Exploring The Role Of Carbon Dots In Enhancing Photocatalytic Hydrogen Generation: A Detail Review

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Abstract:
The global demand for clean and sustainable energy sources has led to the exploration of hydrogen (H_2) as a promising alternative, due to its high energy content and zero-emission characteristics. This review highlights the potential of carbon dots (CDs) in photocatalytic hydrogen production, emphasizing their exceptional optical and electronic properties, including broad-spectrum light absorption, upconverted photoluminescence, and superior electron transfer capabilities. CDs, a novel class of carbon nanomaterials, offer advantages such as low cost, low toxicity, chemical inertness, and ease of functionalization, making them ideal candidates for enhancing photocatalytic systems. Recent advancements in nitrogen doping and synthetic techniques have significantly improved the photocatalytic efficiency of CD-based systems. Integrating CDs with other catalytic materials and exploring their role as standalone materials or as enhancers in semiconductor photocatalysts can lead to improved charge separation and migration efficiency. Future research should focus on optimizing CD synthesis, understanding their structure-property relationships, and developing robust catalytic systems. Continued innovation in this field holds the potential to significantly contribute to sustainable hydrogen production and address global energy and environmental challenges.

Key Word: *Carbon dots; Photocatalytic H_2 Generation; Carbon dots based Hybrid/Composites.*

I. Introduction

In the contemporary context, the world grapples with pressing challenges related to energy demands and environmental sustainability. The exponential increase in global energy consumption, coupled with the detrimental impact of fossil fuel usage on the environment, necessitates the exploration of innovative and sustainable energy sources. Hydrogen (H_2) is gaining prominence as a frontrunner in the pursuit of clean and renewable energy due to its zero-emission characteristics and high energy content per unit mass. Despite being the most abundant element on Earth, the practical extraction of hydrogen requires overcoming hurdles associated with energy-intensive processes involved in breaking chemical bonds within compounds.[1,2]

Efforts have been directed toward developing efficient photocatalytic systems for water splitting, with a focus on three key components: a light harvester, a catalyst, and a sacrificial electron donor. Various studies have explored the use of light-absorbing materials, including organic and inorganic molecules, as well as different type of semiconductor nanomaterials.[3] Traditional photocatalysis leverages semiconductor materials like ZnO, TiO_2, and CdS to absorb light, excite electrons to the conduction band, and generate electron-hole pairs that drive redox reactions. However, current photocatalytic systems often face limitations such as low sunlight utilization and high recombination rates of photogenerated charge carriers, which hinder the overall quantum efficiency of the process. Therefore, designing novel photocatalysts that can enhance visible light utilization and improve quantum efficiency is of paramount interest. [4]

Carbon dots (CDs or CQDs) represent a new class of carbon nanomaterials comprising quasi-spherical particles smaller than 10 nm. First discovered during the purification of single-walled carbon nanotubes in 2004, CDs have since emerged as a prominent material in the carbon family.[5] They offer several advantages, including low cost, low toxicity, chemical inertness, superior water solubility, ease of functionalization, and simple synthetic routes. These properties have propelled CDs to the forefront of photocatalysis research, leading to significant improvements in solar-to-energy conversion efficiency. Carbon dots, in particular, have emerged as promising candidates due to their small size, exceptional electron transfer characteristics, photostability, and low-cost preparation methods. [6,7]

CDs' distinct microstructure and optical characteristics allow them to play a variety of functions in photocatalytic systems. Similar to graphene and carbon nanotubes, CDs have the ability to improve adsorption capacity and efficiently segregate photogenerated electron-hole pairs.[8,9] They also have exceptional upconversion capabilities, which allow them to transform low-energy photons into high-energy ones, and they exhibit great optical absorption in the visible and ultraviolet spectrums. Because of this property, CDs can

function as spectral converters, effectively using the entire spectrum of sunlight. Furthermore, photoexcited CDs' superior electron-donating capacity makes it easier for metal salts to be quickly reduced to metal nanoparticles, which improves photocatalytic activity even more.(10,11)

The promise of CQDs in photocatalytic hydrogen production has been emphasized by recent developments. With their controllable shape and size dependent luminous features, broad absorption profiles, high quantum yields, photostability, and photo-bleaching stability, CQDs are perfect for this kind of application. Though there are still obstacles to overcome, there is potential to improve the light-harvesting capacity and photostability of CQDs, resolve flaws and agglomeration during synthesis, and optimize their optical and electrical properties.(12)(13)

