-CQD mixture. Then,

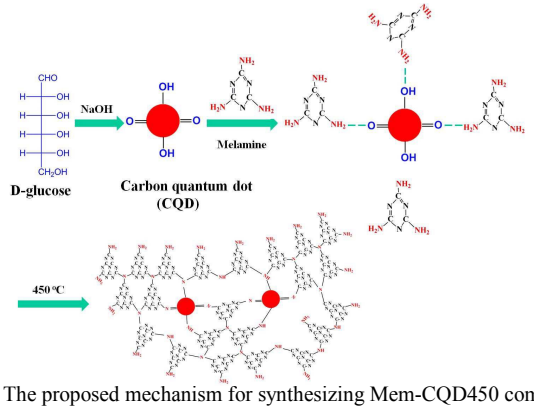
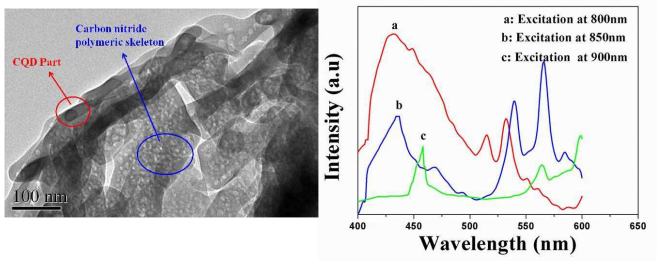


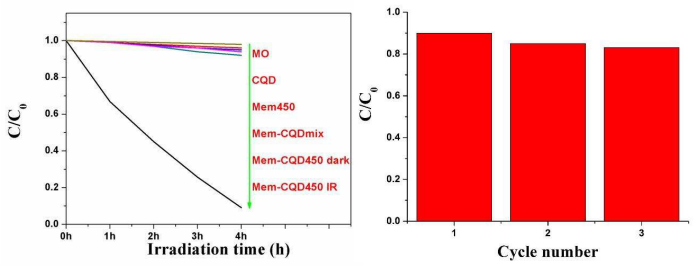
Fig 3. The proposed mechanism for synthesizing Mem-CQD450 composite.

the mixture is heated at 450 °C for 2 h to produce the composite, named as Mem-CQD450. During the heating process, melamine might play three roles: (1) preventing the aggregation of CQDs; (2) polycondensation to form carbon nitride photocatalyst; (3) the released ammonia gas will make an inert atmosphere, which will inhibit in a certain degree the burning of CQD. As shown in Fig S6, the color of Mem-CQD450 is different from that of Mem450 and Mem-CQD-mix, indicating that the reaction between Mem and CQD occurs. From XPS results (Fig S7), the N1s peak of C-N-H group in Mem-CQD450 becomes weaker than that in Mem450, suggesting that these NH_2 groups might have reacted with the surface groups of CQD.[24] Two UV absorption peaks were observed in the UV-vis spectrum of Mem-CQD450 (Fig S8). One is at ~360 nm, which has a red-shift compared to that of Mem450. This might be due to the sensitization of carbon nitride skeleton by CQD. It has been reported that CQD can sensitize TiO_2 to acquire the composite with response under visible light irradiation.[25] Another peak at around 270 nm (Fig S8) could be attributed to the typical absorption of CQD.[21-22, 26] Compared to CQD, this peak becomes broader, which might be explained by the surface reconstruction during the heating process. A long tail appears in UV-vis absorption spectrum of Mem-CQD450 (Fig S8), being attributed to the presence of CQD in Mem-CQD450.[25] According to valence-band x-ray photoelectron spectroscopy (VBXPS) results (Fig S9), the valence bands (VB) of Mem450 and Mem-CQD450 are nearly identical, suggesting that the band gap narrow is mainly due to the CQD part in Mem-CQD450.[27] As shown in Fig 4(a), the surface morphology of Mem-CQD450 has changed compared to Mem450 (Fig S3), a few circles or strips like species could be observed on the surface of carbon nitride skeleton (the area marked by red circle in Fig 4(a)), they are possibly the encapsulated CQD (more TEM images are shown in Fig S10). EDX analysis for the red and blue circled areas in Fig 4(a) shows that the carbon content in the former is 38.1%, while 32.3% in the latter (Fig S11), supporting that this deduction is reasonable. Comparing the photoluminescence spectra of Mem-CQD450 and CQD (Fig 4(b) and Fig 1(b)), the wavelength of light (~420 nm) emitted by Mem-CQD450 excited at 800 nm is shorter than that (~440 nm) of CQD, which is possible due to the change of surface groups on CQD, the passivation by the interaction with carbon nitride polymer and the possible size shrink aroused by the heating treatment. It was reported that surface passivation is essential for fluorescence property of CQD since the surface energy traps could be stabilized by passivation process,[26,28] and the CQD with smaller size usually emits shorter wavelength light than CQD with larger size.[2] In a word, TEM.



(a) (b)

Fig 4. (a) TEM image of Mem-CQD450 at 100 nm scale; (b) Photoluminescence spectra of Mem-CQD450 at the excitation wavelength 800, 850 and 900 nm, respectively.



(a) (b)

Fig 5. (a) The photodegradation of methyl orange (4 mg/L) by CQD, Mem450, Mem-CQDmix and Mem-CQD450 under infrared light irradiation (λ > 800 nm), respectively; (b) The reusability test of Mem-CQD450 photocatalyst under infrared light irradiation (λ > 800 nm).

