

Supporting Information

Graphene Quantum Dots Sensitized Zn-MOF for Efficient Visible-Light-Driven Carbon Dioxide Reduction

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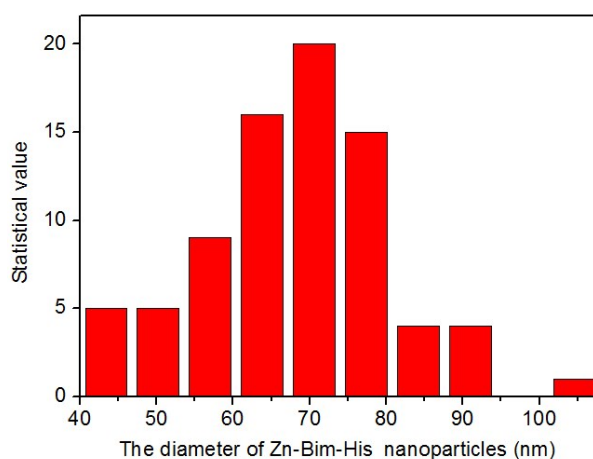


Figure S1. Statistical diameter for the synthesized Zn-Bim-His-1 nanoparticles.

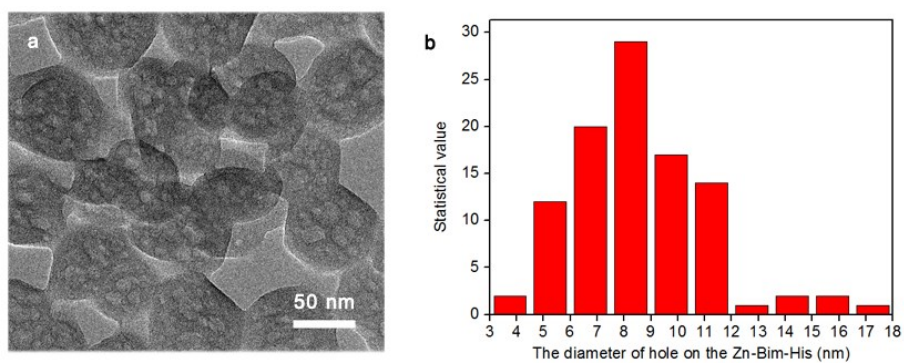


Figure S2. Statistical diameter for the hole on the surface of Zn-Bim-His-1 nanoparticles.

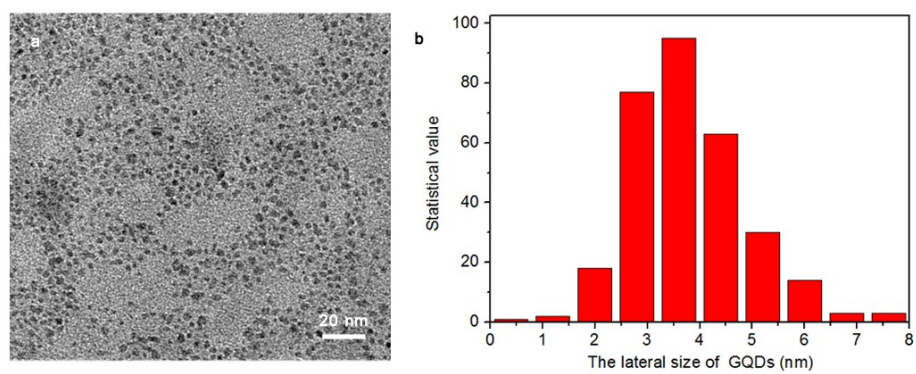


Figure S3. Statistical lateral size for GQDs.

