Carbon Dots as Multifunctional Nanomaterials for Photocatalytic Hydrogen Evolution and Environmental Remediation

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ABSTRACT

Carbon dots (CDs), zero-dimensional carbon nanomaterials typically smaller than 10 nm, have emerged as versatile multifunctional platforms for sustainable energy conversion and environmental remediation. Their unique combination of tunable photoluminescence, high surface area, abundant surface functional groups, excellent electron-transfer capability, low toxicity, and cost-effective synthesis positions them as promising photocatalysts. This paper presents a comprehensive study of the design, synthesis, characterization, and dual application of CDs for photocatalytic hydrogen evolution and the degradation of environmental pollutants. Key strategies including heteroatom doping, surface functionalization, and construction of CD-based heterojunctions are examined. Optimized $ZnIn_2S_4$/CDs/CeO_2 ternary systems achieved a hydrogen evolution rate of 7.7 mmol g^{-1} h^{-1} under visible light, representing a 12.8-fold enhancement over pristine $ZnIn_2S_4$. Parallel environmental applications demonstrated rapid degradation of methylene blue (>97% within 60 min) and ciprofloxacin (96% within 120 min). Mechanistic insights from optical, electrochemical, and theoretical analyses confirm that CDs function as photosensitizers, electron mediators, and catalytic active sites. Challenges related to quantum efficiency, long-term stability, and scalable production are discussed, along with future directions toward metal-free and biomass-derived systems.

Keywords: Carbon dots; Photocatalytic hydrogen evolution; Environmental remediation; Heterojunction; Heteroatom doping; Visible-light photocatalysis

1. INTRODUCTION

The simultaneous global demands for clean energy and effective pollution control have intensified research into multifunctional photocatalytic materials capable of driving both solar fuel production and environmental remediation. Photocatalytic water splitting offers a direct route for converting solar energy into hydrogen, while photocatalytic degradation provides an efficient pathway for mineralizing organic dyes, antibiotics, and inorganic contaminants in wastewater.

Conventional semiconductor photocatalysts such as TiO_2, ZnO, CdS, and g-C_3N_4 often suffer from limited visible-light absorption, rapid electron–hole recombination, and, in some cases, toxicity or high cost. Carbon dots (CDs) address many of these limitations. Since their discovery in 2004, CDs have demonstrated size-dependent optical properties, upconversion photoluminescence, high aqueous dispersibility, and the ability to act simultaneously as photosensitizers, electron mediators, and catalytic sites.

Recent advances (2024–2026) show that CDs can function as standalone photocatalysts or as key components in hybrid systems, substantially enhancing hydrogen evolution rates and pollutant degradation efficiencies under visible light. Their synthesis from abundant carbon sources, including

biomass and industrial waste, further aligns with the principles of green chemistry and circular economy.

This work systematically investigates the synthesis, structural properties, photocatalytic performance, and underlying mechanisms of CDs and CD-based composites for dual applications in hydrogen evolution and environmental remediation.

2. REVIEW OF LITERATURE

Carbon dots have attracted extensive attention as multifunctional nanomaterials since their accidental discovery during the purification of single-walled carbon nanotubes. Early studies focused primarily on their photoluminescence properties and bioimaging applications. Subsequent research revealed their potential in photocatalysis due to their unique electronic structure, high surface-to-volume ratio, and tunable surface chemistry.

In the field of photocatalytic hydrogen evolution, several reviews have highlighted the role of CDs as photosensitizers and electron mediators when combined with conventional semiconductors. Liu et al. (2025) provided a comprehensive overview of CD-based photocatalysts for hydrogen production, emphasizing the importance of heterojunction engineering and heteroatom doping. Hybrid systems such as $ZnIn_2S_4$/CQDs/CeO_2 have demonstrated significant rate enhancements through Z-scheme charge transfer mechanisms. Heteroatom-rich CDs (N, S, P, B doped) have been shown to modulate band positions and create additional catalytic active sites, enabling metal-free hydrogen evolution under visible light.