Despite these challenges, the unique properties of CQDs, including their biocompatibility, abundance, low toxicity, and resistance to photo-bleaching, position them as promising materials for photocatalytic hydrogen production. Ongoing research focuses on atom-precise structural synthesis, controllable functionalization, and doping of CQDs to enhance their performance. With continued advancements, CQDs hold the potential to significantly contribute to the development of efficient and sustainable photocatalytic systems for hydrogen production, offering a viable solution to the global energy crisis and environmental issues.(14,15)

This comprehensive review seeks to provide insights into the diverse strategies employed in harnessing carbon-based nanomaterials, such as carbon dots, graphene quantum dots, and carbon quantum dots, for efficient photocatalytic hydrogen production. By understanding their unique properties and optimizing their synthesis, these carbon-based materials offer potential solutions to address the challenges posed by the global energy crisis and environmental issues.

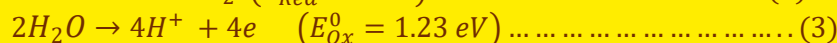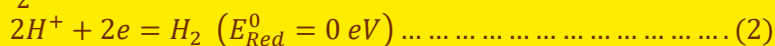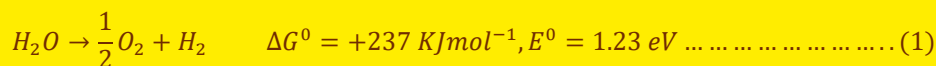## II. Basic Principles Of Photocatalytic Water Splitting

Since Honda and Fujishima's pioneering work in 1972 demonstrating photo assisted electrochemical water splitting into hydrogen (H_2) and oxygen (O_2), significant progress has been made in the field of photocatalytic H_2 production driven by solar light. This process is particularly attractive due to its potential to convert sunlight and water—the cleanest and most abundant resources on Earth—directly into hydrogen, a promising alternative fuel.(2)

Semiconductor systems are most extensively used for this purpose. Semiconductor systems are characterized by a valence band (VB) containing the highest occupied energy states and a conduction band (CB) with the lowest unoccupied energy states, separated by a band gap. Semiconductors are pivotal in photocatalysis, where light absorption induces the generation of electron-hole pairs (e^-, h^+). The process of photocatalytic water splitting typically unfolds in several steps, illustrated in Figure 1. Firstly (i), photons with sufficient energy excite electrons from the VB to the CB, creating electron-hole pairs. These charge carriers are then separated (ii): electrons might migrate to the semiconductor surface, while holes may either recombine or participate in surface reactions. The third step (iii) involves the catalytic reactions: electrons (e^-) reduce water molecules, producing H_2, while holes (h^+) oxidize water to generate O_2. This entire sequence relies on the semiconductor's ability to facilitate these reactions through its band structure and surface properties.(2,3)
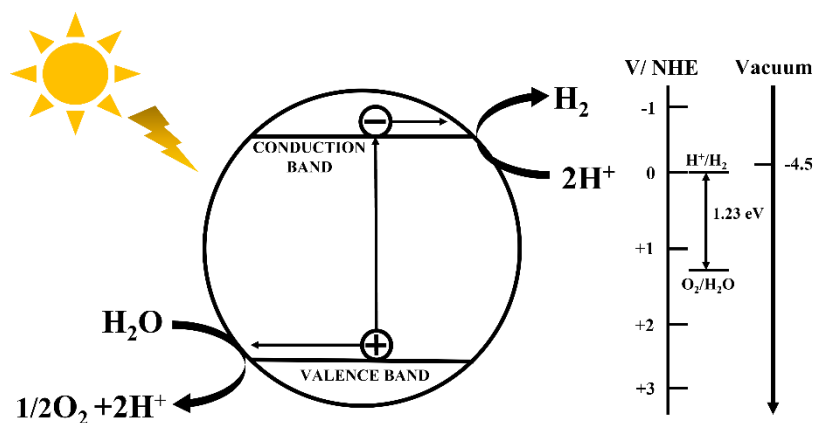
Figure 1: Schematic representation of semiconductor-based photocatalytic overall water splitting

Photocatalytic reactions are initiated when photons with energy equal to or greater than the semiconductor's band gap are absorbed, promoting electrons to the CB and leaving holes in the VB. Unlike traditional thermal reactions, photocatalysis is relatively independent of temperature, operating efficiently even at room temperature due to the energetic photoexcited state of the semiconductor.