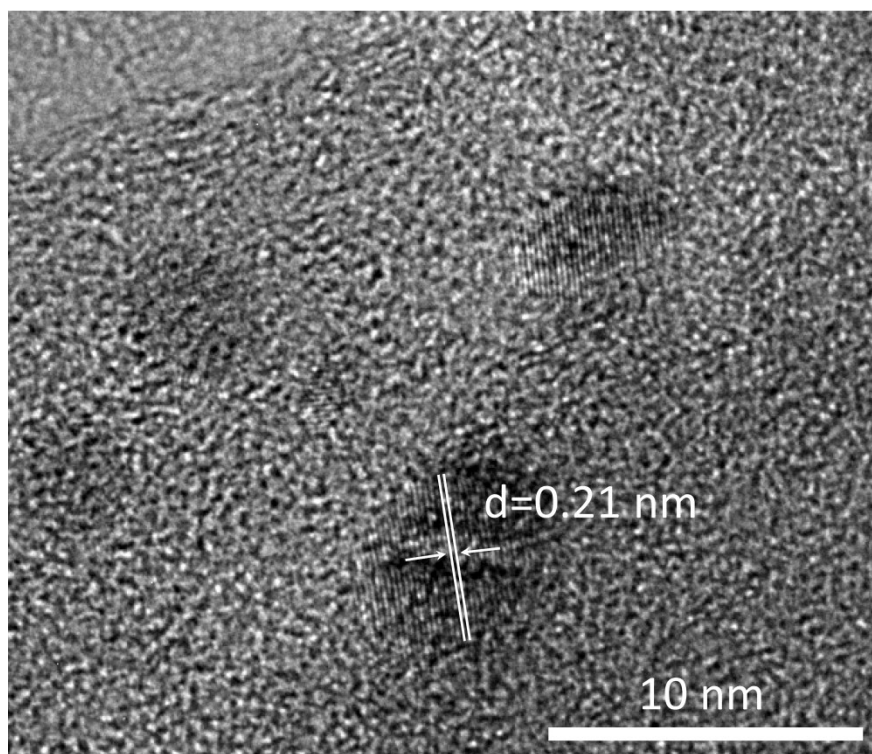


Figure S4. HRTEM image of Zn-Bim-His-1@GQDs in higher resolution.

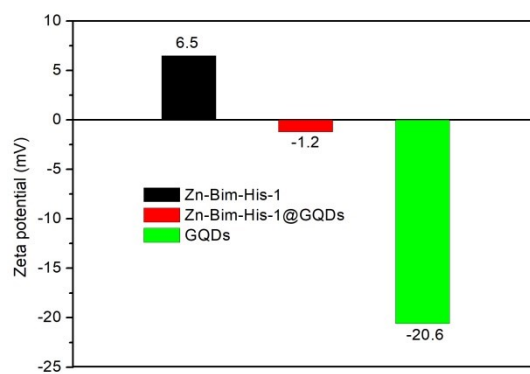


Figure S5. Histogram of the zeta potential value of Zn-Bim-His-1, GQDs and Zn-Bim-His-1@GQDs.

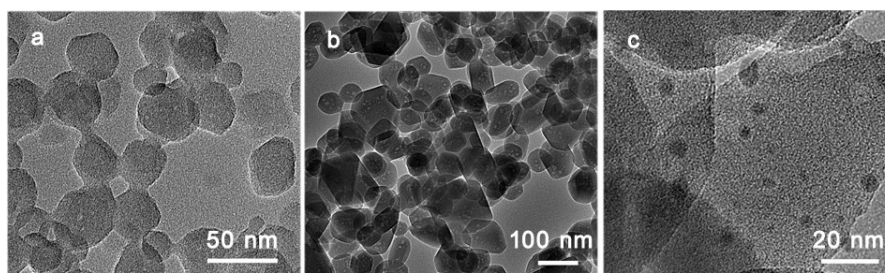


Figure S6. TEM of Zn-Bim@GQDs (a), Zn-Bim-His-2 (b) and Zn-Bim-His-2@GQDs (c).

