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Supporting Information

Efficient photocatalysts of tetraphenylporphyrin/P25 hybrid for visible-light photoreduction of CO_2

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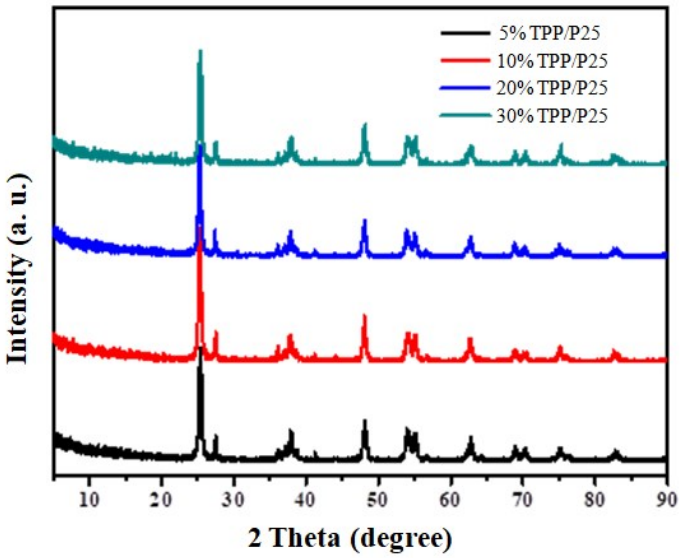

Fig. S1 XRD patterns of TPP/P25 with different addition of TPP.

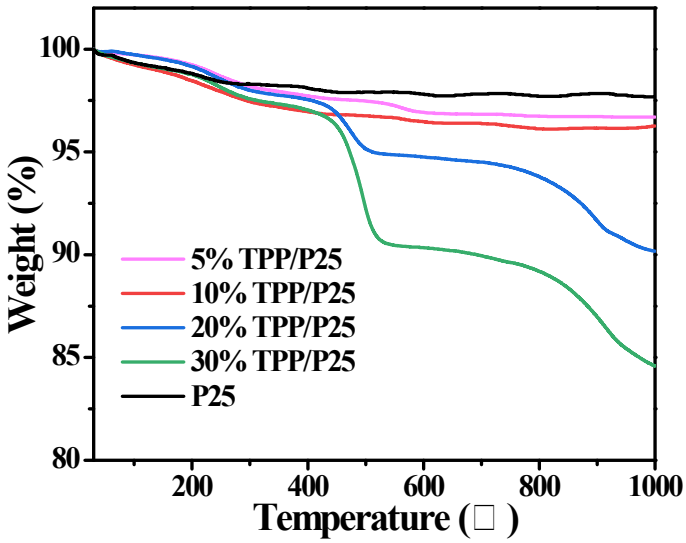

Fig. S2 TG curves of the P25 and TPP/P25 composite with different loading amount of TPP.

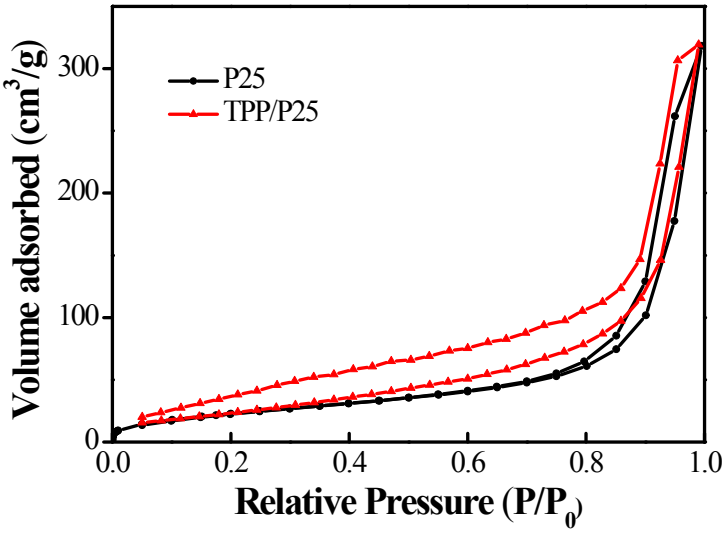

Fig. S3 N_2 adsorption-desorption isotherms of the TPP/P25 and P25.

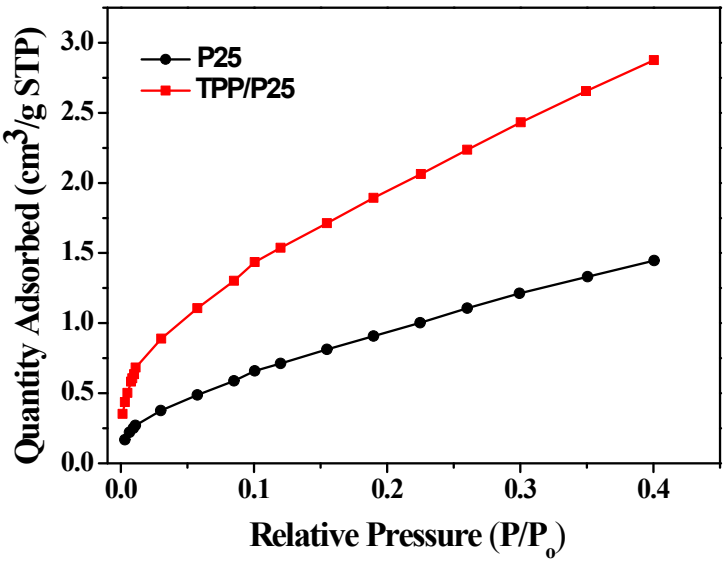

Fig. S4 CO_2 adsorption isotherms of the TPP/P25 and P25.

