

Supporting Information

Quantum effect and Mo-N surface bonding states of α -MoC_{1-x} modified carbon nitride for boosting photocatalytic performance

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Photocatalyst Synthesis

1) Synthesis of g-C₃N₄ (CN)

Melamine (3.0 g) was calcined in temperature-programmed muffle furnace for 2 h at 500 °C, then heated up to 550 °C for another 2 h, with the same heating rate (2.3 °C · min⁻¹) under N₂ atmosphere, then get the pure CN.

2) Synthesis of α -MoC_{1-x} quantum dot (α -MoC_{1-x}-QDs)

0.5 g (NH₄)₆Mo₇O₂₄·4H₂O and 3.0 g melamine are grinding evenly. Then the hybrid precursor was annealed in N₂ atmosphere at 400 °C for 2 h with a heating rate of 1 °C min⁻¹, then 800 °C for 2 h with heating rate of 2 °C min⁻¹, naturally cooled to ambient temperature under N₂. The obtained quantum dot cocatalyst is denoted as α -MoC_{1-x}-QDs.

3) Synthesis of α -MoC_{1-x} quantum dot modified CN (α -MoC_{1-x}-QDs/CN)

Different amount of the obtained α -MoC_{1-x}-QDs (0.01, 0.05, 0.1 g) and melamine (3.0 g) are grinding evenly, respectively. After that, the above mixture is dispersed into 20 mL solution ($V_{\text{ethanol}}/V_{\text{water}} = 1:3$) within ultrasonic 5.0 h, and then evaporated in a water bath to get a well-dispersed mixture. Finally, transferred it to a temperature-programmed muffle furnace for calcining 2 h at 500 °C, then heated it up to 550 °C for another 2 h, with the same heating rate (2.3 °C · min⁻¹) under N₂ atmosphere, get the α -MoC_{1-x}-QDs/CN. Finally, the product named of α -MoC_{1-x}-QDs/CN-0.01, α -MoC_{1-x}-QDs/CN-0.05, α -MoC_{1-x}-QDs/CN-0.1 corresponding the content α -MoC_{1-x}-QDs (0.01, 0.05, 0.1 g).

Photoelectrochemical Measurements

Photo-electrochemical performance of the as-prepared photocatalyst is investigated by photocurrent response by CHI 660C electrochemical station. Briefly, 0.01 g photocatalyst is dispersed in 0.5 mL ethanol and 0.1 mL oleic acid, and then take 100 μ L of the catalyst colloid was spread on the pretreated FTO (1.0 \times 1.0 cm²), dried in air at room temperature and used as corresponding working electrodes. A Pt electrode is used as the counter electrode and an Ag/AgCl electrode in saturated KCl solution is employed as the reference electrode.

Adsorption Experiments.

The adsorption performances of different catalyst investigated by batching adsorbing experiment. In brief, 80 mg of photocatalysts was mixed with 100 mL of tetracycline aqueous solution (initial concentrations: 20 mg L⁻¹). After an immersion of 1.0 h, the solution was separated and analyzed to 150 determine the remaining concentration of tetracycline by using a UV-vis spectrophotometer. The adsorption quantity of tetracycline by difference photocatalyst was calculated according to final and initial concentrations of the solution.

Photocatalytic Experiments

The photocatalytic performance of the prepared photocatalyst was evaluated by decomposition

of tetracycline. a 250 W xenon lamp covered with a UV filter ($\lambda > 420$ nm) was used as the light source, at room temperature (25 °C). 50 mg of the as-prepared photocatalyst was totally suspended in an aqueous solution of tetracycline (100 mL, 20 mg L⁻¹). For optimally dispersed system, the suspension was magnetically stirred in dark 1.0 h to reach adsorption/desorption equilibration. Air was blown into the aqueous solution during the whole reaction process. At irradiation time interval of 30 min, 2 mL solution was taken out and magnet separated, and then the absorbance of tetracycline (TC) was determined by UV/visible spectrum. The free radicals capture experiments were put into force by adding EDTA-2Na and isopropanol (IPA) and VC during the photocatalytic degradation process, respectively. The change in the concentration of tetracycline solution was measured by UV/visible spectrophotometer. The degradation efficiency was computed by $\eta = (C_0 - Ct)/C_0$, where η is the photocatalytic degradation efficiency, C_0 is the original concentration before illumination, and Ct is the concentration of tetracycline after visible light irradiation.