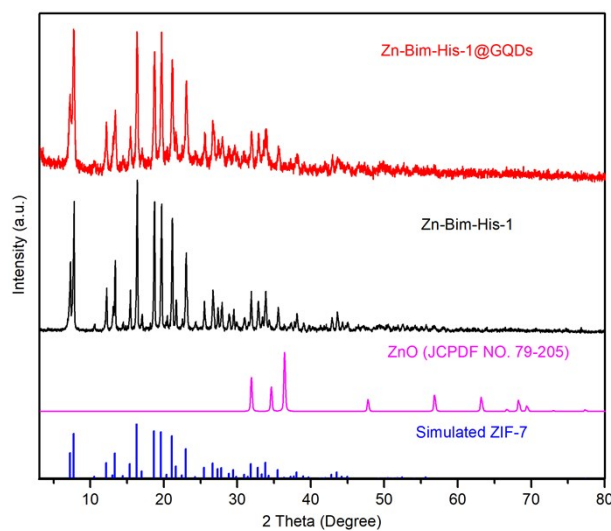


Figure S7. PXRD patterns of Zn-Bim-His-1, Zn-Bim-His-1@GQDs, pure ZnO (JCPDF NO. 79-205) and that simulated from crystal structure data for ZIF-7.^{S1} The result shows the absence of impurities such as ZnO from the as prepared samples.

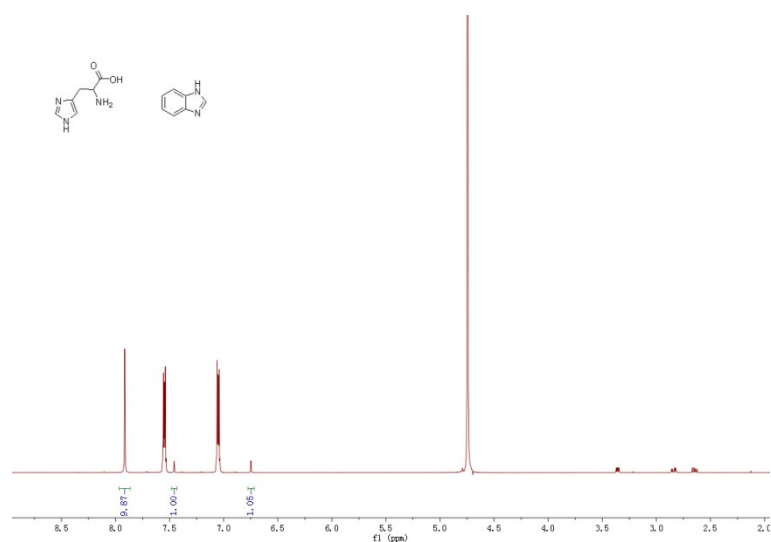


Figure S8. ^1H -NMR spectra for the Zn-Bim-His-1 sample. For ^1H -NMR analysis, the solution was prepared by digesting 20 mg of Zn-Bim-His-1 sample in NaOH (1 M)- D_2O solution for 24 h.

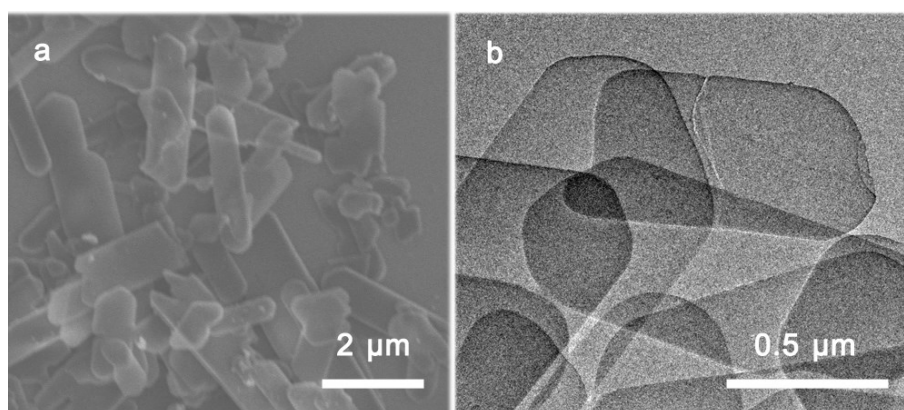


Figure S9. SEM and TEM of Zn-Bim-NH₂.