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \qquad \Delta G^0 = +237 \ KJmol^{-1}, E^0 = 1.23 \ eV \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(1)$$

$$2H^+ + 2e = H_2 \ \left(E_{Red}^0 = 0 \ eV\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2)$$

$$2H_2O \rightarrow 4H^+ + 4e \ \left(E_{Ox}^0 = 1.23 \ eV\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(3)$$

To achieve a thermodynamically non-spontaneous process via photocatalysis, additional photon energy exceeding the 1.23 eV energy barrier must be supplied to the reaction by the photocatalyst. This energy is subsequently converted into chemical energy within the products. Therefore, the band gap energy (E_g) of the photocatalyst needs to be greater than 1.23 eV (corresponding to an absorption edge wavelength $\lambda < 1000$ nm) for effective water splitting. For utilization of visible light, E_g should be less than 3.0 eV ($\lambda > 400$ nm). Additionally, for efficient reduction/oxidation of H_2O by photoexcited electrons/holes, the band positions of the photocatalyst must align with the redox potentials of water. Specifically, the conduction band (CB) of the photocatalyst should be more negative than the reduction potential of H^+/H_2 (0 eV vs. the normal hydrogen electrode (NHE) at pH=0), while the valence band (VB) should be more positive than the oxidation potential of O_2/H_2O (1.23 eV vs. NHE at pH=0). This alignment ensures the necessary driving force for both H_2O reduction and oxidation processes.

Photocatalytic Efficiency in Water Splitting: Measuring and Comparing

The efficiency of photocatalytic hydrogen generation from water splitting can be assessed through direct measurement of the evolved hydrogen or oxygen gas, or indirectly by quantifying the electrons transferred from the semiconductor to water during a defined period of light exposure. Various experimental setups and light sources are employed by different research groups, leading to potential differences in measured gas evolution rates even when using the same photocatalyst. This variability complicates direct comparisons across studies.

To facilitate comparability, researchers often normalize gas evolution rates to the amount of photocatalyst used within a specific time frame. This normalization typically uses units such as $\mu mol \cdot h^{-1}$ and $\mu mol \cdot h^{-1} \cdot g^{-1}$ catalyst. Such normalization helps in assessing and comparing the efficiency of different photocatalysts under similar experimental conditions, despite variations in setup configurations and light sources.(3)

Quantum Yield in Photocatalytic Water Splitting

The (apparent) quantum yield (QY) plays a crucial role in evaluating photocatalytic activity for water splitting. It is an extension of the overall quantum yield used in homogeneous photochemical systems. The overall quantum yield (QY) and the apparent quantum yield (AQY) are defined by equations (4) and (5) respectively. The apparent quantum yield is typically lower than the total quantum yield because number of absorbed photons is usually smaller than that of incident photons.(3)

$$\text{Quantum Yield (\%)} = \frac{\text{Number of reacted electrons}}{\text{Number of absorbed photons}} \times 100\% \dots\dots\dots\dots\dots\dots\dots.(4)$$

$$\text{Apparent Quantum Yield (\%)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%$$

$$= \frac{2 \ \times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\% \dots\dots\dots\dots..(5)$$

$$= \frac{4 \ \times \text{Number of evolved } O_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\%$$

Moreover, the solar-to-hydrogen conversion (STH) efficiency under air mass 1.5 global (AM 1.5G) lighting is another parameter generally used for calculating the efficiency.

$$\text{STH (\%)} = \left[\frac{\text{Output energy of hydrogen evolved}}{\text{Energy of incident solar light}}\right] \times 100\% \dots\dots\dots\dots(6)$$

III. Carbon Dots Based Hybrid/Composite Systems

Various strategies have been employed to integrate Carbon dots with other materials to create synergistic effects that further improve photocatalytic efficiency. These hybrid systems leverage the complementary properties of Carbon dots and their counterparts, leading to enhanced light harvesting, better charge separation, and increased surface area for catalytic reactions. In this context, this study provides an overview of the recent advancements in the development of carbon dots-based hybrid/composite systems for

photocatalytic hydrogen generation, highlighting their potential, current challenges, and the strategies being employed to overcome these obstacles.