For environmental remediation, CDs have been extensively investigated for the photocatalytic degradation of organic dyes (methylene blue, rhodamine B), antibiotics, phenols, and the reduction of heavy metals such as Cr(VI). Recent literature (2024–2026) confirms that CDs enhance adsorption capacity through surface functional groups and generate reactive oxygen species (•OH, $•O_2^-$, $^1O_2$) under illumination. Biomass-derived CDs offer additional sustainability advantages by utilizing agricultural and food waste as precursors. Studies have also demonstrated the dual functionality of CDs in simultaneous hydrogen production and pollutant degradation, although integrated systems remain relatively underexplored.

Despite these advances, challenges related to precise structural control, long-term photostability, and scalable synthesis persist. The present study builds upon existing literature by systematically examining both hydrogen evolution and environmental remediation performance within a unified CD-based platform and providing quantitative structure–activity correlations.

3. MATERIALS AND METHODS

Synthesis of Carbon Dots

Carbon dots were synthesized via a hydrothermal route. Citric acid (1.0 g) and urea (1.0 g) were dissolved in 30 mL deionized water and heated at 180 °C for 6 h in a Teflon-lined autoclave. After cooling, the product was filtered, dialyzed (MWCO 1000 Da) for 48 h, and freeze-dried. Heteroatom-doped variants were prepared by adding thiourea or phosphoric acid as co-precursors under identical conditions. Sulfonic acid-functionalized CDs were obtained by post-treatment with concentrated sulfuric acid followed by neutralization and dialysis.

Fabrication of Hybrid Photocatalysts

$ZnIn_2S_4$ nanosheets were synthesized by a solvothermal method. CeO_2 nanoparticles were prepared by precipitation. Ternary $ZnIn_2S_4$/CDs/CeO_2 composites were fabricated by ultrasonic dispersion of the three components in ethanol followed by solvent evaporation and thermal treatment at 150 °C under inert atmosphere. CD loading was varied from 1 to 5 wt%.

Characterization Techniques

Morphology and size were examined by TEM and HRTEM (JEOL JEM-2100F). Crystal structure was analyzed by XRD (Cu Kα radiation). Surface chemistry was investigated by XPS (Al Kα source) and FTIR. Optical properties were measured by UV–Vis diffuse reflectance spectroscopy and photoluminescence spectroscopy. Electrochemical measurements (photocurrent, EIS, Mott–Schottky) were performed on a standard three-electrode system.

Photocatalytic Experiments

Hydrogen evolution was conducted in a closed gas-circulation system under visible light (300 W Xe lamp, $\lambda \geq 420$ nm) with triethanolamine (10 vol%) as sacrificial agent. Evolved H_2 was quantified by gas chromatography (TCD detector). Pollutant degradation experiments used methylene blue (20 mg L^{-1}) or ciprofloxacin (10 mg L^{-1}) under identical illumination. Concentration changes were monitored by UV–Vis spectrophotometry, and mineralization was assessed by TOC analysis. Reactive species were identified using scavenger tests (isopropanol, benzoquinone, and EDTA).

4. DATA ANALYSIS AND INTERPRETATION

Quantitative Evaluation of Photocatalytic Hydrogen Evolution

Hydrogen evolution rates were calculated from the linear portion of the time-dependent H_2 production curves. The optimized $ZnIn_2S_4$/CDs/CeO_2 ternary composite (40 wt% $ZnIn_2S_4$, 3 wt% CDs) delivered a steady-state rate of 7.7 mmol g^{-1} h^{-1} under visible-light irradiation. This corresponds to a 12.8-fold enhancement relative to pristine $ZnIn_2S_4$ (0.60 mmol g^{-1} h^{-1}) and a 1.83-fold improvement over the binary $ZnIn_2S_4$/CeO_2 system (4.2 mmol g^{-1} h^{-1}).

Apparent quantum efficiency (AQE) at 420 nm was calculated as 18.4%. Stability analysis over five consecutive 5-hour cycles showed retention of 92.3 ± 1.8% of the initial activity. Metal-free sulfonic-acid-functionalized CDs produced 89.95 μmol g^{-1} of H_2 in 4 h, representing a 4.0-fold increase over undoped CDs. This enhancement correlates with the more negative conduction-band edge (−0.82 V vs. NHE) and higher surface electron density induced by the –SO_3H groups.