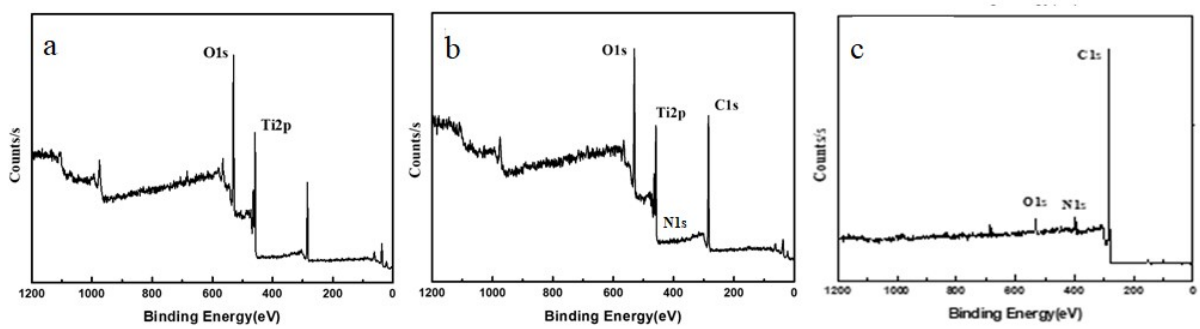

Fig. S5 XPS spectra (survey) of (a) P25, (b) TPP/P25 composite and (c) TPP.

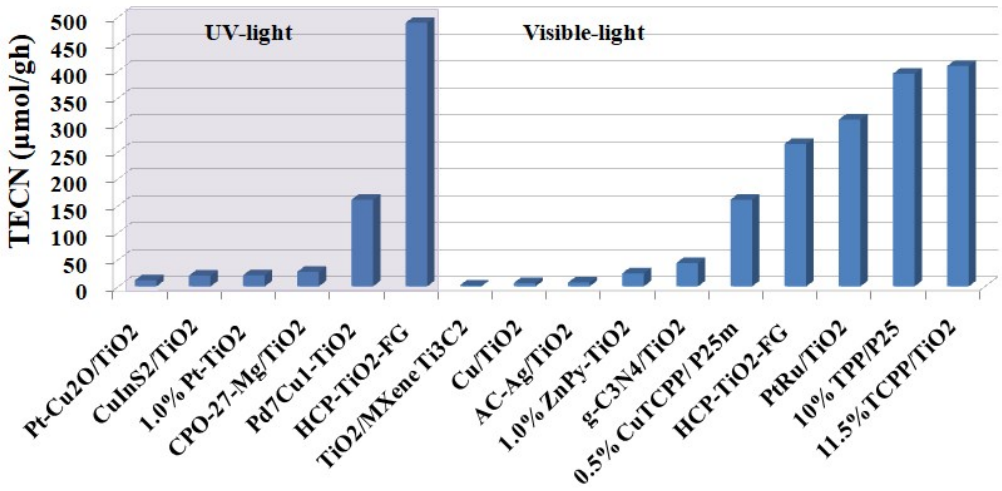

Fig. S6 Comparison of photocatalytic CO_2 reduction performance of different TiO_2-based photocatalysts.

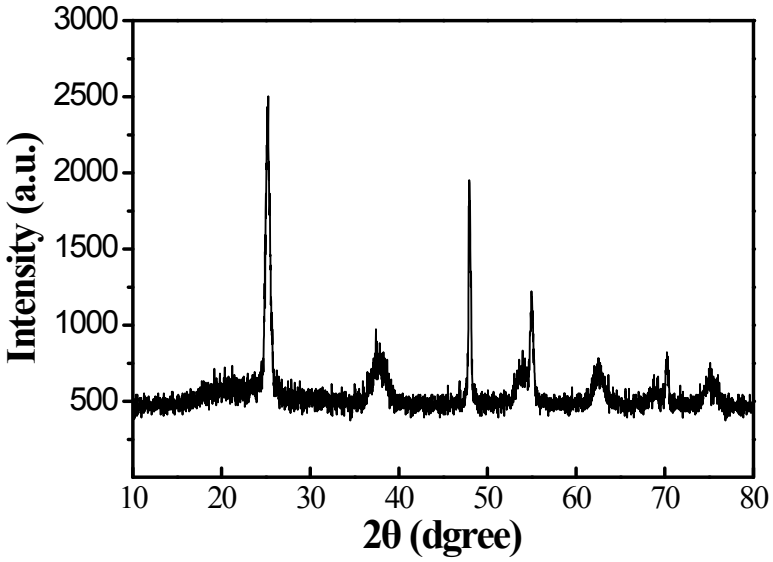

Fig. S7 XRD patterns of the TPP/P25 after reaction.