Carbon dots/TiO₂ Systems:

Carbon dots/TiO_2 composite system was developed by Zhang et al. for studying the photocatalytic H_2 evolution reaction.(16) Carbon quantum dots (CQDs) and P25 TiO_2 come together through a straightforward hydrothermal synthesis, creating a unique "dyade" structure that significantly enhances photocatalytic activity. In this composite, CQDs perform two crucial roles: under UV light, they serve as electron reservoirs, trapping electrons and improving the separation of electron-hole pairs. Under visible light, CQDs act as photosensitizers, similar to organic dyes, enabling P25 to respond to visible light and thus driving hydrogen production. The photocatalytic performance sees a remarkable boost: under UV-Vis light, the CQDs/P25 composite achieves a hydrogen evolution rate of 9.1 mmol/h, four times higher than that of pure P25, which suffers from rapid electron-hole recombination. Under visible light ($\lambda > 450$ nm), where pure P25 shows almost no activity due to its wide band gap, the CQDs/P25 composite reaches a hydrogen evolution rate of 0.5 mmol/h as CQD content increases. Methanol plays a critical role in this enhanced performance. Under UV light, methanol scavenges holes in P25, improving the hydrogen evolution rate. Under visible light, holes induced by CQDs can oxidize methanol, enhancing hydrogen production, unlike in pure water where this reaction is less efficient. The preparation method contributes significantly to the improved activity. The hydrothermal method leads to strong chemical interactions between CQDs and P25, evidenced by the formation of Ti–O–C bonds, which facilitate efficient charge transfer. This contrasts with composites prepared by physical adsorption, which show less enhancement. Surface area measurements indicate no significant differences between P25 and CQDs/P25 composites, suggesting that the enhanced photocatalytic activity is not due to surface area variations but rather the chemical interactions and roles of CQDs.

This study was further modified by Ghosh and co-workers where they have prepared graphene quantum dots (GQDs) via liquid phase exfoliation of graphite powder and created composites with various TiO_2 morphologies, including nanotubes, nanorods, P-25, and anatase and rutile nanoparticles.(17) Initial optimization was done using TiO_2 nanotubes (TNT) with varying GQD loadings, identifying 15 wt% GQDs as optimal. This optimal loading was then used to prepare and evaluate composites with TiO_2 nanorods (TNR), nanoparticles (TNP), and anatase nanoparticles (ANP), with CTNP-3 (15 wt% GQDs with P-25 TiO_2) showing the highest H_2 production at 29,548 $\mu mol.h^{-1}.g^{-1}_{cat}$. Stability tests under solar light irradiation indicated that CTNP-3 maintained consistent H_2 production over four cycles, demonstrating stability and potential for practical applications. Additionally, the solar-to-hydrogen efficiency (SHE) of CTNP-3 was 9.84%, significantly higher than pristine TNT (0.4%) and CTNT-3 (4.28%), due to better light utilization and charge carrier separation facilitated by GQDs. Overall, GQDs enhanced photocatalytic performance by improving electron transfer, light absorption, and charge separation in TiO_2. Based on experimental results and literature, they proposed that GQDs exhibit a synergistic role, especially in 0D-0D systems compared to 0D-1D systems. Additionally, the biphasic nature of P-25 (anatase and rutile) TiO_2 facilitates better charge transfer than single-phase TiO_2 (anatase). The narrow bandgap of GQDs (2.26 eV) aids in harnessing visible solar light, suggesting their role as photosensitizers on TiO_2, improving electron charge transfer and H_2 generation under UV irradiation. GQDs enhance charge carrier separation in TiO_2 by trapping photoinduced electrons, preventing recombination, and thereby improving photocatalytic performance.

Carbon dots/ Molecular catalyst system:

According to the aforementioned research, semiconductor hybrid systems based on carbon dots have a significant deal of potential as photocatalytic H_2 production materials. The Reisner group is also investigating whether or if carbon dots-based systems based on molecular catalysts offer comparable potential.(18) For this purpose, water-soluble, carboxylic acid-terminated carbon quantum dots (CQDs) were synthesized from citric acid at 180 °C for 40 hours, resulting in spherical nanoparticles with an average size of 6.8 ± 2.3 nm. The CQDs showed broad UV absorption and excitation-wavelength-dependent photoluminescence emission, shifting from 464 nm to 532 nm as the excitation wavelength varied. For solar-driven hydrogen production, CQDs were combined with a nickel bis(diphosphine) complex (NiP) and EDTA as an electron donor. This system was optimized to achieve a turnover frequency (Ni) of 41 (mol_{H2}) $(mol_{NiP})^{-1}$ h^{-1} and a turnover number (TON_{Ni}) of 64 (mol_{H2}) $(mol_{NiP})^{-1}$ after 4 hours at pH 6. The highest activity of 398 μmol_{H2} $(g_{CQD})^{-1}$ h^{-1} was obtained with 0.5 mg of CQD and 30 nmol of NiP. The CQD-NiP system's hydrogen production ceased without one of its components and declined due to catalyst degradation, not CQD instability. Reintroduction of NiP restored activity, confirming the catalyst as the limiting factor. The system achieved an internal quantum efficiency (IQE) of $1.40 \pm 0.08\%$, higher than previously reported noble-metal-free systems. Ongoing studies aim to enhance charge separation and improve efficiency.

Few years later Reisner group again modified the carbon dots/NiP system with the carbon dots synthesized from lignocellulosic waste.(19) They have synthesized CDs from α-cellulose-rich waste such as commercial cotton wool and recyclable cotton fabric, achieving the highest H_2 yield with α-cellulose CDs. The optimized conditions (320-340°C) resulted in CDs that outperformed other carbon-based photocatalysts, achieving specific activities up to 13,450 μmol_{H2} $(g_{CDs})^{-1}$ h^{-1}. Photocatalytic experiments, conducted under simulated solar light, showed that α-cellulose CDs, combined with EDTA and NiP, produced significant amounts of H_2. Control experiments confirmed the necessity of both CDs and NiP for H_2 generation, highlighting the importance of a sacrificial electron donor (SED) like EDTA. The structural properties of the CDs, such as smaller size, more graphitic cores, and higher surface coverage by carboxylate groups, correlated with improved photocatalytic performance.

Different cobalt based molecular catalyst-carbon dots composite systems were examined by Ladomenou et al.(20) In this study, carbon dots (CDot) and nitrogen-doped carbon dots (NCDot) were synthesized and employed as light harvesters for the photocatalytic reduction of protons to hydrogen (H_2) using molecular cobalt catalysts. The selected catalysts were the macrocyclic cobalt complex denoted as CatCo(III)1, the cobaloxime CatCo(III)2, and the porphyrin-based catalyst CatCo(II)3. These molecular catalysts offer the advantage of easy synthetic preparation and future modification to explore a series of molecules. The synthesized carbon dot materials were characterized physically and structurally, with additional studies on their UV-Vis, fluorescence properties, and electron transfer capabilities.

Initial catalytic experiments with CDot, pure NCDot, and impure NCDotMix as photosensitizers and CatCo(III)1 in 0.1 M or 1 M ascorbic acid (Asc) as SED at pH 5 under UV or visible white LED light did not produce any H_2. This was attributed to the formation of dehydroascorbic acid (DHA) during catalysis, which inhibits Asc's ability to provide electrons to the photosensitizer. To address this, a mixture of TCEP/Asc (1:1) 0.1 M each at pH 5 was used, resulting in H_2 production in the presence of CatCo(III)1. The TCEP regenerates oxidized ascorbic acid, overcoming Asc's instability and extending the system's lifetime. Optimization led to a maximum TON_{CAT} of 859 with NCDot after 52 hours of irradiation, the highest reported for a carbon dot and cobalt molecule system.

The CatCo(III)1 catalyst was chosen for its stability and activity in aqueous media. It outperformed a system using CdTe quantum dots, which achieved a lower TON_{CAT} of 650 in 1.5 hours, highlighting that CdTe components are unnecessary for better performance. N-doped carbon dots synthesized from low-cost materials proved more efficient than CDot, with pure NCDot achieving a maximum TON_{CAT} of 859 and impure NCDotMix achieving 334. The presence of citric acid or low molecular weight carbonated products in NCDotMix likely hindered light absorption. NCDot began producing H_2 after about 10 hours of irradiation, slower than CDot, which achieved 52 TON_{CAT} in 7 hours. The superior performance of NCDot is attributed to nitrogen's role in enhancing charge transfer. Stability tests showed that the system remained stable for about 6 days under UV LED irradiation. After this period, the carbon dots photobleached, stopping H_2 production. TEM images confirmed that the carbon dots retained their spherical shape but reduced in diameter upon irradiation, with fewer spheres present. XRD measurements showed structural changes in NCDot after the photocatalytic experiment. Control experiments without CatCo(III)1, NCDot, SED, or light produced negligible H_2, confirming all components' necessity. Using $CoCl_2$ as an alternative cobalt catalyst resulted in insignificant H_2 production. Lower photocatalytic H_2 production was observed when using TCEP alone as SED, indicating that the combination of TCEP/Asc is essential for efficient H_2 production. Emission experiments revealed that Asc is primarily responsible for quenching photoinduced holes.

