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Electronic Supplementary Information

Muti-stepwise Charge Transfer *via* MOF@MOF/TiO_2 Dual-heterojunction Photocatalysts towards Hydrogen Evolution

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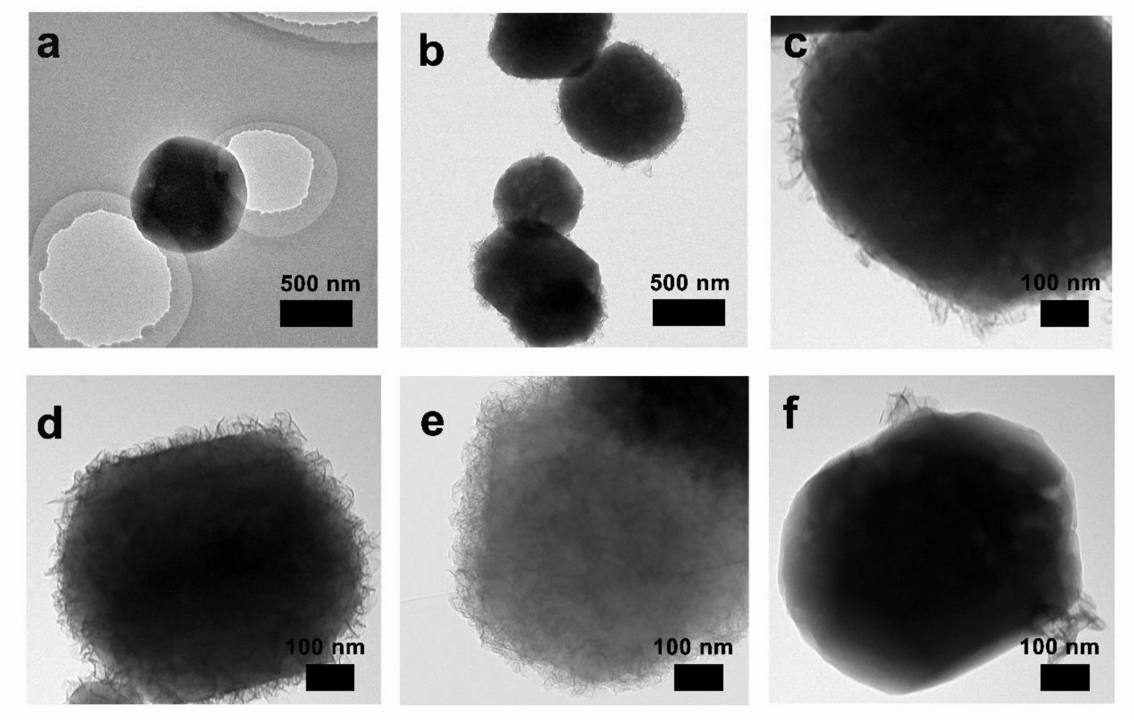

Fig. S1. TEM images of (a) NM, (b, c) NM@OM-1, (d) NM@OM-2, (e) NM@OM-6 and (f) NM@OM-10.

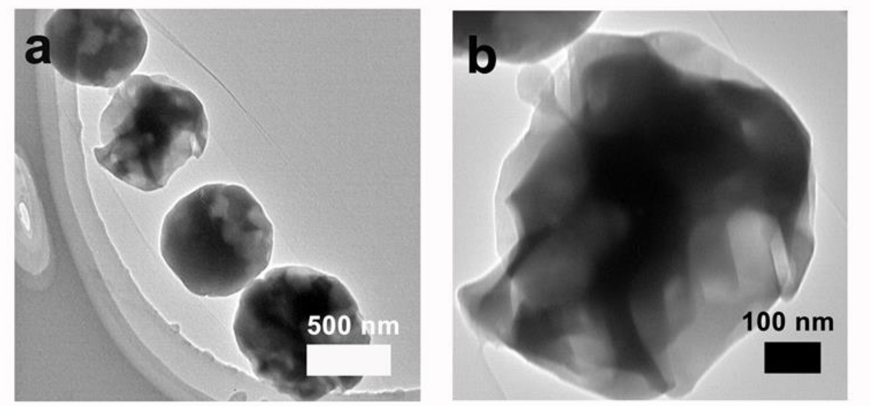

Fig. S2. TEM images of (a, b) OM.

