Frontiers of Materials Science

Electronic Supplementary Material

ReS_2 quantum dots and AgBr nanoparticles co-anchored on porous g-C_3N_4 for visible-light pollutant degradation and hydrogen evolution

Dunhua Hong[1], Wei Zhu[1], Mingjiang Wang[1], Qibin Liu (✉)[2], Lan Liu[1], Jiaxin Yuan[1], Jiayuan Chen[1], Wuying Chen[3], Wenfei Li[4], Fengxia Wang[4], Hongguang Zhang[5], and Yuwei Guo[6]

1 School of Physical and Electronic Science, Zunyi Normal College, Zunyi 563006, China
2 School of Materials and Metallurgy, Guizhou University, Guiyang 550025, China
3 College of Chemistry and Chemical Engineering, Zunyi Normal College, Zunyi 563006, China
4 State Key Laboratory of Green and Efficient Development of Phosphorus Resources, Guiyang 550081, China
5 College of Pharmacy, Qiqihar Medical University, Qiqihar 161006, China
6 Department of Chemistry, Baotou Normal College, Baotou 014030, China

E-mail: qbliugzu@163.com

S1 Computational details

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with projector-augmented-wave (PAW) potentials and the Perdew–Burke–Ernzerhof (PBE) functional within the generalized-gradient approximation. Dispersion interactions were treated with the DFT-D3 correction. A plane-wave cutoff energy of 480 eV was used. The self-consistent iteration energy convergence criterion was set to 10^{-5} eV, and the atomic force convergence criterion during geometry optimization was below 0.05 eV·Å^{-1}. A vacuum layer of 20 Å was set perpendicular to the heterojunction slab to eliminate spurious interactions between adjacent layers under periodic boundary conditions. Structures and charge distributions were visualized with VASPKIT and VESTA.

The adsorption energy E_{ads} of RhB on different surfaces is defined as:

$$E_{ads} = E_{A/B} - E_A - E_B \quad (S1)$$

where $E_{A/B}$ is the total energy of the A/B system formed by RhB adsorbed on the substrate A, and E_A and E_B are energies of the isolated substrate and the isolated RhB molecule, respectively.

The charge density difference $\Delta\rho$ is defined as:

$$\Delta\rho = \rho_{A/B} - \rho_A - \rho_B \quad (S2)$$

which is used to characterize the interfacial charge redistribution upon heterojunction formation and RhB adsorption. Here, $\rho_{A/B}$, ρ_A, and ρ_B are charge densities of the heterostructure, the substrate, and the adsorbed molecule, respectively.

The Gibbs free energy change ΔG for intermediates in the hydrogen evolution reaction (HER) is estimated as:

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S \quad (S3)$$

where ΔE_{DFT} is the energy difference calculated by DFT, ΔE_{ZPE} is the zero-point energy difference, and $T\Delta S$ is the entropy term (temperature taken as 298.15 K).

S2 Control experiments for RhB degradation

To isolate the photocatalytic contribution from the H_2O_2-assisted oxidation, control experiments were performed under conditions identical to the standard RhB degradation test, except for the specified variations. The optimal composite (OC) refers to (ReS_2 QDs(5%) + AgBr NPs(15%))@PCN. The catalyst dosage was 20 mg, the RhB solution was 100 mL at 20 mg·L^{-1}, and the light source was a 300 W Xe lamp equipped with a 420 nm long-pass filter (100 mW·cm^{-2}). HCl (0.5 mL, 3%) and H_2O_2 (one drop, 30%) were added immediately before irradiation unless otherwise stated.

S3 Analysis on experimental results

In Fig. S1, following control curves are revealed:

OC + H_2O_2 (dark): no further removal after t = 0, confirming negligible dark oxidation by H_2O_2;

OC (light, no H_2O_2): approximately 85% RhB removal within 20 min, demonstrating intrinsic photocatalytic activity;

OC + H_2O_2 (light): 96.4% removal within 20 min (standard condition);

H_2O_2 only (dark) and H_2O_2 only (light): no obvious RhB degradation, confirming that the catalyst is essential.

These results collectively demonstrate that the observed RhB removal is predominantly driven by photocatalysis, with H_2O_2 acting as an auxiliary electron acceptor and oxidant.

