

† **Electronic Supplementary Information (ESI) available**

**A new type of hybrid nanostructures: complete photo-generated
carriers separation and ultrahigh photocatalytic activity**

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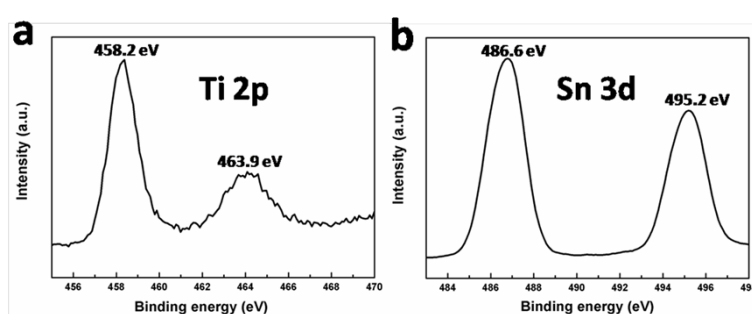


Figure S1. (a) and (b) are the XPS spectra for Ti2p, Sn3d of the pure TiO₂ and SnO₂ hollow spheres respectively.

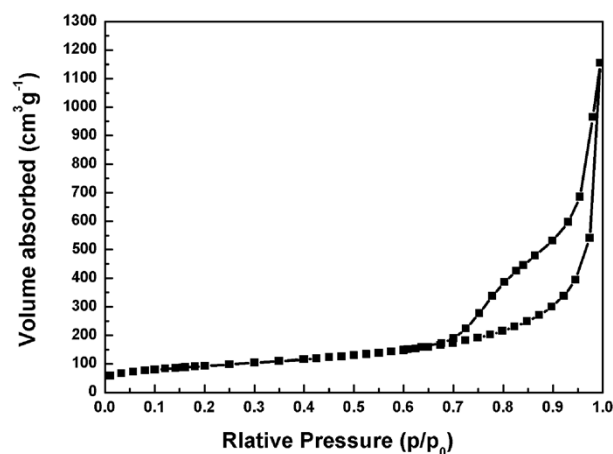


Figure S2. The nitrogen adsorption/desorption isotherms of TiO₂/SnO₂ hybrid nanostructures.

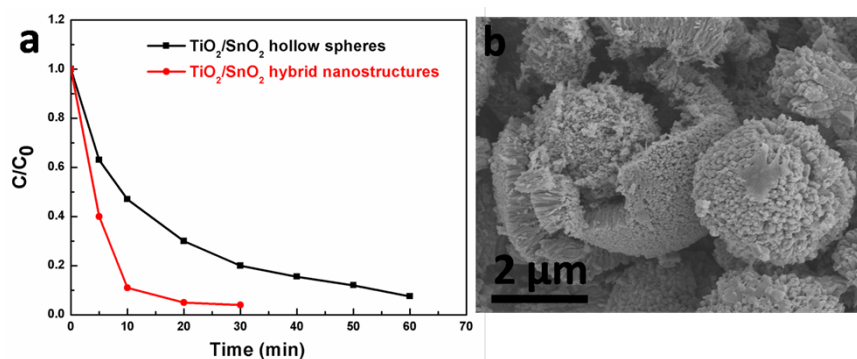


Figure S3. (a) The concentration changes of RhB dye as a function of irradiation time under full range light with our TiO₂/SnO₂ nanostructures and the TiO₂/SnO₂ hollow spheres reported by Huang et al²¹. (b) SEM image of the TiO₂/SnO₂ hollow spheres reported by Huang et al²¹.

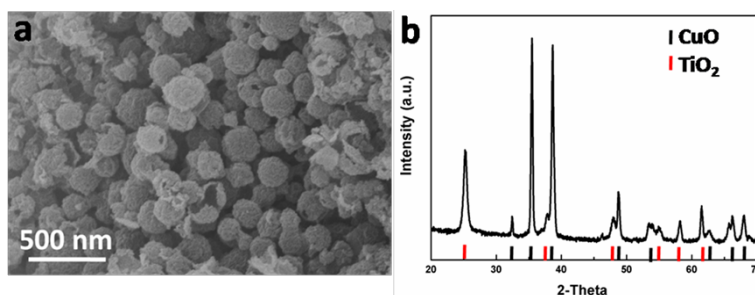


Figure S4. (a) and (b) are the SEM image and XRD pattern of the TiO₂/CuO hollow spheres.

The typical SEM image of the TiO₂/CuO hollow spheres was shown in Figure S4a. It clearly illustrated the perfect hollow spheres morphology of the TiO₂/CuO. The XRD results of the TiO₂/CuO hollow spheres in Figure S4b showed the pure TiO₂ (PDF#65-1119) and CuO (PDF#65-2309) diffraction peaks were coexisted in this chart.

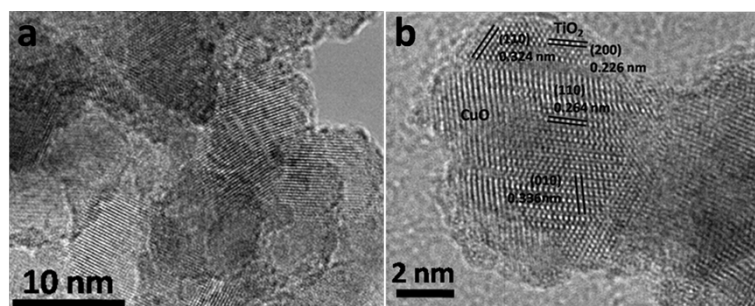


Figure S5. (a) is the enlarged TEM image of the shell of TiO₂/CuO hollow spheres and (b) is the HRTEM image of the TiO₂/CuO nanoheterojunctions.