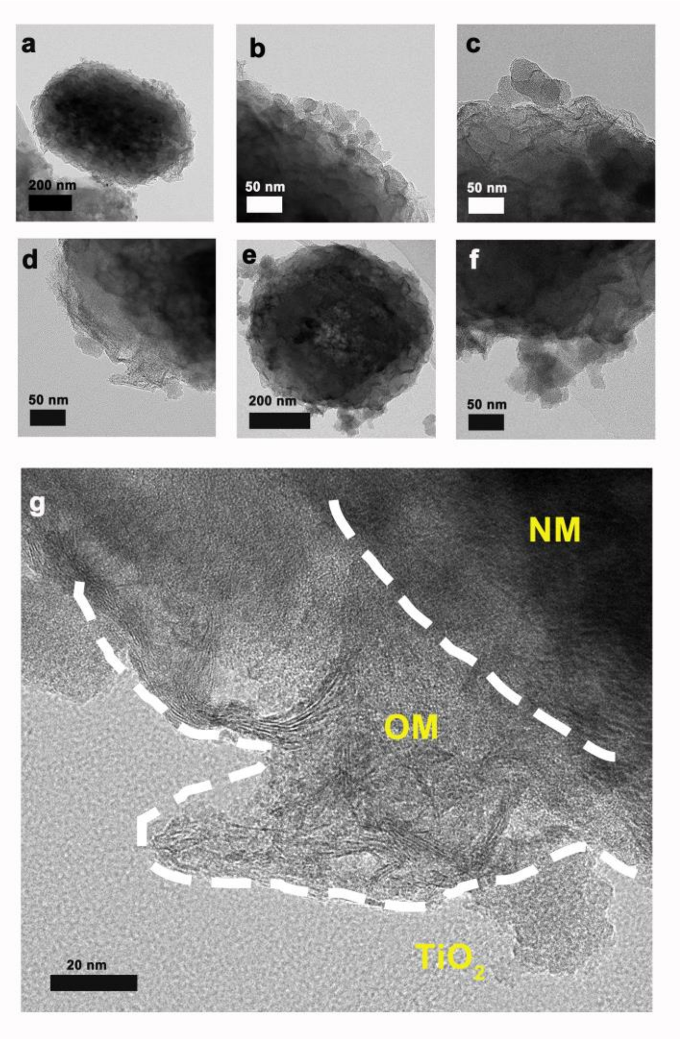

Fig. S3. TEM images of NM@OM/TiO_2 before (a-d) and after (e-f) photocatalytic reaction, (g) an HRTEM image of NM@OM/TiO_2 with circled three regions.

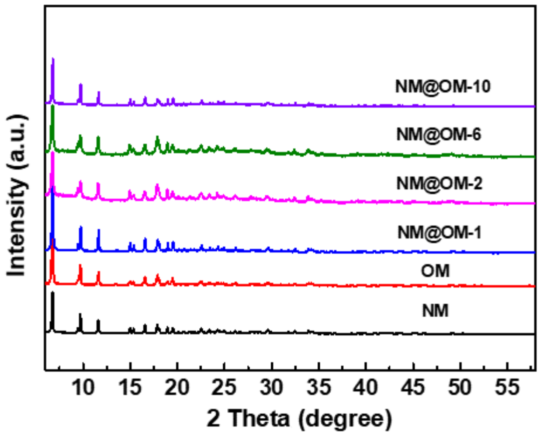

Fig. S4. XRD patterns of NM@OM-n, OM and NM samples.

