

**Uniform decoration of UiO-66-NH₂ nanooctahedra onto TiO₂ electrospun nanofibers
for enhancing photocatalytic H₂ production based on multi-step interfacial charge
transfer**

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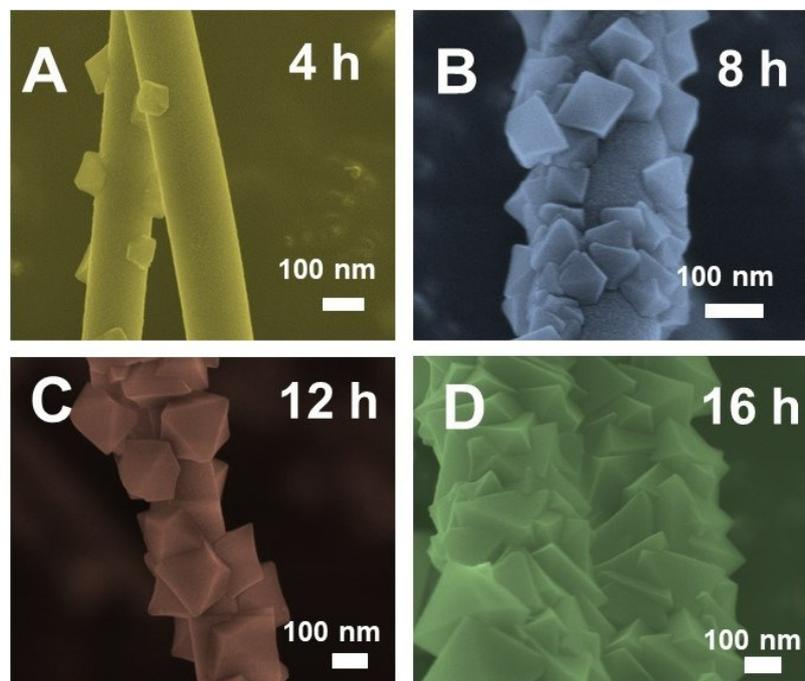
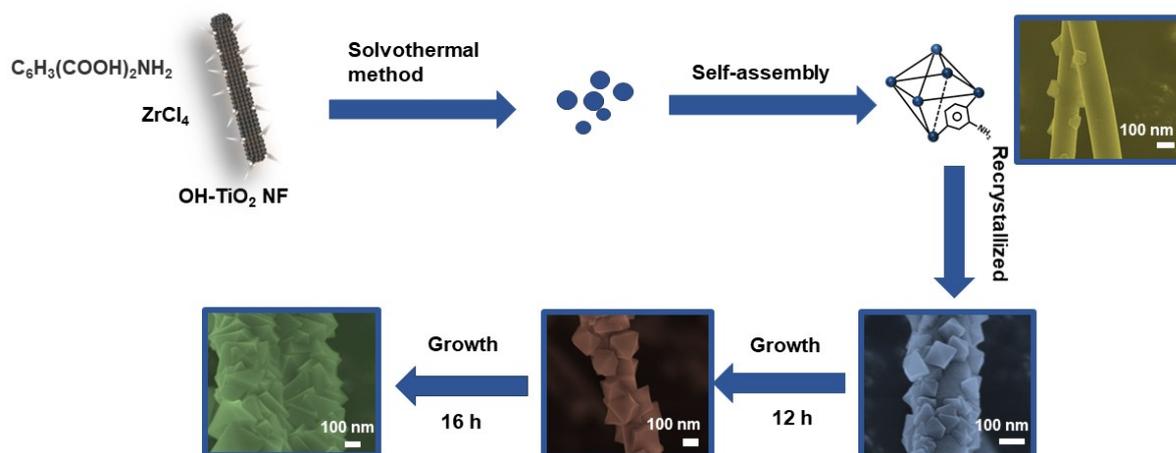


Fig. S1 SEM images of the UiO-66-NH₂/TiO₂(A) heterostructures obtained at different reaction time: (A) 4 h, (B) 8 h, (C) 12 h, (D) 16 h.



Scheme S1 A schematic illustration of the morphological evolution process of the UiO-66-NH₂/TiO₂(A) heterostructures.

Fig. S1 shows the SEM images of the products that were obtained at 120 °C at different growth stages. At the early stage, as shown in Fig. S1A, the irregularly-shaped UiO-66-NH₂ particles with the size of less 60 nm on the TiO₂(A) nanofibers were obtained by solvothormal reaction. As observed in Fig. S1B, when the reaction time reaches 8 h, the regularly-shaped UiO-66-NH₂ nanooctahedra with the average edge-length of 100 nm appear on the TiO₂(A) nanofibers. When the reaction time was prolonged from 8 to 12 h, the average edge-length of UiO-66-NH₂ nanooctahedra was increased to 200 nm. (Fig. S1C). Further prolonging the reaction time to 16 h, the average edge-length of the octahedral UiO-66-NH₂ nanostructures was about 240 nm, and lots of octahedral UiO-66-NH₂ nanostructures were found on the surface of the TiO₂(A) nanofibers (Fig. S1D). Combining our experimental results with the theory of Ostwald ripening, we concluded a formation mechanism of the UiO-66-NH₂ nanooctahedra on TiO₂(A) nanofibers (Scheme S1). At first, the activated TiO₂(A) nanofibers (OH-TiO₂) were added to the precursor of BDC-NH₂/ZrCl₄ that spontaneously precipitates to form the nuclei on the TiO₂(A) nanofibers through Zr-O coordination. Then, the nuclei on the TiO₂(A) electrospun nanofibers aggregate to form microspheres, the core of the octahedral structure, that further orient, agglomerate, and recrystallize on the surfaces of the spherical structures. Next, the spherical structures on the TiO₂(A) nanofibers grows into the octahedral nanostructure due to the different growth rates of different crystal facets. Finally, with prolonged reaction time, the octahedral nanostructures were formed on the TiO₂(A) nanofibers. ^[1-2]