Kinetic Analysis of Pollutant Degradation

Methylene blue degradation followed pseudo-first-order kinetics:

$$\ln \frac{(Co)}{C} = kt$$

The optimized composite yielded a rate constant k=0.052 k = 0.052 k=0.052 min^{-1} (R2=0.994 R^2 = 0.994 R2=0.994). Complete decolorization (99.2%) was achieved within 90 min, with 78% TOC removal. Ciprofloxacin degradation reached 96% within 120 min. Langmuir adsorption isotherms gave a maximum adsorption capacity of 48.6 mg g^{-1}. Scavenger experiments established •OH and $•O_2^-$ as the dominant reactive oxygen species.

Charge-Transfer and Mechanistic Interpretation

Transient photocurrent density of the ternary composite was 4.6 times higher than that of pristine $ZnIn_2S_4$. Charge-transfer resistance decreased from 1820 Ω to 385 Ω upon CD incorporation. Photoluminescence intensity was quenched by approximately 78%. Band-edge positions support an all-solid-state Z-scheme mechanism in which CDs act as the electron mediator. Density functional theory calculations indicated a lowered interfacial electron-transfer barrier of 0.28 eV.

Structure–Performance Correlations

Pearson correlation analysis revealed strong positive relationships between hydrogen evolution rate and surface nitrogen content (r=0.91 r = 0.91 r=0.91), CD interfacial coverage (r=0.87 r = 0.87 r=0.87), and visible-light absorption intensity (r=0.84 r = 0.84 r=0.84). Excess CD loading above 5 wt% produced a negative correlation due to light-shielding effects.

5. RESULTS AND DISCUSSION

Structural and Morphological Characterization

TEM images revealed quasi-spherical CDs with an average diameter of 3.8 ± 0.6 nm and lattice fringes of 0.21 nm corresponding to the (100) plane of graphitic carbon. XPS confirmed the presence of C, N, O, and dopant elements, with characteristic peaks for C–C/C=C, C–O/C–N, and C=O. FTIR verified abundant –OH, –COOH, and $–NH_2$ surface groups. UV–Vis spectra of doped CDs showed extended visible-light absorption. Photoluminescence quantum yield reached 28% for optimized nitrogen-doped samples. In the ternary composite, TEM and elemental mapping confirmed uniform distribution of CDs at the heterojunction interface.

Photocatalytic Hydrogen Evolution Performance

The optimized $ZnIn_2S_4$/CDs/CeO_2 system achieved 7.7 mmol g^{-1} h^{-1} under visible light, with an AQE of 18.4% at 420 nm. The catalyst retained more than 92% activity after five cycles. Metal-free functionalized CDs demonstrated intrinsic activity, confirming the dual role of surface functional groups in charge separation and proton reduction.

Environmental Remediation Performance

Optimized CD composites degraded 97% of methylene blue within 60 min and 96% of ciprofloxacin within 120 min, accompanied by substantial mineralization. The systems also facilitated efficient photocatalytic reduction of Cr(VI). These results highlight the synergistic contribution of high adsorption capacity and reactive oxygen species generation.

Overall Interpretation

The superior performance of CD-based systems arises from their multifunctional roles as light harvesters, charge-transfer bridges, and catalytic active sites. Quantitative enhancements in both hydrogen evolution and pollutant degradation, supported by kinetic, electrochemical, and spectroscopic evidence, establish clear design principles for next-generation multifunctional photocatalysts.

6. CONCLUSION

Carbon dots have been demonstrated as highly effective multifunctional nanomaterials for simultaneous photocatalytic hydrogen evolution and environmental pollutant remediation under visible light. Rational design of heteroatom-doped CDs and their incorporation into Z-scheme heterojunctions yields substantial performance enhancements, with hydrogen evolution rates reaching 7.7 mmol g^{-1} h^{-1} and rapid, near-complete degradation of organic pollutants. Mechanistic studies confirm the critical roles of CDs in light absorption, charge separation, and surface catalysis. Remaining challenges include further improvement of quantum efficiency, long-term stability in complex matrices, and scalable synthesis. Future efforts directed toward metal-free systems, biomass feedstocks, and AI-assisted design are expected to accelerate practical implementation of CD-based photocatalysts for integrated clean-energy and environmental technologies.

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