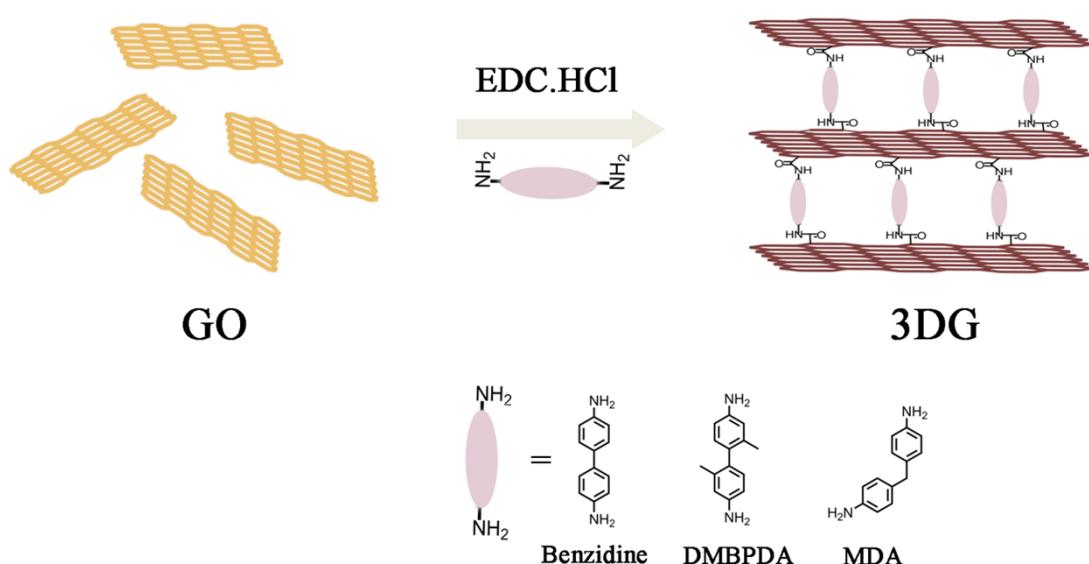


*Supporting Information*  
*for*

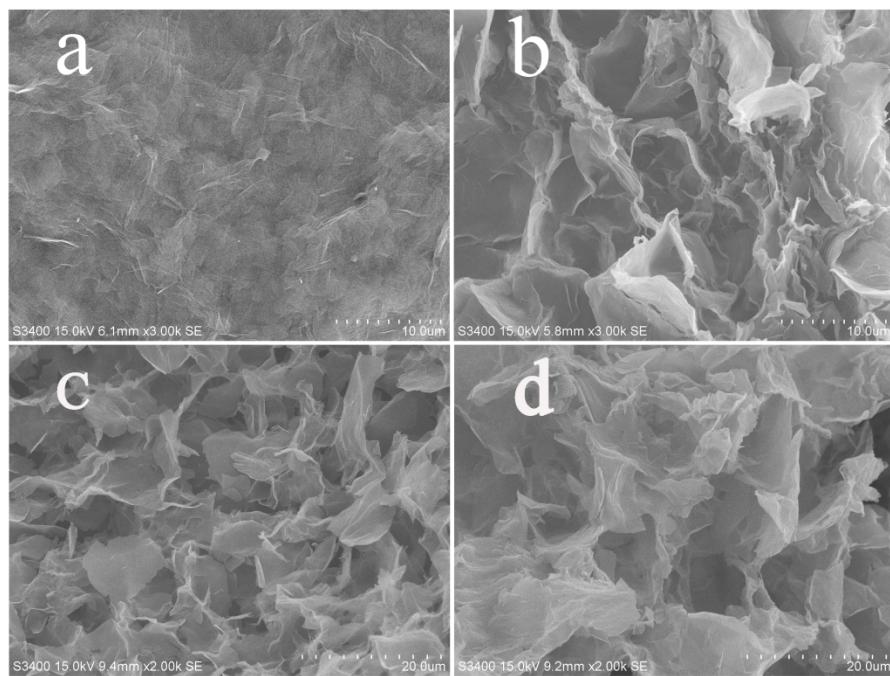
## Three-Dimensional Graphene Oxide Cross-Linked by Benzidine as an Efficient Metal-free Photocatalyst for Hydrogen Evolution