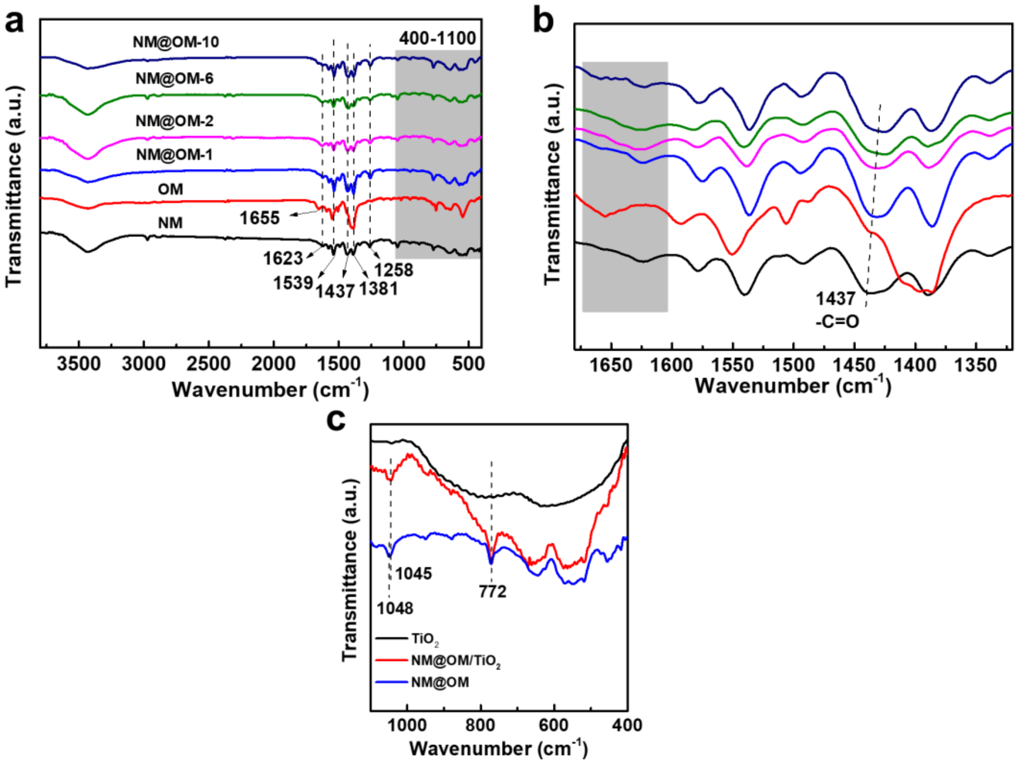

Fig. S5. (a) Full and (b) partial-enlarged FTIR spectra of NM@OM-n, NM and OM samples. (c) partial-enlarged FTIR spectra of NM@OM/TiO$_2$, NM@OM and NM samples.

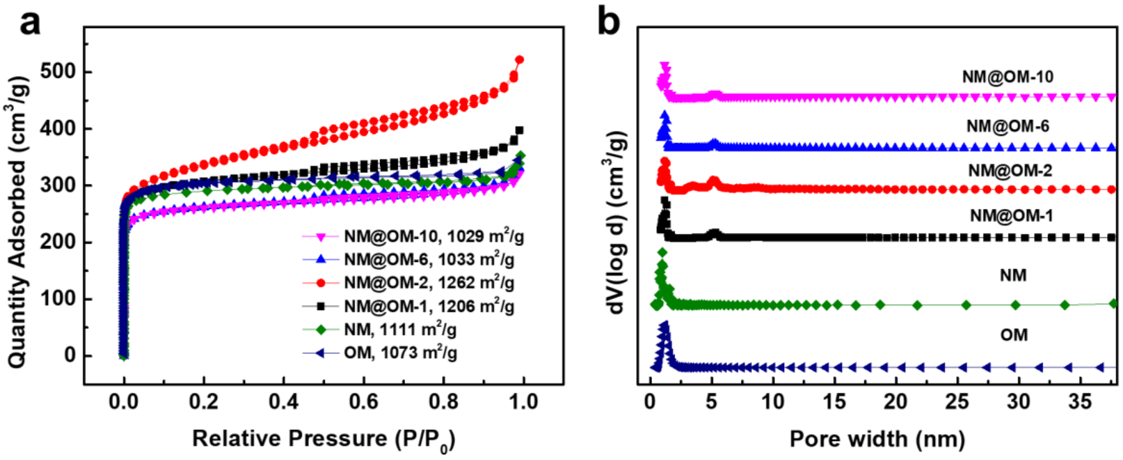

Fig. S6. (a) N_2 adsorption-desorption isotherms (b) and the pore size distribution of NM@OM-n, NM and OM samples, respectively.

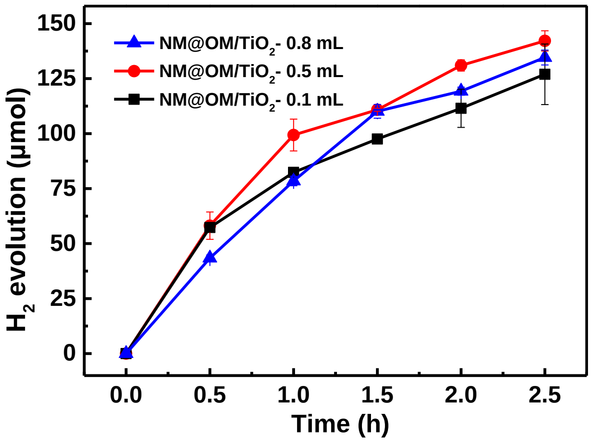

Fig. S7. Photocatalytic H_2 evolution curves of NM@OM/TiO_2 with different TiO_2 deposition quantity.