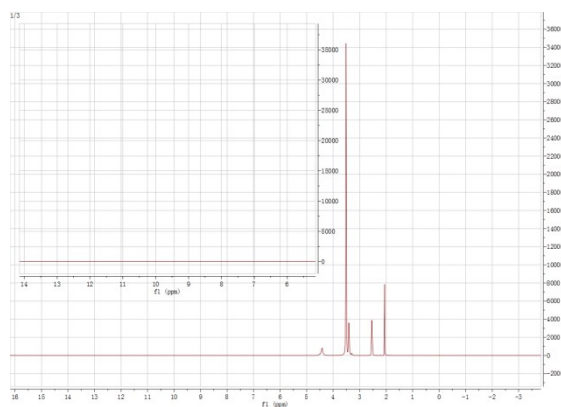


Figure S10. ^1H NMR spectra for the supernatant taken from the Zn-Bim-His-1@GQDs photocatalytic reaction system under visible light irradiation for 12 h.

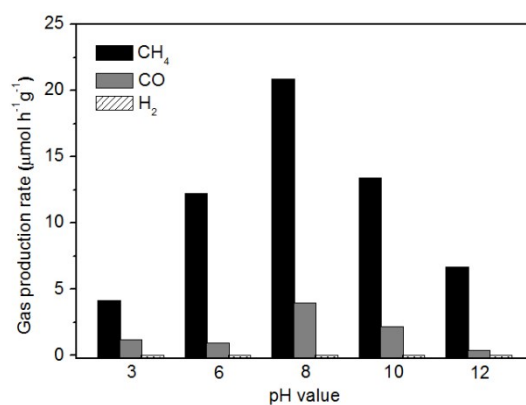


Figure S11. Product distribution during the photocatalytic CO_2 reduction using Zn-Bim-His-1@GQDs preparing in different pH values.

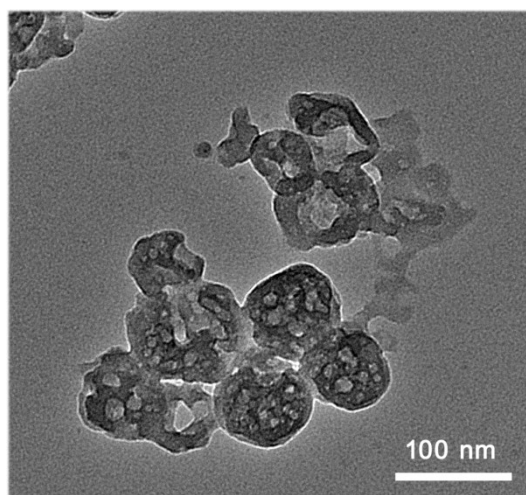


Figure S12. TEM of Zn-Bim-His-1@GQDs prepared under pH3.

Table S1. Comparison of photocatalytic performance for reduction of CO₂ with carbon dots catalyst and some noble-metal-containing systems reported in literature.

Catalyst	Light source	Sacrificial agent	Major product evolution rate $\mu\text{mol h}^{-1} \text{g}^{-1}$	Reference
Zn-Bim-His-1@GQDs	$420 < \lambda < 750 \text{ nm}$	TEOA	CH ₄ : 20.9	This work
gold-doped carbon dots	$405 < \lambda < 720 \text{ nm}$	--	HCOO ⁻ : 8.5 ppm	S2
GQD-BNPTL	$420 < \lambda < 800 \text{ nm}$	--	CH ₃ OH: 0.7	S3
CQDs/Cu ₂ O	$\lambda > 400 \text{ nm}$	--	C ₂ H ₆ : 16.9	S4
ZrOCo ^{II} /IrOx/ SBA-15 silica	355 nm	--	CO: 1.7	S5
ZnCr-LDH@Pt	UV	--	CO: 7.6	S6
C ₃ N ₄ /MgAl-LDH/Pd	500 W Hg(Xe) lamp without filter	--	CH ₄ : 0.8	S7
RuRu' /NS-C ₃ N ₄ , Ag	$\lambda > 400 \text{ nm}$	EDTA·2Na	COOH ⁻ : 57.5	S8
Pd-TiO ₂	$\lambda > 310 \text{ nm}$	--	CO: 0.4	S9
Cu ₂ S/Pt NR	450 W Xe lamp with a cutoff water filter for the IR wavelengths	Na ₂ SO ₃	CO: 3.0	S10
Pt-g-C ₃ N ₄ /NaNbO ₃	$\lambda > 420 \text{ nm}$	--	CH ₄ : 6.4	S11
Pt/SiC	simulated sunlight	--	CH ₄ : 13.6	S12
PbS/TiO ₂	$420 < \lambda < 610 \text{ nm}$	--	CO: 0.8	S13
Cu/Pt/TiO ₂	$320 < \lambda < 780 \text{ nm}$	--	CH ₄ : 33.0	S14
rGO/NiWO ₄ @Au	simulated sunlight	--	CO: 0.9	S15