Xin Zhou, Shi-Cong Cui, \* and Jin-Gang Liu\*

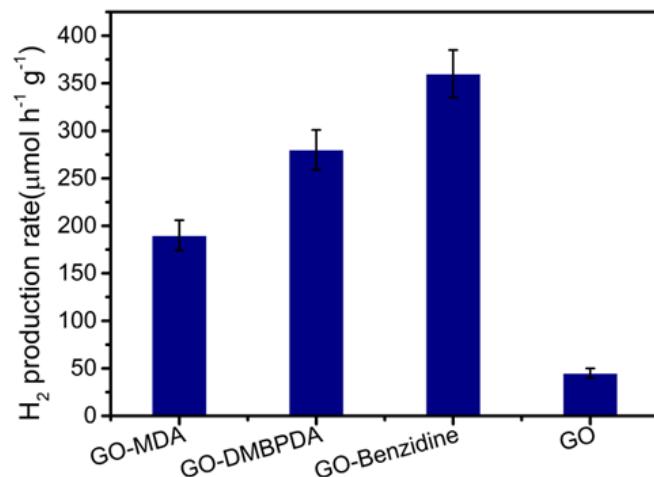
*Key Lab for Advanced Materials, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai, 200237, P. R. China, E-mail:*  
*liujingang@ecust.edu.cn*



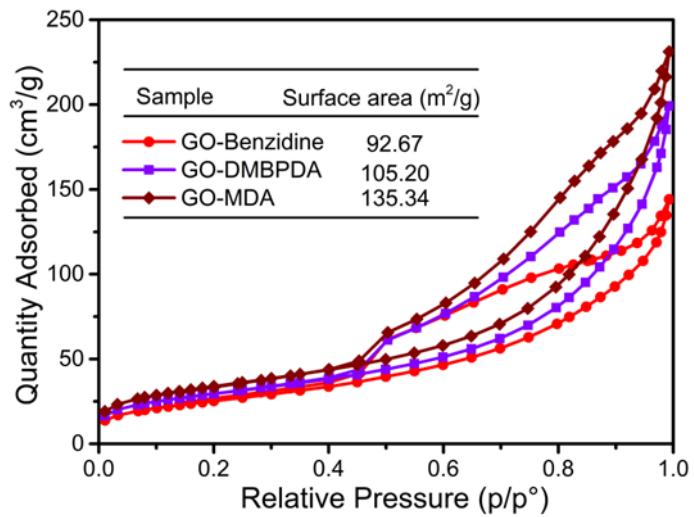
**Fig. S1** Preparation scheme of the 3DG materials with benzidine, DMBPDA, and MDA as the cross-linker.



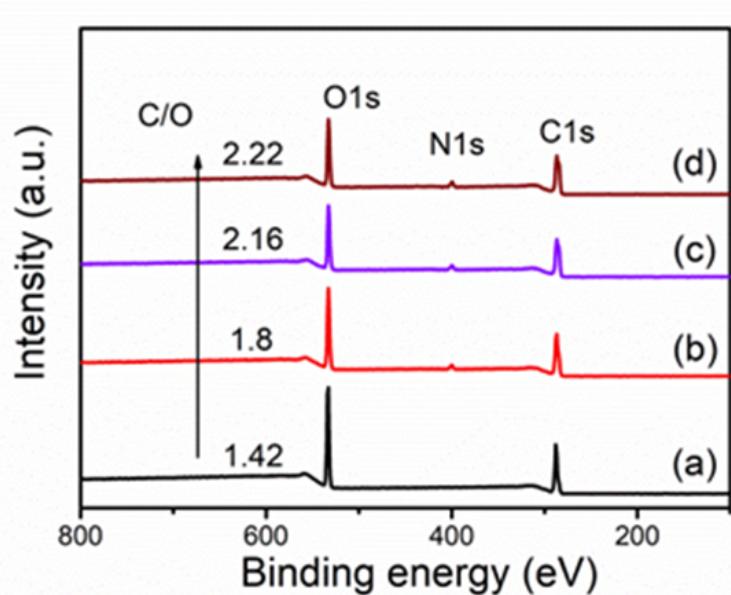
**Fig.S2** SEM images of (a) GO, (b) GO-Benzidine (3DG-1), (c) GO-DMBPDA, (d) GO-MDA.