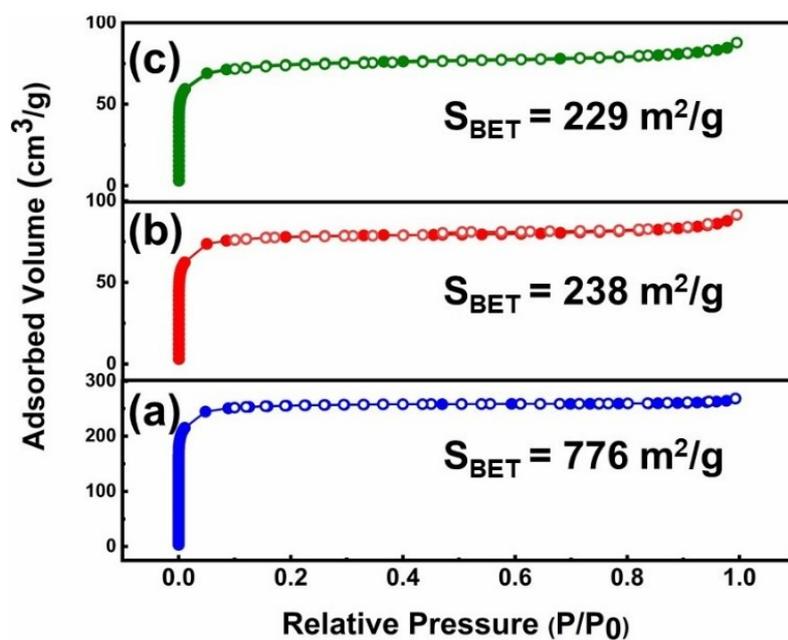


Fig. S2 Nitrogen adsorption-desorption isotherm of the as-synthesized samples: (a) UiO-66-NH₂ nanooctahedra, (b) UiO-66-NH₂/TiO₂(A) heterostructures, (c) UiO-66-NH₂/TiO₂(AR) heterostructures.

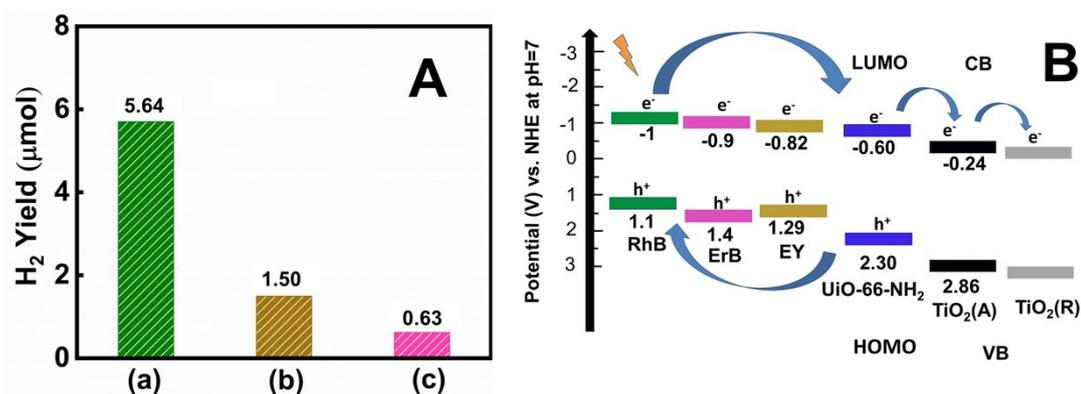


Fig. S3 (A) The amount of H₂ production through UiO-66-NH₂/TiO₂(AR) heterostructures for (a) RhB, (b) EY, (c) ErB systems under visible-light irradiation for 2 hours; (B) band structures of different dyes

As observed in Fig. S3A, the amount of H₂ production over a period of two hours for RhB, EY, ErB systems was 5.64 μmol, 1.50 μmol, and 0.63 μmol, respectively. And the photocatalytic activities of H₂ production in the RhB system was ~3.76 and ~8.95 times as compared to that in the EY and ErB system, respectively, which may be due to the difference of the band structures for RhB, EY, and ErB. According to the literatures [3-6], the LUMO position of RhB (-1 V) is higher than that of EY (-0.82 V) and ErB (-0.9 V), and HOMO position of RhB (+1.1 V) is lower than that of EY (1.29 V) and ErB (1.4 V) (Fig. S3B), leading to an easier redox reaction of RhB than that of EY and ErB. That is to say, the higher LUMO position make it easier that the photoinduced electrons on the LUMO level transfer to the LUMO of UiO-66-NH₂, which could further transfer to the CB of TiO₂ to reduce protons for H₂ production. And the lower HOMO position of RhB could lead photoinduced holes on the HOMO of UiO-66-NH₂ to transfer to HOMO level of RhB. Thus, the RhB is the optimal photosensitizer for the photocatalytic H₂ production of UiO-66-NH₂/TiO₂(AR) heterostructures under visible light irradiation. Moreover, due to the LUMO position of EY and ErB are similar, but the HOMO position of EY is obviously lower than ErB, so the photoinduced holes on the HOMO of UiO-66-NH₂ are easier to transfer to HOMO level of EY which promotes the effective separation of electrons and holes. Thus, the H₂ production of EY is higher than ErB.

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