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金属碳化钨与液相染料光敏剂协同促进光催化制氢

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Metallic Tungsten Carbide Coupled with Liquid-Phase Dye Photosensitizer for Efficient Photocatalytic Hydrogen Production

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Computational details

The Dmol3 module of the Materials Studio software (Accelrys Inc.) was employed for the quantum chemistry calculations. Based on XRD and TEM results, W(001) (W riched WC (001) surface), W(001) + V_W (W riched WC(001) surface with W vacancy), C(001) (C riched WC(001) surface), C(001) + V_C (C riched WC(001) surface with C vacancy) were chosen to be calculated the ability of H_2 production.

The Tri (light absorbing) molecule was used to calculate the energy of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LOMO). During the calculations, the structural properties were obtained by the local density approximation (LDA) method in the form of the PWC exchange-correlation energy [1]. The 3 × 3 × 1 *k*-points samplings were used with smearing 0.005 Ha. And the global orbital cutoff is 4.9 Å. DNP (Double-Numeric basis with polarization functions) atomic orbital basis set will be used in the calculation [2]. All electrons are included in the calculation. Gibbs free energy of adsorption hydrogen atom are calculated by the following equation.

$$\Delta G_H = E[\text{surface} + H^*] - E[\text{surface}] - 1/2E[H_2] + \Delta E_{ZPE} - T\Delta S_H$$

where E[surface + H*] is the total energy of the system, including the adsorbed molecules and facet; E[surface] is the energy of the facet; $E(H_2)$ represents the total energy of a gas phase H_2 molecule; ΔE_{ZPE} denotes the zero-point energy of the system simplified as 0.05 eV; The $-T\Delta S_H$ is the contribution from entropy at temperature T, taken as 0.20 eV at 298 K.

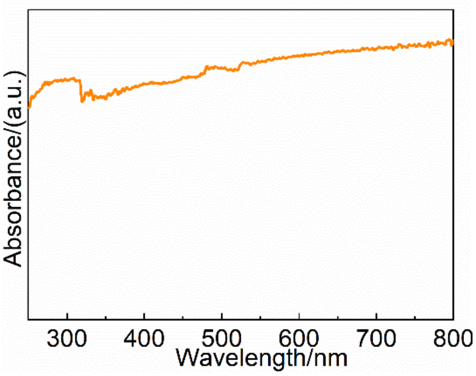

Fig. S1 **UV-Vis absorption spectrum along with the color of WC catalyst.**

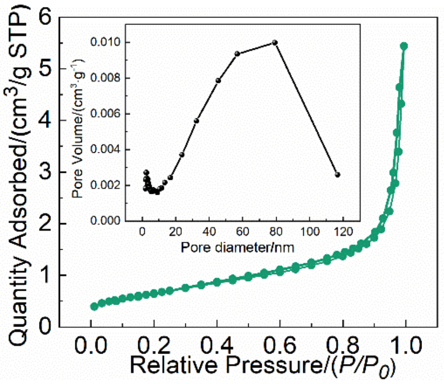

Fig. S2 **N_2 adsorption-desorption isotherm and pore size distribution (inset) of WC.**

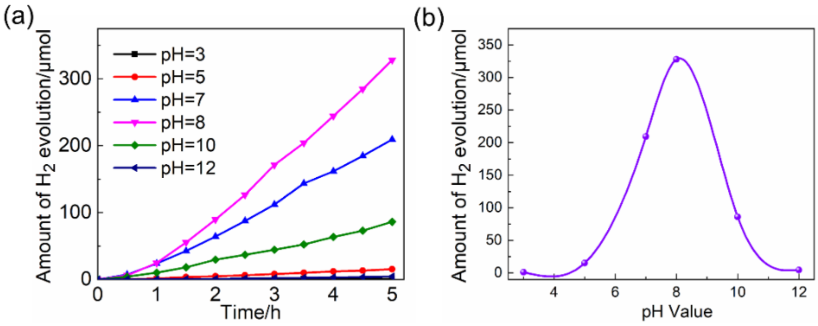

Fig. S3 **H_2 evolution from TEOA (10% (volume fraction, *φ*), 100 mL) solution containing WC (4 mmol·L^{-1}) and ErB (1 mmol·L^{-1}) at different pH values.**

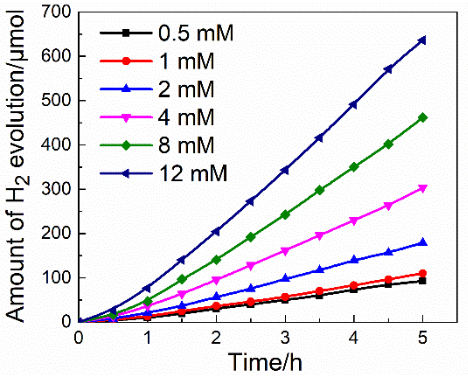

Fig. S4 H_2 evolution from systems containing 0.5 mmol·L^{-1} ErB and different concentrations of WC catalyst.