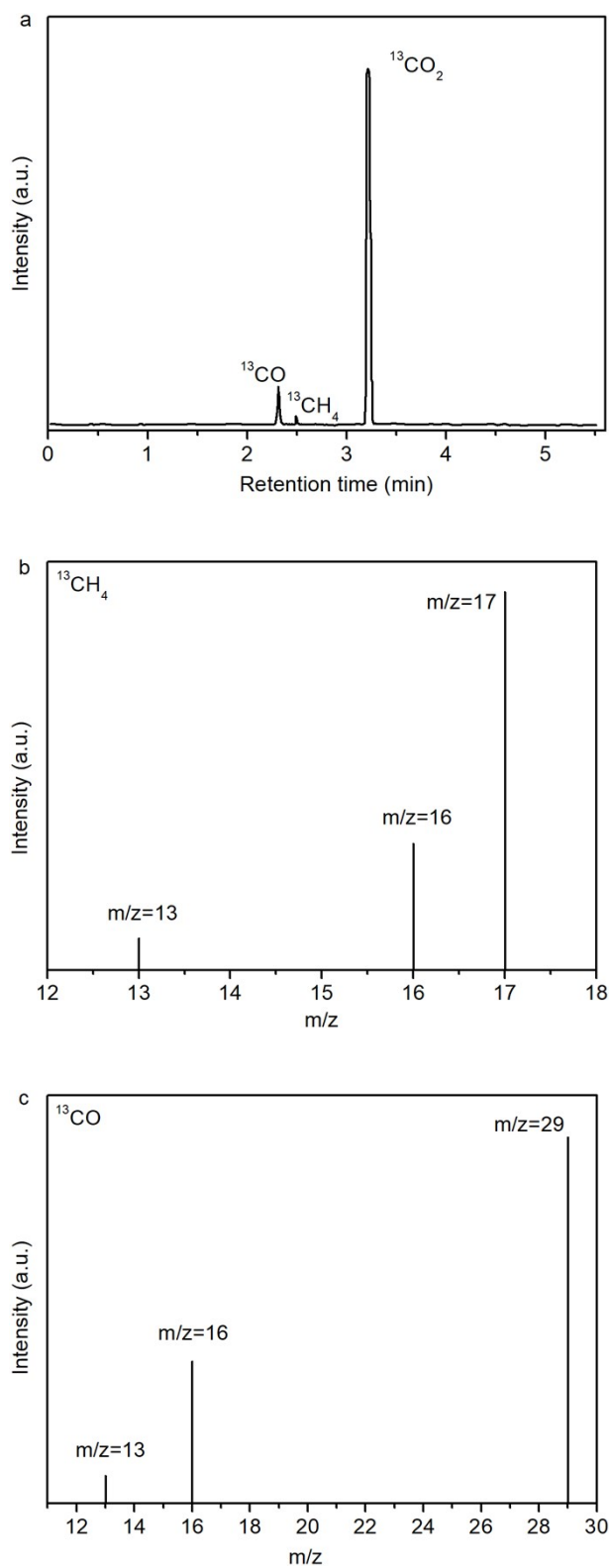


Figure S13. GC-MS spectras of the products generated from the $^{13}\text{CO}_2$ isotope experiments. (a) GC spectrum, (b, c) mass spectra showing $^{13}\text{CH}_4$ ($m/z = 17$) and ^{13}CO ($m/z = 29$) produced over Zn-Bim-His-1@GQDs.