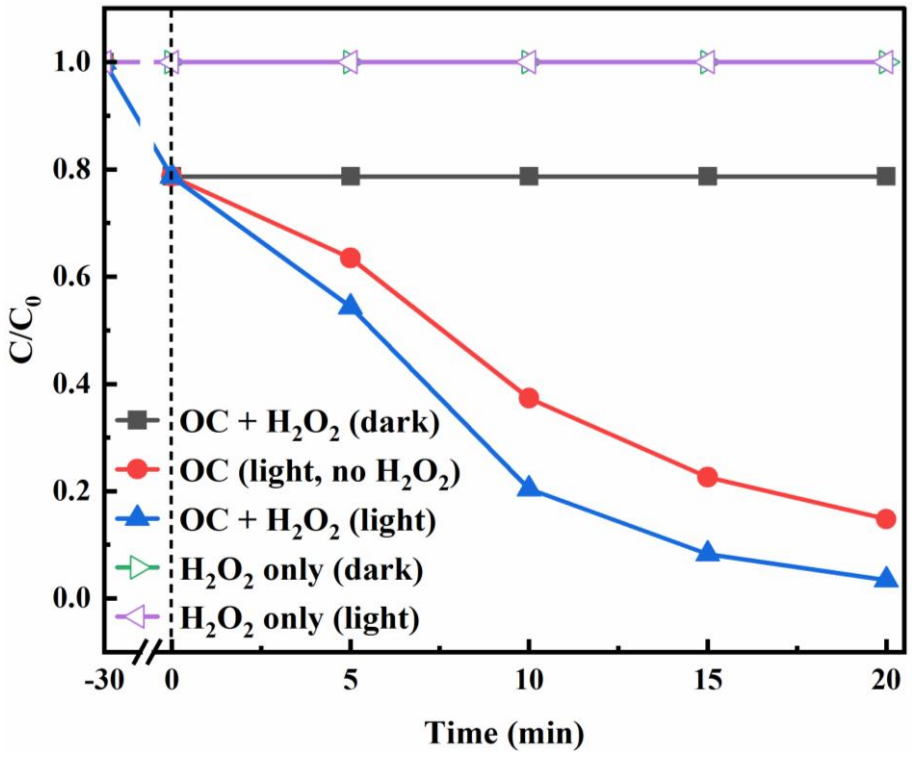

Fig. S1 Control experiments for the RhB removal over the optimal composite (OC) of (ReS_2 QDs(5%) + AgBr NPs(15%))@PCN. Conditions: catalyst 20 mg, RhB 20 mg·L^{-1} (100 mL), and visible light (300 W Xe lamp, 420 nm cutoff, 100 mW·cm^{-2}). The period from −30 to 0 min corresponds to the dark adsorption equilibrium, and the dashed line indicates the light-on point (t = 0).

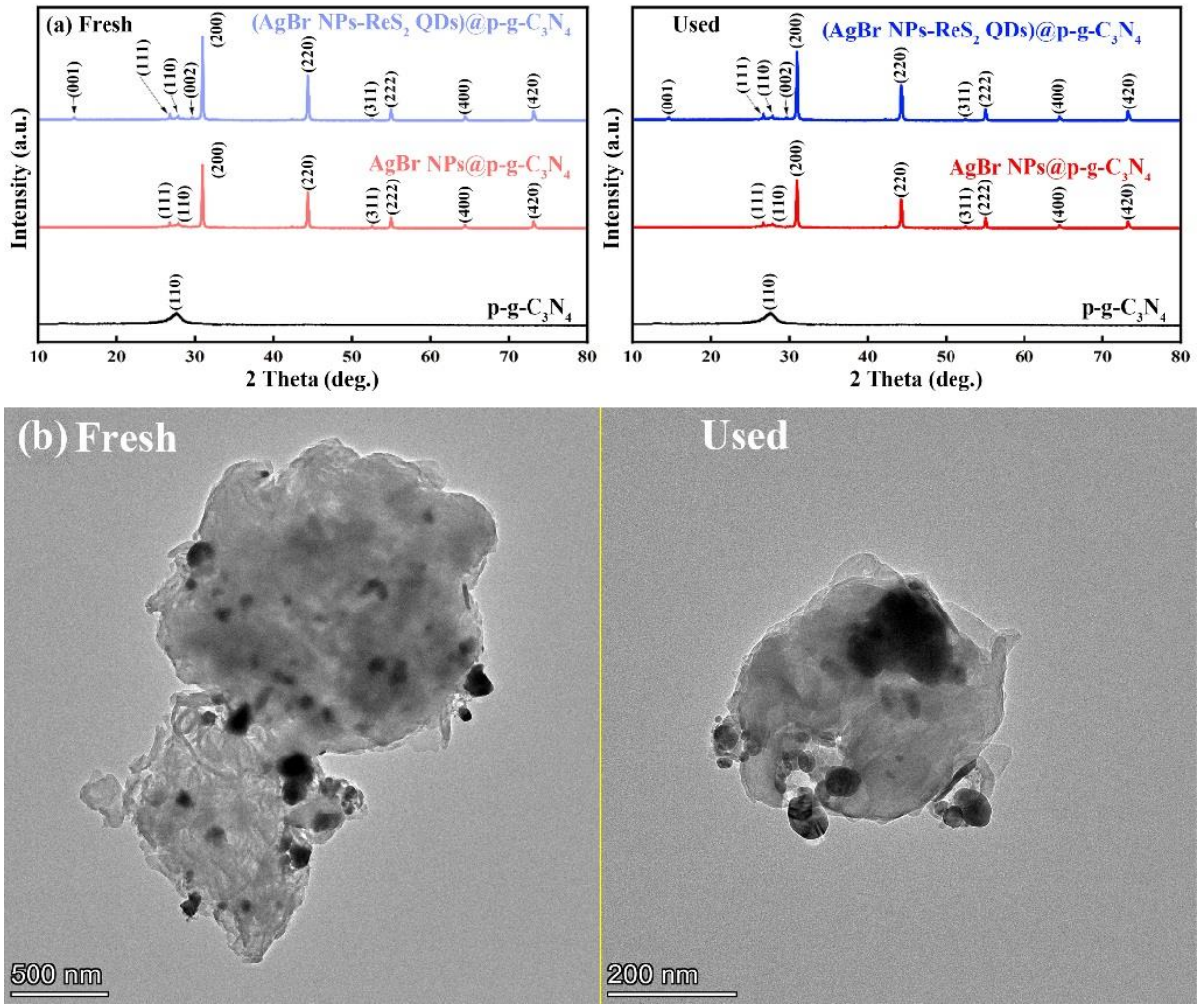

Fig. S2 (a) XRD patterns and **(b)** TEM images of the fresh and used optimal composite after four consecutive degradation cycles. The used sample retains all characteristic reflections of PCN, AgBr, and ReS_2, with no detectable metallic Ag^0 phase. The TEM images confirm that ReS_2 QDs and AgBr NPs remain uniformly anchored on the PCN surface without significant agglomeration or detachment.