Additional experiments with CatCo(III)2 and CatCo(II)3 showed lower H_2 production than CatCo(III)1, likely due to their lower stability in acidic media. The highest H_2 production was 17.1 μmol with CatCo(III)1 after 52 hours, demonstrating its superiority. H_2 production plateaued after several hours, with no further production upon adding more catalyst or SED, but regeneration occurred with the addition of more photosensitizer. Under real solar irradiation, the NCDot system remained stable for 21 days without photobleaching, producing 5.3 μmol of H_2 (TON_{CAT}=264). Emission spectroscopy with NCDot and CatCo(III)1 showed significant quenching, indicating efficient electron transfer from NCDot to the catalyst. Quenching constants calculated from Stern-Volmer plots suggested a reductive quenching mechanism where electrons are transferred from the SED to NCDot's conduction band, then to the catalyst, facilitating H_2 production. The photocatalytic mechanism involves solar irradiation exciting the carbon dots, with electron transfer from the valence band to the conduction band. The hole formed in the valence band is filled by an electron from the SED. This electron transfer reduces the cobalt catalyst from Co(III) to Co(II). The process repeats, with a second reduction believed to be ligand-based, leading to the formation of $[Co^{II}(L^{--})]^+$ species, which produce H_2 upon protonation. This mechanism aligns with previously reported systems using similar cobalt catalysts.

Carbon dots/ g-C₃N₄ systems:

Carbon dots based nonmetal systems are quite rare in this purpose. g-C₃N₄/Graphene Quantum Dots Hybrid system one such system, developed by Zou and coworkers.(21) In this study, the authors have methodically investigated the connections between the structures and morphologies of g-C₃N₄ made from several precursors (urea, melamine, and dicyandiamide) for photocatalytic hydrogen evolution. The photocatalytic performance of H_2 production is influenced by the method and degree of polymerization, the degree of protonation, and the morphology of g-C₃N₄. g-C₃N₄ is prepared by heat-treating urea, melamine, and dicyandiamide at 550°C for 2 hours in air. SEM and TEM analysis revealed that CN-U (g-C₃N₄ obtained from urea) formed thin, porous nanosheets, while CN-D and CN-M formed thicker layers. CN-U had the highest surface area (77 m²/g) and the best photocatalytic activity for hydrogen production, producing 8.2 times more H_2 than CN-M and 6.3 times more than CN-D. Elemental analyses showed that the C/N molar ratio followed the order CN-U < CN-D < CN-M, correlating with the stability of tri-s-triazine versus s-triazine ring units, and explaining the higher photocatalytic activity of CN-U. Additionally, combining g-C₃N₄ with N-GQDs significantly improved its performance, with 15N-CNU showing the best activity, achieving a H_2 evolution rate of 2.18 mmol·h^{-1}·g^{-1}, 2.16 times that of CN-U, and a quantum efficiency of 5.25% at 420 nm. N-GQDs also enhanced the visible light absorption of CN-U by converting long-wavelength light (600-800 nm) into shorter wavelengths (400-600 nm), facilitating better photocatalytic hydrogen production under longer wavelength irradiation. This upconversion property of N-GQDs allowed CN-U to utilize NIR light effectively for H_2 evolution. The proposed mechanism involves CN-U absorbing light (420-470 nm) to generate electrons and holes, while N-GQDs absorb visible light (600-800 nm) and emit shorter wavelengths absorbed by CN-U, promoting effective charge separation and enhanced hydrogen production on the surface of N-GQDs.