Figure S5a showed that the shell of the TiO₂/CuO hollow spheres was composed of nanoparticles in a football-like structure. And in Figure S5b, the interplanar distances of 0.336 nm and 0.264 nm were close to the d spacings of the (010) and (110) planes of the monoclinic CuO. The interplanar distances of 0.324 nm and 0.226 nm were agreed well with the lattice spacing of the (110) and (2 0 0) planes of the tetragonal TiO₂ respectively.

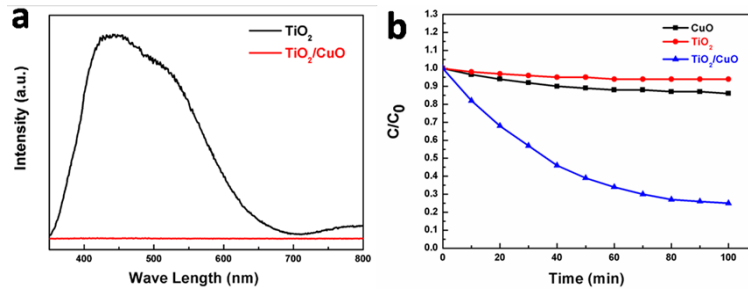


Figure S6. (a) is the PL spectra of the TiO₂ hollow spheres and TiO₂/CuO hybrid nanostructures, respectively. And (b) is the concentration changes of RhB dye as a function of irradiation time under visible light ($\lambda > 420$ nm) with TiO₂, CuO hollow spheres and TiO₂/CuO hybrid nanostructures, respectively.

As a nanoheterojunction between the indirect and direct gap semiconductors, the PL emission of TiO₂/CuO hybrid nanostructures in Figure S6a exhibited a quenching phenomenon, indicating that the recombination of the photo-generated charge carrier was almost vanished in this system. And in the visible light, the photocatalytic of CuO and TiO₂ hollow spheres were not impressive under visible light (Figure S6b). However a significant degradation of RhB dye was observed in the TiO₂/CuO nanoheterojunctions under the same light irradiation. As we all known TiO₂ was a wide-gap semiconductor, therefore, the excellent photocatalytic of the TiO₂/CuO hollow spheres under visible light should be attributed to the formation of TiO₂/CuO nanoheterojunctions.

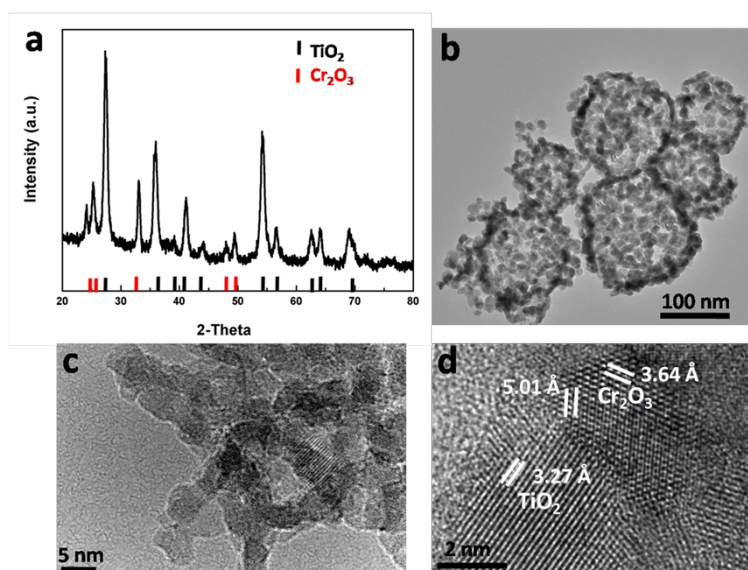


Figure S7. (a) and (b) are the XRD pattern and TEM image of the $\text{TiO}_2/\text{Cr}_2\text{O}_3$ hollow spheres. (c) is the enlarged TEM image of the shell of $\text{TiO}_2/\text{Cr}_2\text{O}_3$ hollow spheres and (d) is the HRTEM image of the $\text{TiO}_2/\text{Cr}_2\text{O}_3$ hybrid nanostructures.

The XRD pattern of the $\text{TiO}_2/\text{Cr}_2\text{O}_3$ hollow spheres in Figure S7a showed the pure TiO_2 (PDF#65-1119) and Cr_2O_3 (PDF#38-1479) diffraction peaks. The typical TEM image of the $\text{TiO}_2/\text{Cr}_2\text{O}_3$ hollow spheres clearly illustrated the perfect hollow characteristic (Figure S7b). Figure S7c showed that the shell of the $\text{TiO}_2/\text{Cr}_2\text{O}_3$ hollow spheres was composed of nanoparticles in a map-like structure. And in Figure S7d, the interplanar distances of 0.501 nm and 0.364 nm were close to the d spacings of the (010) and (012) planes of the Cr_2O_3 . The interplanar distances of 0.327 nm was agreed with the lattice spacing of the (110) plane of the tetragonal TiO_2 .