Supporting Information

Boosting Photocatalytic CO₂ Reduction of Metal-Organic Frameworks by Encapsulating Carbon Dots

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S1. Experimental

Synthesis of CD@NH₂-UiO-66-G particles by *in situ* generating CDs in the MOF pores. Using the pores of MOFs as templates, small CDs could be *in situ* generated inside the MOF pores. According to a previous report, we have also prepared CD@NH₂-UiO-66 by carbonizatino of glucose inside NH₂-UiO-66(Zr) particles and the sample was denoted as CD@NH₂-UiO-66-G. In a typical synthesis, 50 mg presynthesized NH₂-UiO-66(Zr) were dispersed in a mixed solvent of 0.5 mL DI water and 4.5 mL ethanol. Then, 9 mg glocuse were added and dessolved in the solution. After stirring overnight, the solvent was slowly evaporated and the collected powder was transferred to a crucible in a tube furnance. Under N₂ protection, the powder was heated at 200 °C for 2 h. After cooling down to room temperature, the product was collected and washed with ethanol and DI twice, respectively. Finally, the product was dried at 60 °C in vacuum overnight.



Scheme S1. Schematic illustration of the formation mechanism of CD-embedded NH₂-UiO-66 particles. At the beginning, the pre-synthesized CDs were used as seeds and added into the starting reagents for growing NH₂-UiO-66 particles (Zr^{4+} and H₂ATA). Because CDs could be well dispersed in solution (DMF) and absorb some Zr^{4+} ions on their surface, they would act as heterogeneous seeds and participate in the assembly of MOF units. Under solvothermal condition, along with the assembly of Zr^{4+} and H₂ATA in solution, these CDs seeds were also crosslinked by the MOF units. As a result, they were encapsulated inside MOF matrixes, leading to the formation of CD-embedded NH₂-UiO-66 particles.



Fig. S1. Zeta potentials of the prepared CDs and NH_2 -UiO-66 particles dispersed in water. The NH_2 -UiO-66 particles are positively charged due to their surface coordination unsaturated Zr^{4+} ions. In contrast, the CDs are negatively charged owing to some residual groups from citric acid after polymerization (e.g., -OH and - COOH). The difference in surface charge can lead to the electrostatic combination between CDs and NH_2 -UiO-66.



Fig. S2. (A) SEM and (B) TEM images of the pristine NH₂-UiO-66 particles prepared without the addition of CDs seeds. The average diameter of these particles is about 180 nm.



Fig. S3. FTIR spectrum of the prepared CDs by copolymerization of citric acid and ethylenediamine followed by carbonization. Because of the copolymerization and sequential carbonization process, many functional groups were simultaneously produced among the CDs. As such, there is a wide FTIR absorption below 1700 cm⁻¹ observed. The peaks at 1570 cm⁻¹ and 1240 cm⁻¹ are originated from -COOH and - C-NH- groups, respectively.



Fig. S4. Characterizations of the CDs collected from the dissolution of $CDs@NH_2$ -UiO-66 particles by 1 M NaOH: (A) TEM image; (B) excitation-dependent PL spectra. In concentrated NaOH solution, the NH₂-UiO-66 framework was dissolved while the CDs remained stable. The TEM image and PL spectra of these CDs are the same as the pristine CDs used as seeds during the synthesis of $CDs@NH_2$ -UiO-66 particles, confirming that these CDs have been encapsulated inside the NH₂-UiO-66 framework.



Fig. S5. Photocatalytic CO₂ reduction rates in the system under different experimental conditions: (1) without light; (2) without TEOA; (3) without CO₂ (bubbled with N₂); (4) without catalyst (CD@NH₂-UiO-66); (5) using CDs as catalyst instead of CD@NH₂-UiO-66. Without light irradiation, CO₂ input, catalyst, or using CDs as catalyst instead of CD@NH₂-UiO-66 is indeed the photocatalyst for CO₂ reduction. Prior to the addition of TEOA, a typical sacrificial electron donor, the activity of photocatalysts is also pretty low. Since the photogenerated electrons were consumed by the reduction of CO₂, the consummation of photogenerated holes is thus a rate-limiting step. Therefore, the use of sacrificial electron donor in this system could help to establish a steady-state path for CO₂ reduction under light irradiation.



Fig. S6. Mass spectrum of ¹³CO (m/z=29) produced over CD@NH₂-UiO-66 using $^{13}CO_2$ as the gas source instead of CO₂. The m/z=29 in the spectrum is assigned to $^{13}CO_2$, indicating that the generated ^{13}CO is from $^{13}CO_2$ rather from other possible sources (i.e., catalyst, sacrificial agent or solvent).



Fig. S7. Characterizations of CD@NH₂-UiO-66 particles after photocatalytic reactions: (A) SEM image; (B) XRD patters. The results indicate that the morphology and phase of CD@NH₂-UiO-66 particles keep unchanged after the catalytic reaction, confirming their good photocatalytic stability.



Fig. S8. (A) Comparison of photocatalytic activity between CD@NH₂-UiO-66 and NH₂-UiO-66 under 420 nm and 475 nm irradiation bands, respectively; (B) Comparison of photocurrents under 420-nm irradiation; (C) Comparison of photocurrents under 475-nm irradiation; (D) Comparison of photocatalytic activity of CD@NH₂-UiO-66 under visible light (420~780 nm) and NIR light (780~2500 nm), respectively.



Fig. S9. UV-Vis absorption spectra of the prepared CDs and NH_2 -UiO-66 before hybridization, respectively. The absorption of NH_2 -UiO-66 mainly locates in the short-wavelength visible region (<440 nm) while the CDs have a wide absorption in the whole visible range.



Fig. S10. (A) PL spectra of CDs under different long-wavelength excitations of the Xe lamp; (B) Comparison of PL emissions of CDs under three different exciting conditions. With a cutoff filter (e.g., 420 nm) between the sample and Xe lamp, no obvious PL emission was observed under the long-wavelength excitation (e.g., 640 nm in Fig. B). This result implies that the 'upconversion' emission from CDs (see Fig. A) might be originated from the excitation of half-wavelength incident light from the Xe lamp, not a real upconversion emission.



Fig. S11. (A) Schematic illustration of the synthetic process toward CD@NH₂-UiO-66-G by *in situ* generating CDs in the MOF pores. The glucose molecules were loaded in the pores of NH₂-UiO-66 particles and then cross-linked and carbonized into CDs; (B, C) TEM and XRD characerizations of the prepared CD@NH₂-UiO-66-G particles; (D) PL spectra of CDs prepared by the *in situ* generating method (denoted as CDs-G). In comparison, the PL spectrum of CDs prepared by hydrothermal method is much higher, showing a better quality than those from the *in situ* generating method.



Fig. S12. Comparision of PL emission of CDs prepared with different routes (solvothermal *vs*. MOF pores-templating). Above result suggests that the CD@NH₂-UiO-66-G particles prepared by *in situ* generating CDs in MOF pores have an inferior activity, compared to the CD@NH₂-UiO-66 particles prepared by the encapsulating method. We infer that this result may attribute to the relatively poor quality of CDs generated from polymerization of glucose molecules in the MOF pores, as suggested by the PL spectra of two kinds of CDs (see Fig. S11D).