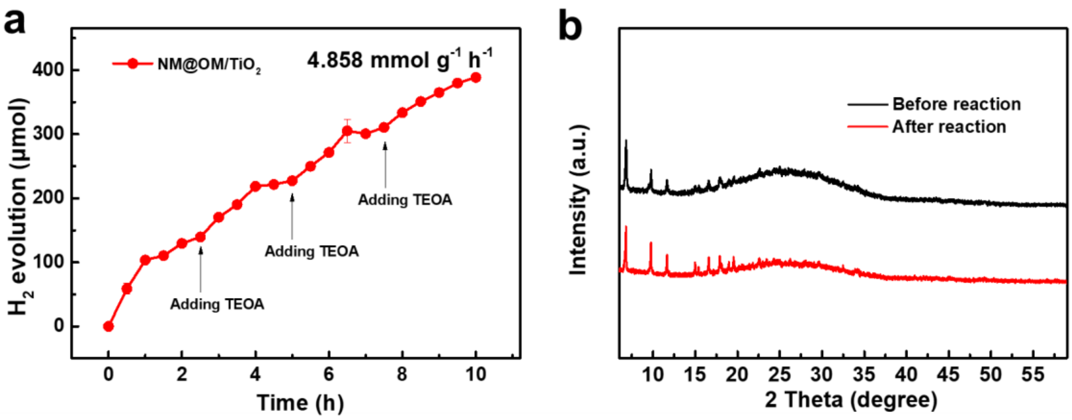

Fig. S8. (a) A long-term hydrogen evolution curve over NM@OM/TiO_2 under full-spectrum irradiation; (b) the XRD curves of NM@OM/TiO_2 before and after photocatalytic reaction.

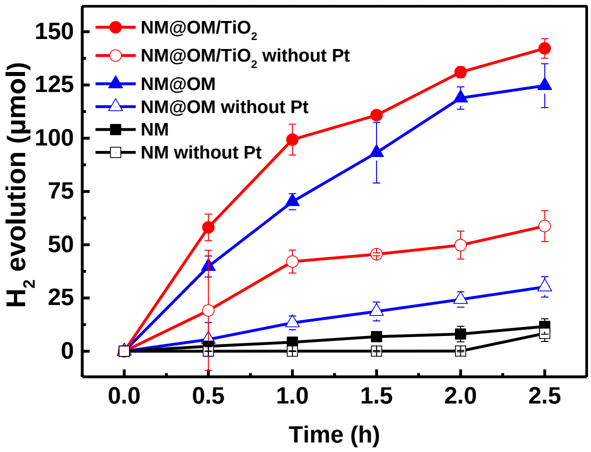

Fig. S9. Comparison of Photocatalytic H_2 evolution curves of NM@OM/TiO_2, NM@OM and NM with/without Pt co-catalysts.

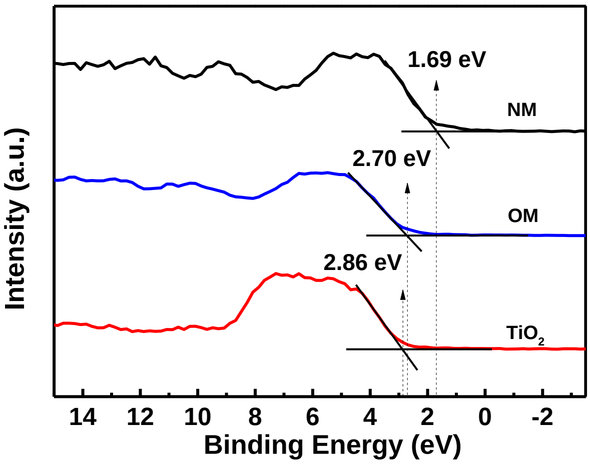

Fig. S10. VB-XPS spectra of NM, OM and TiO_2.