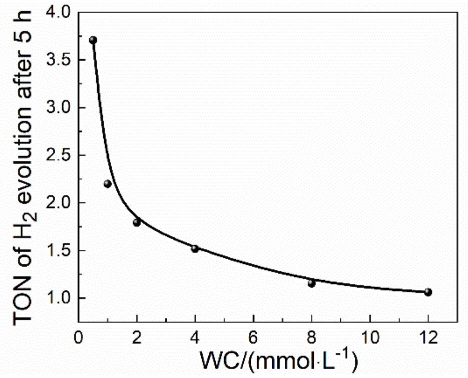

Fig. S5 TON of H_2 evolution from TEOA solution (10% (*φ*), 100 mL, pH 8) containing ErB (0.5 mmol·L^{-1}) and different concentrations of WC catalyst.

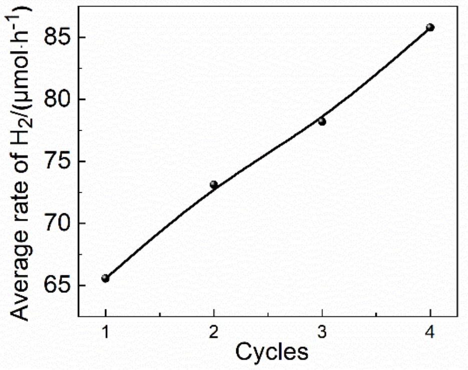

Fig. S6 Average rate of H_2 evolution after 5 h reaction per cycle.

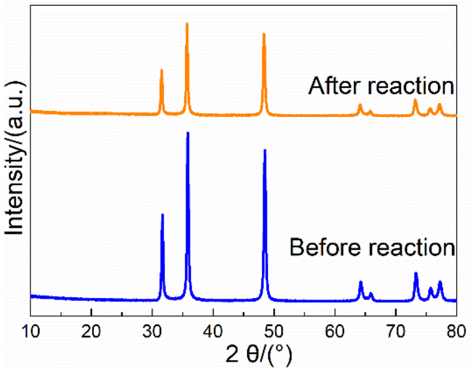

Fig. S7 XRD patterns of WC catalyst before and after reactions.

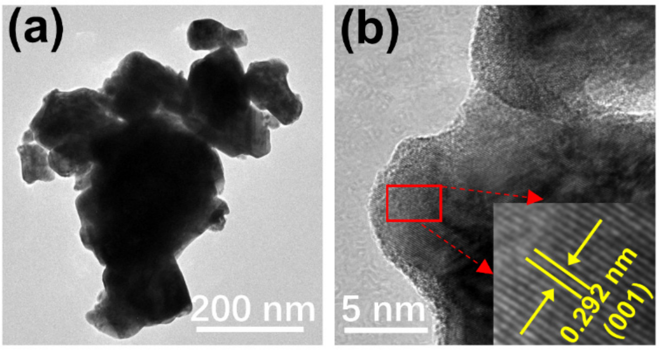

Fig. S8 TEM image of WC after stabilization reaction.

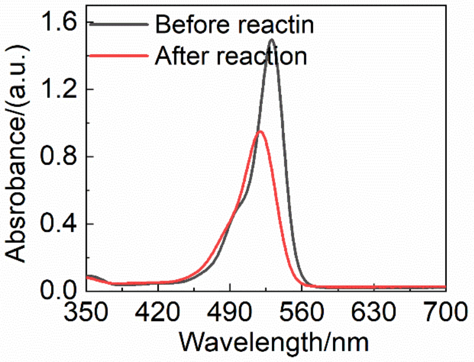

Fig. S9 UV-Vis absorption spectra before and after the reaction for the dye ErB.

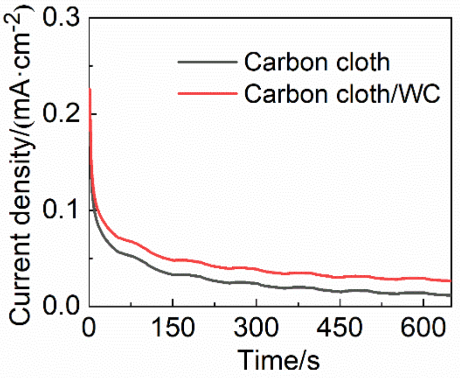

Fig. S10 Photocurrent responses of Carbon cloth, Carbon cloth/WC electrodes recorded in Na_2SO_4 (0.5 mol·L^{-1}) containing TEOA (10% (φ), pH 8) at bias of 0.5 V *vs*. Ag/AgCl.

References

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