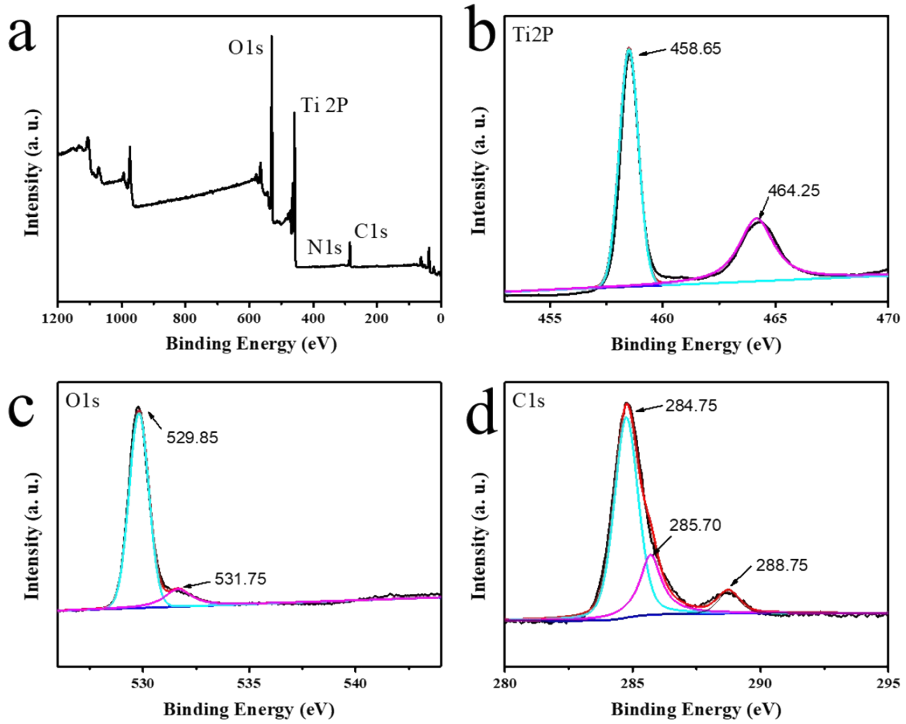

Fig. S8 XPS spectra of TPP/P25 composite after reaction: (a) full XPS spectra, (b) Ti 2p, (c) O 1s and (d) C 1s.

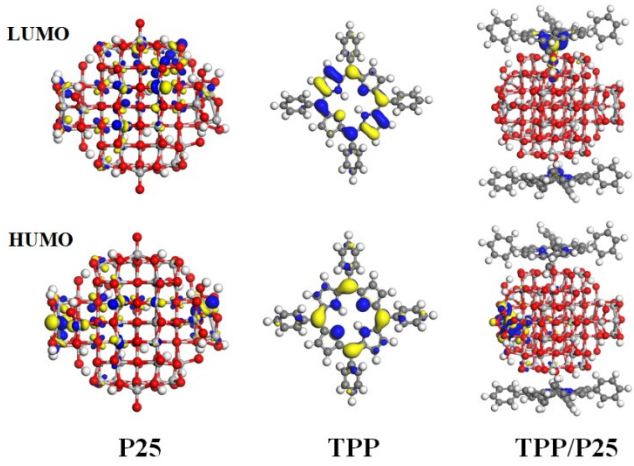

Fig. S9 Calculated LUMOs and HOMOs for P25, TPP and TPP/P25.

Computational details: All the theoretical calculations were based on the density functional theory (DFT) with the linear combination of atomic orbitals (LCAO) method. For the electron-electron exchange and correlation interactions, functional that parametrized by Becke-Lee-Yang-Parr (BLYP), a form of general gradient

approximation (GGA) was applied in all the calculations unless otherwise stated. The van der Waals interactions were handled with the DFT-D2 dispersion correction. The core-electrons interactions were described by the DFT semi-core pseudopototential (DSPP). The double numerical plus polarization (DNP) basis set was used to expand the wave functions. The P25 clusters are modeled with a nanocluster structure with a diameter of 8.0 angstrom, which is sufficient to simulate the P25 nanocluster according to our test. The surface dangling bonds was saturated with OH. The hybrids of P25 and porphyrin molecules were modeled with the surface Ti atoms of P25 nanocluster bonded with four N atoms in the center of the porphyrin molecules. During the optimization process, the central bulk phase atom of the P25 nanocluster was frozen at the fixed position, and all the structure was optimized until the max force is below 0.001 Ha A^{-1}. Due to the DFT usually underestimated the gap between LUMO and HOMO, the orbital was calculated with the B3LYP functional, a kind of hybrid functionals, to obtain a more accurate result of gap.