Computational method

We have employed the Vienna Ab Initio Package (VASP) ^{11, 21} to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE ¹³ formulation. We have chosen the projected augmented wave (PAW) potentials ^{14, 51} to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10⁻⁵ eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å. Grimme’s DFT-D3 methodology ¹⁶ was used to describe the dispersion interactions.

The equilibrium lattice constant of hexagonal g-C₃N₄ monolayer unit cell in a vacuum in the depth of 20 Å was optimized, when using a 9×9×4 Monkhorst-Pack k-point grid for Brillouin zone sampling, to be $a=7.136$ Å. We then use it to construct a g-C₃N₄(001) monolayer model with p (3×3) periodicity in the x and y directions and a vacuum layer in the depth of 20 Å in the z direction in order to separate the surface slab from its periodic duplicates. This g-C₃N₄(001) model contains 54 C and 72 N atoms. In another model, a Mo₁₃C₁₃ cluster cut out of MoC was put onto the g-C₃N₄(001) model. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and all atoms allowed to relax.

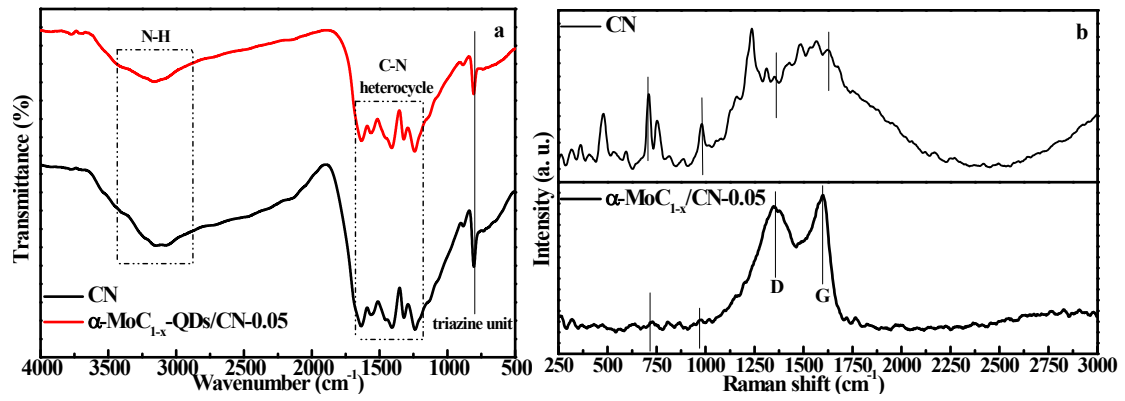


Fig. S1. FTIR and Raman data of pure CN, $\alpha\text{-MoC}_{1-x}\text{/CN-0.05}$

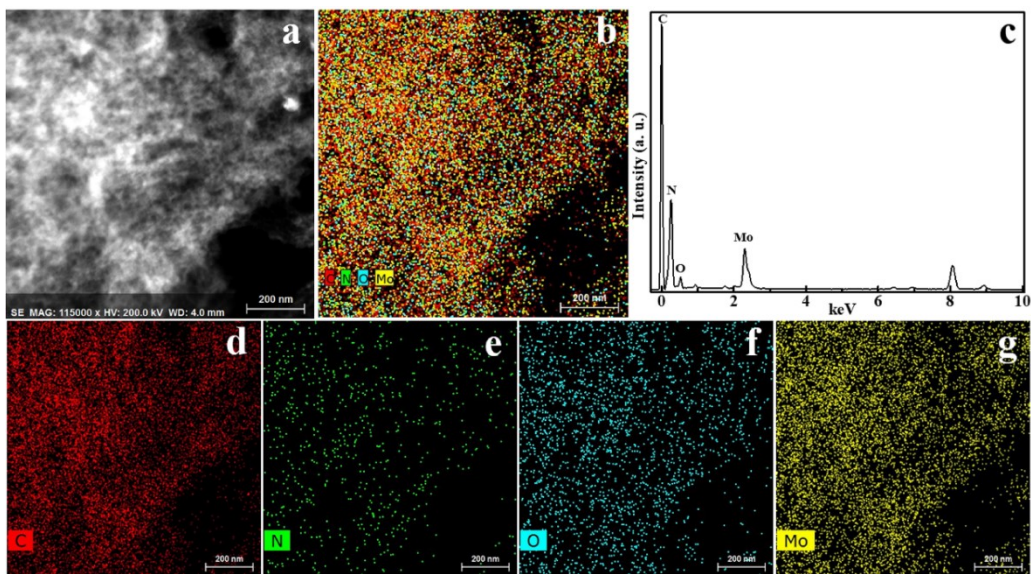


Fig. S2 EDX elemental mapping for C, N, O, Mo elements over $\alpha\text{-MoC}_{1-x}\text{-QDs}$ photocatalyst.