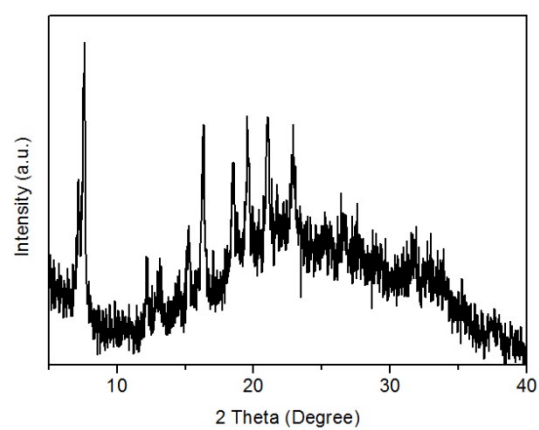


Figure S14. XRD patterns for Zn-Bim-His-1@GQDs hybrid nanoparticles after 48 h photocatalytic test.

References

- S1 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186-10191.
- S2 S. Sahu, Y. Liu, P. Wang, C. E. Bunker, K. A. S. Fernando, W. K. Lewis, E. A. Gulians, F. Yang, J. Wang and Y. P. Sun, *Langmuir*, 2014, **30**, 8631-8636.
- S3 Y. Yan, J. Chen, N. Li, J. Tian, K. Li, J. Jiang, J. Liu, Q. Tian and P. Chen, *ACS Nano*, 2018, **12**, 3523-3532.
- S4 T. Kulandaivalu, S. Abdul Rashid, N. Sabli and T. L. Tan, *Diamond Relat. Mater.*, 2019, **91**, 64-73.
- S5 W. Kim, G. Yuan, B. A. McClure and H. Frei, *J. Am. Chem. Soc.*, 2014, **136**, 11034-11042.
- S6 K. I. Katsumata, K. Sakai, K. Ikeda, G. Carja, N. Matsushita and K. Okada, *Mater. Lett.*, 2013, **107**, 138-140.
- S7 J. Hong, W. Zhang, Y. Wang, T. Zhou and R. Xu, *ChemCatChem*, 2014, **6**, 2315-2321.
- S8 R. Kuriki, M. Yamamoto, K. Higuchi, Y. Yamamoto, M. Akatsuka, D. Lu, S. Yagi, T. Yoshida, O. Ishitani and K. Maeda, *Angew. Chem. Int. Ed.*, 2017, **56**, 4867-4871.
- S9 T. Yui, A. Kan, C. Saitoh, K. Koike, T. Ibusuki and O. Ishitani, *ACS Appl. Mater. Inter.*, 2011, **3**, 2594-2600.
- S10 A. Manzi, T. Simon, C. Sonleitner, M. Döblinger, R. Wyrwich, O. Stern, J. K. Stolarczyk and J. Feldmann, *J. Am. Chem. Soc.*, 2015, **137**, 14007-14010.
- S11 H. Shi, G. Chen, C. Zhang and Z. Zou, *ACS Catal.*, 2014, **4**, 3637-3643.
- S12 C. Han, B. Wang, N. Wu, S. Shen and Y. Wang, *Appl. Surf. Sci.*, 2020, **515**, 145952.
- S13 C. Wang, R. L. Thompson, P. Ohodnicki, J. Baltrus and C. Matranga, *J. Mater. Chem.*, 2011, **21**, 13452-13457.
- S14 Q. Zhai, S. Xie, W. Fan, Q. Zhang, Y. Wang, W. Deng and Y. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 5776-5779.
- S15 J. Shin, J. N. Heo, J. Y. Do, Y. I. Kim, S. J. Yoon, Y. S. Kim and M. Kang, *J. Ind. Eng. Chem.*, 2020, **81**, 427-439.