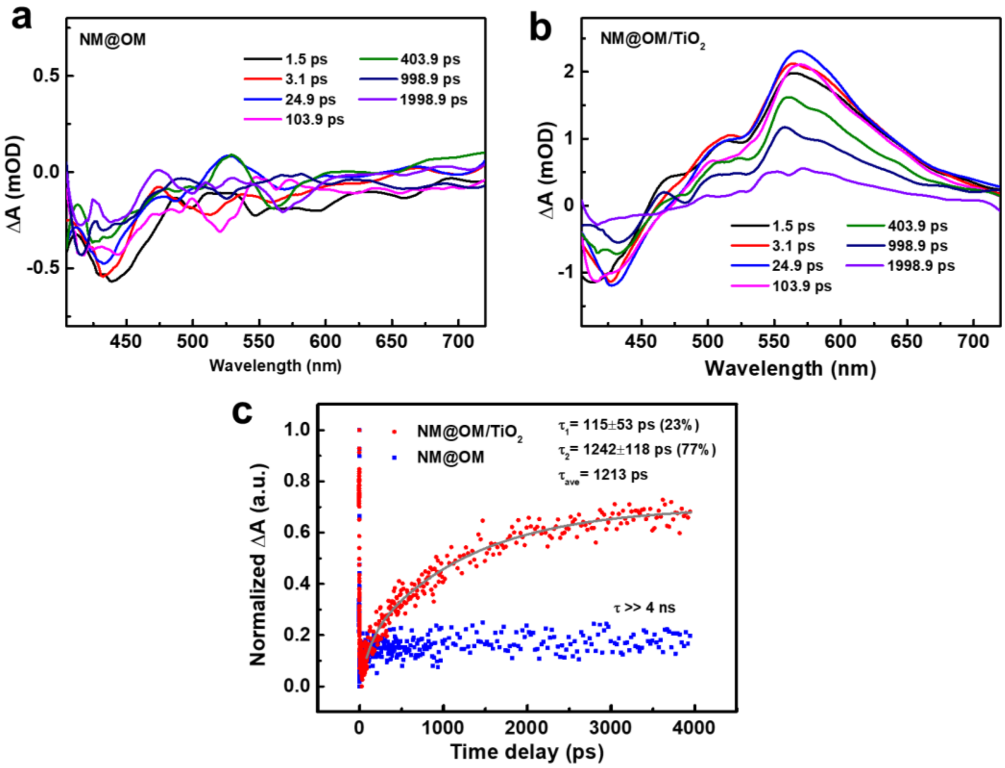

Fig. S11. Fs-TA spectra of (a) NM@OM and (b) NM@OM/TiO_2 (pumped at 370 nm) with TA signal given in mOD (OD: optical density); (c) The comparison of kinetic traces probed at 440 nm between NM@OM and NM@OM/TiO_2.

In the fs-TA test, the liquid sample was prepared by dispersing the powder in DMF followed by sonication for 0.5 h, and the concentration was adjusted to achieve an optical density of 0.35-0.45 in a 1 mm cuvette measured by the UV-Vis spectrum before the fs-TA test.

The fs-TA results are shown in **Fig. S11**, in which distinct differences can be observed between NM@OM and NM@OM/TiO_2. NM@OM shows a broad and unobvious negative absorption ranging up to 600 nm and a relatively obvious negative absorption in the range of 420-450 nm, which can be attributed to the ground state bleach (GSB). It probably covers the positive excited state absorption (ESA) since only weak and fluctuant signals ranging from 450-550 nm appear. In contrast, enhanced GSB and the stronger positive signals from 500 to 700 nm belonging to ESA can be observed for NM@OM/TiO_2, arising from the electron transfer from NM@OM to TiO_2. The comparison of kinetic traces probed at 440 nm between NM@OM and NM@OM/TiO_2 is given in **Fig. S11c**. It can be seen that NM@OM displays an extremely long GSB recovery (>> 4 ns), which is unable to accurately determine the lifetime from the fitting results[1]. The GSB of NM@OM/TiO_2 decays much faster than that in NM@OM, featuring an obvious acceleration of the TA kinetics. The biexponential fitting results for NM@OM/TiO_2 are $\tau_1 = 115 \pm 53$ ps (23%) and $\tau_2 = 1242 \pm 118$ ps (77%), with an average relaxation lifetime of 1213 ps, which is remarkably shorter than that of NM@OM, suggesting that more efficient charge transfer and separation are achieved in NM@OM/TiO_2[2].

Notes and references

1 X. Z. Fang, Q. C. Shang, Y. Wang, L. Jiao, T. Yao, Y. F. Li, Q. Zhang, Y. Luo and H. L. Jiang, *Adv. Mater.*, 2018, **30**, 1705112.

2 H. Q. Xu, S. Z. Yang, X. Ma, J. Huang and H. L. Jiang, *ACS Catalysis*, 2018, **8**, 11615-11621.