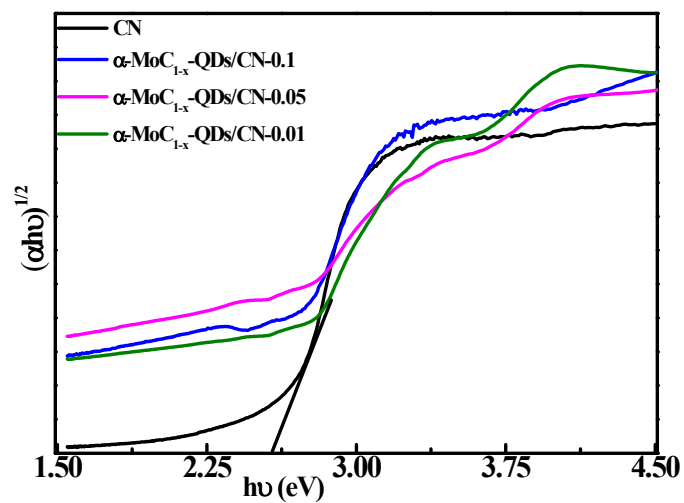


Fig. S3 Tauc plots of CN and $\alpha\text{-MoC}_{1-x}\text{-QDs/CN}$ photocatalyst.

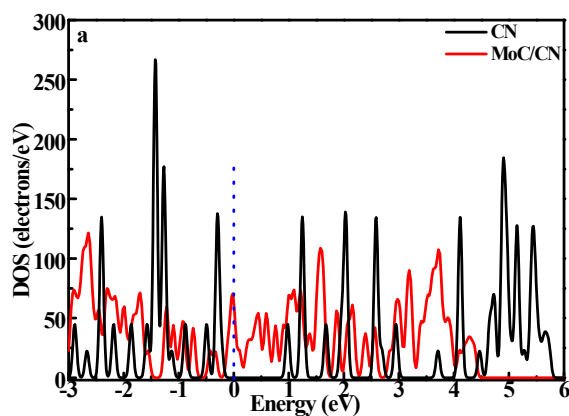


Fig. S4 The total density of states of CN and α -MoC_{1-x}/CN (the dash line is the Fermi level set at zero).

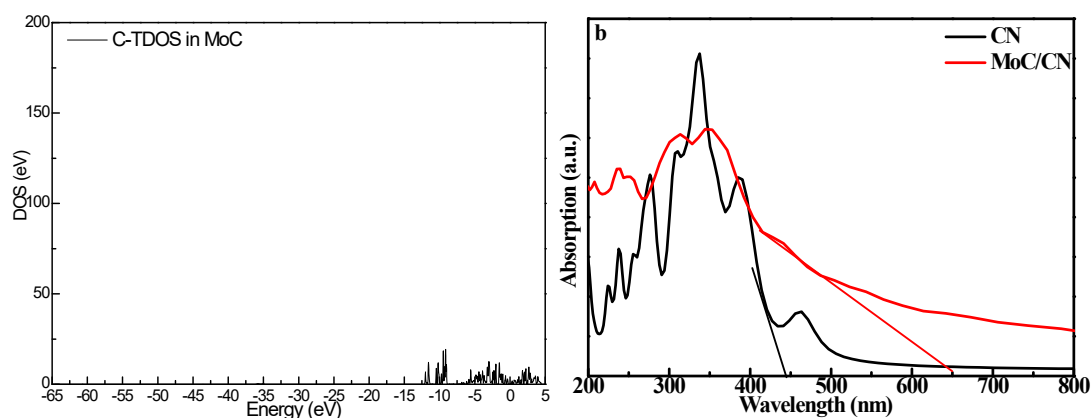


Fig. S5 The total density of states of C of α -MoC_{1-x} from MoC_{1-x}/CN (a), light absorption curves by DFT of CN and α -MoC_{1-x}/CN (b)

References

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