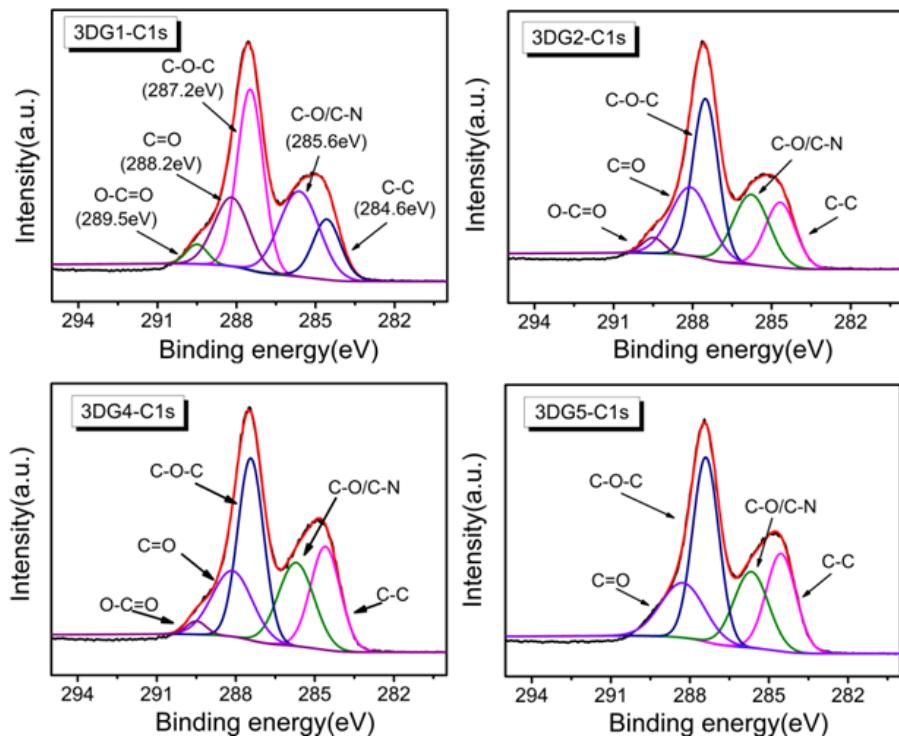
**Fig.S3** Photocatalytic activity for  $H_2$  production of GO-MDA, GO-DMBPDA, GO-Benzidine(3DG-1) and GO.



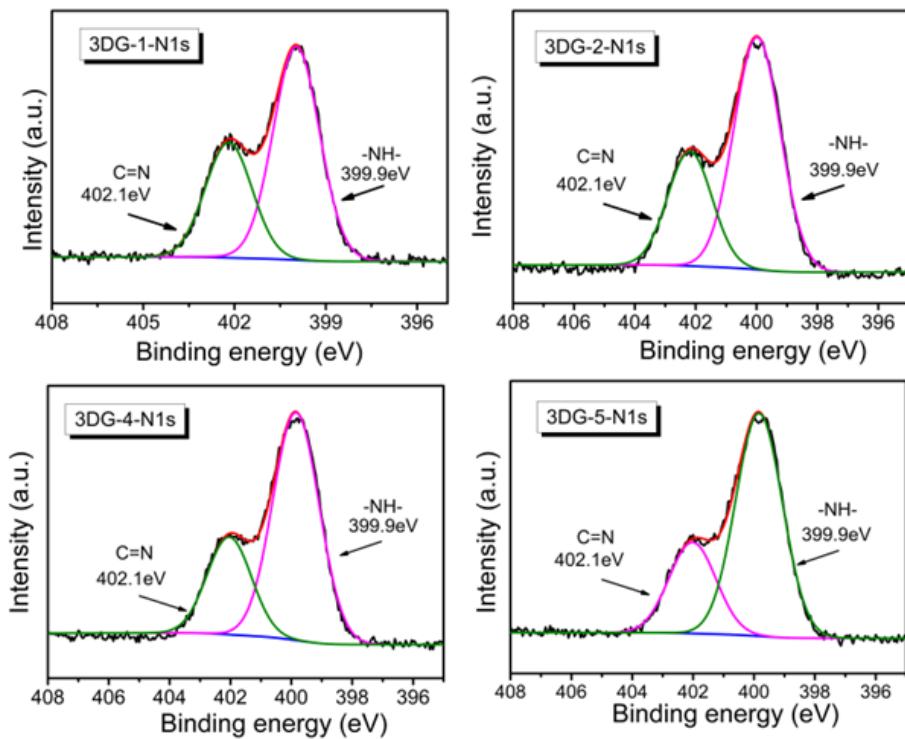
**Fig.S4**  $\text{N}_2$  adsorption-desorption isotherms of GO-MDA, GO-DMBPDA and GO-Benzidine(3DG-1).