EDX, Uv-vis spectra and photoluminescence spectra of Mem-CQD450 together will support that CQD exists in Mem-CQD450.

The photocatalytic activity of Mem-CQD450 was evaluated by photodegradation of MO (4 mg/L) under infrared light irradiation (λ > 800 nm). As shown in Fig 5(a), MO is stable under infrared light irradiation, and CQD, Mem450 as well as Mem-CQDmix can not degrade MO by irradiation of infrared light. However, nearly 90% of MO could be photodegraded by Mem-CQD450 under infrared irradiation within 4 h (Fig 5(a) and Fig S12). This indicates that combining CQD with carbon nitride prepared by our strategy could acquire infrared-responsive photocatalyst. To investigate the effect of CQD amount on the activity of synthesized photocatalyst, Mem-CQD(4mL)450, Mem-CQD(6mL)450 and Mem-CQD(10mL)450 were also synthesized following the similar procedures of Mem-CQD450 as described in Fig.3, except using 4, 6 and 10 mL CQD solution, respectively. According to Fig S13, all Mem-CQD450 samples have MO photodegradation activity, which follows the order as: Mem-CQD450 > Mem-CQD(6mL)450 > Mem-CQD(10mL)450 > Mem-CQD(4mL)450. Since CQD in the composite acts as the light source to emit visible light under infrared irradiation, it is reasonable that higher photodegradation activity could be expected as the CQD/Mem ratio increases. However, with the increase of CQD amount, the possibility for CQD interacting with each other to form aggregation also increases, which would reduce the intensity of the emitted light and further decrease the photocatalytic performance of the synthesized composite. This might explain why the photodegradation activity of Mem-CQD(10mL)450 is lower than that of Mem-CQD450. The reusability of Mem-CQD450 was also investigated (Fig 5(b)). On the third cycle, ~80% of MO could be degraded in 4 h, which is just a little lower than that on the first use (90%), implying that Mem-CQD450 is a good photocatalyst with high reusability under infrared light irradiation.

It is well known that graphitic carbon nitride (g-C_3N_4) is a well-developed photocatalyst,[7, 13-19] which can be synthesized by heating melamine at 550 ^oC.[13-19] So, the composite Mem-CQD550 was also synthesized based on the procedure in Fig. 3 by heating the mixing of melamine and CQD at 550 ^oC for two hours. From the TEM results (Fig. S14), the surface of Mem550 is relatively dense, while there are lots of pores on the surface of Mem-CQD550. This difference between the surface of Mem550 and Mem-CQD550 may be from the burning of CQD at 550 ^oC. The photocatalytic performance of Mem-CQD550 was also evaluated by photodegradation of methyl orange (MO, 4 mg/L) under infrared light irradiation (λ > 800 nm). According to Fig. S15, Mem-CQD550 cannot photodegrade MO under infrared light irradiation (λ > 800 nm). It is well known that ammonia gas will be released during the thermal polycondensation of melamine.[7-8, 23-24] At 450 ^oC, the thermal polycondensation is not complete, implying that there is still ammonia gas in the crucible, which can in a certain degree to provide inert atmosphere for preventing the combustion of CQD. At 550 ^oC, the thermal polycondensation of melamine is complete and there is no too much ammonia gas in the crucible, which will lead to the combustion of CQD. This results in the formation of pore on the surface of Mem-CQD550 and no CQD exists in Mem-CQD550. So, Mem-CQD550 cannot use infrared light to photodegrade MO.

In summary, a novel method has been developed to synthesize CQD/carbon nitride composite at 450 ^oC to form an infrared-responsive photocatalyst. The XPS, TEM, UV-vis and photoluminescence spectrophotometers all confirmed the formation of the CQD/carbon nitride composite, and the new material shows good performance for MO photodegradation under infrared light irradiation. This research would provide insights for developing new infrared-responsive photocatalyst and promote the application of CQD in photocatalytic field.

Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental details, and TEM, Uv-vis, XRD, XPS characterization for the samples are provided]. See DOI: 10.1039/c000000x/

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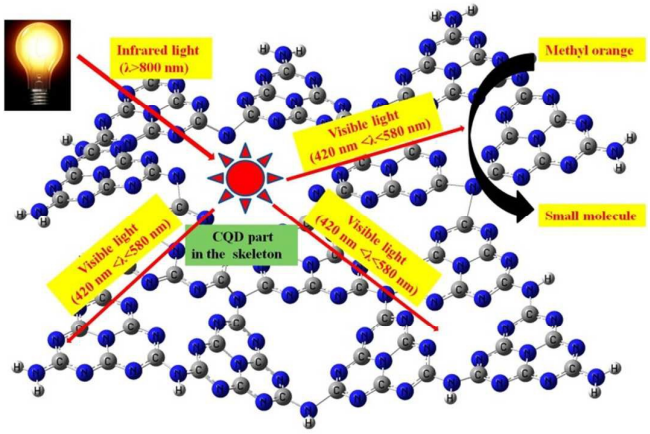

A facile strategy has been developed to combine carbon quantum dot and hydrophobic carbon nitride photocatalyst together to form infrared-responsive photocatalyst. The photodegradation experiment has confirmed that the obtained material can effectively degrade methyl orange under infrared light irradiation. This work will be helpful to develop novel infrared photocatalyst and promote the application of carbon quantum dot in photocatalytic field.