**Fig.S5** The full XPS spectra of (a)GO, (b) GO-Benzidine(3DG-1), (c) GO-DMBPDA and (d) GO-MDA.



**Fig. S6** C1s XPS spectrums of 3DG-1, 3DG-2, 3DG-4 and 3DG-5.



**Fig. S7** N1s XPS spectra of 3DG-1, 3DG-2, 3DG-4 and 3DG-5.

Table S1 Metal-free photocatalysts for H<sub>2</sub> production

| Photocatalyst   | H <sub>2</sub> evolved<br>(μmolg <sup>-1</sup> h <sup>-1</sup> ) | Sacrificial<br>agents                             | Light source<br>(W) | λ                   | Ref.      |
|---|--|---|---------------------|---------------------|-----------|
| 3DG-3   | 690  | TEOA  | Xe lamp (300)       | 320–780 nm          | This work |
| 3DG-650   | 270  | EtOH  | Xe lamp (200)       | 320–780 nm          | S1        |
| GO-0.47   | 1104   | Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub> | Xe lamp (500)       | 320–780 nm          | S2        |
| 3D N-doped<br>g-C <sub>3</sub> N <sub>4</sub>   | 480  | HL  | Xe lamp (300)       | > 420 nm            | S3        |
| g-C <sub>3</sub> N <sub>4</sub> /B-rGO  | 273  | TEOA  | Xe lamp (500)       | simulate<br>sunligh | S4        |
| C-I codoped<br>g-C <sub>3</sub> N <sub>4</sub><br>C <sub>3</sub> N <sub>4</sub><br>(1.0 wt% Pt) | 168  | TEOA  | Xe lamp (300)       | > 400 nm            | S5        |
| g-C <sub>3</sub> N <sub>4</sub> @C  | 772  | TEOA  | Xe lamp (350)       | > 420 nm            | S6        |
| g-C <sub>3</sub> N <sub>4</sub><br>( 3 wt% Pt)  | 16885  | TEOA  | Xe lamp (500)       | > 420 nm            | S7        |
|   | 459  | HL  | Xe lamp (300)       | > 400 nm            | S8        |

### References:

- S1. Y. Lu, B. Ma, Y. Yang, E. Huang, Z. Ge, T. Zhang, S. Zhang, L. Li, N. Guan, Y. Ma and Y. Chen, *Nano Res.*, 2017, **10**, 1662-1672.
- S2. L. K. Putri, B. J. Ng, K. H. Tan, F. S. Lim, W. J. Ong, W. S. Chang and S. P. Chai, *Catal. Today*, 2018, **315**, 93-102.
- S3. N. Tian, Y. Zhang, X. Li, K. Xiao, X. Du, F. Dong, G. I. N. Waterhouse, T. Zhang and H. Huang, *Nano Energy*, 2017, **38**, 72-81.
- S4. L. K. Putri, B. J. Ng, W. J. Ong, H. W. Lee, W. S. Chang and S. P. Chai, *J. Mater. Chem. A*, 2018, **6**, 3181-3194.
- S5. C. Yang, W. Teng, Y. Song and Y. Cui, *Chin. J. Catal.*, 2018, **39**, 1615-1624.
- S6. J. Cheng, Z. Hu, K. Lv, X. Wu, Q. Li, Y. Li, X. Li and J. Sun, *Appl. Catal. B Environ.*, 2018, **232**, 330-339.
- S7. Q. Han, B. Wang, J. Gao and L. Qu, *Angew. Chem. Int. Ed.*, 2016, **55**, 10849-10853.
- S8. F. Yang, D. Liu, Y. Li, L. Cheng and J. Ye, *Appl. Catal. B Environ.*, 2019, **240**, 64-71.