Along with N-GQDs and g-C₃N₄, Shi et al. have introduced $ZnNb_2O_6$ to construct three materials based heterostructures as the hydrogen evolving catalysts.(22) These NGQDs-$ZnNb_2O_6$/g-C₃N₄ heterostructures exhibit excellent light-harvesting and charge-separation properties. The optical properties of NGQDs were investigated using up-converted photoluminescence (PL) spectra under excitation wavelengths of 550-800 nm. NGQDs absorb visible light and emit shorter wavelengths (400-500 nm), effectively exciting g-C₃N₄ and enhancing photocatalytic performance. Photocatalytic H_2 production was tested in a 20% methanol solution with 1% Pt under a 300 W Xe lamp. The optimal Zn/7CN ratio achieved a hydrogen evolution rate of 223.2 μmol g^{-1} h^{-1}, more than double that of pure g-C₃N₄ (103.7 μmol g^{-1} h^{-1}). Increasing NGQDs content from 1% to 5% improved H_2 production to 340.9 μmol g^{-1} h^{-1}, but further increase led to decreased efficiency. Reusability tests showed that the 5% NGQDs-Zn/7CN photocatalyst maintained a hydrogen production rate of 335.2 μmol g^{-1} h^{-1} after 9 hours of irradiation, indicating excellent stability. They have proposed that under visible light, NGQDs absorb wavelengths ≥550 nm and convert them to <460 nm, exciting g-C₃N₄ to generate electron-hole pairs. Methanol is oxidized by holes in the valence band of g-C₃N₄, while electrons are injected from the conduction band of g-C₃N₄ to $ZnNb_2O_6$ and then trapped by Pt nanoparticles, enhancing charge separation and photocatalytic efficiency.

By fabricating Ag nanoparticles on Carbon Quantum Dots/Graphitic Carbon Nitride system Zeng et al. have studied the photocatalytic performance of the system.(23) The Ag/CQDs/g-C₃N₄ composite harnesses a broad spectrum of light. CQDs play a crucial role by converting longer wavelengths into shorter ones, allowing g-C₃N₄ to utilize a wider range of light. This broad-spectrum absorption capability is critical for maximizing the efficiency of the photocatalytic process. Enhanced charge separation is another key feature of this composite. Ag NPs and CQDs act as electron reservoirs, effectively separating photo-generated electron-hole pairs. Photoluminescence (PL) spectra indicate a significant reduction in emission intensity for the composite, which signifies a suppression of electron-hole recombination. This enhanced separation is crucial for improving photocatalytic efficiency. The composite demonstrates remarkable photocatalytic efficiency, achieving a hydrogen evolution rate (HER) of 626.93 μmol g^{-1} h^{-1} under visible light. This rate is 6.7 times higher than that of pure g-C₃N₄ and 2.8 times higher than the best CQDs/g-C₃N₄ composite. The optimal performance is observed with 3 wt% Ag in the composite. However, adding more than 3 wt% Ag results in a decline in activity due to the accumulation of Ag NPs, which block active sites and hinder the suppression of carrier recombination. Stability and reusability are essential for practical applications. The Ag/CQDs/g-C₃N₄ composite maintains consistent performance over four consecutive photocatalytic cycles (20 hours). X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectra confirm the photostability and thermal stability of the photocatalyst, ensuring its long-term effectiveness. In optimizing hydrogen generation, various sacrificial agents were tested. Triethanolamine (TEOA) proved to be the most effective, facilitating the consumption of photo-generated holes. The presence of TEOA ensures that more photoelectrons are released to combine with H^+ for hydrogen evolution, enhancing the overall efficiency of the process. The synergistic effects of the composite are critical for its enhanced performance. The surface plasmon resonance (SPR) effect of Ag NPs and the upconversion properties of CQDs complement each other, enhancing light absorption and charge transfer. The

combination of g-C_3N_4, CQDs, and Ag NPs creates a beneficial interface for high-efficiency photoelectron generation and separation, further boosting photocatalytic performance.

Carbon dots/Noble metal systems:

The remarkable catalytic activity of noble metal systems has drawn more attention to carbon dots based on these systems. Carbon dots (CDs) with tunable sizes were synthesized from coal tar pitch using a simple hydrothermal method with NaOH as an additive by Qiu and co-workers.[24] The CDs exhibited high crystallinity, and their size was controlled by varying the NaOH concentration. Increasing the size of the CDs from 1.9 to 5.8 nm resulted in a 70% improvement in solar-to-hydrogen efficiency. The synthesis involved nitrating coal tar pitch in HNO_3, followed by dispersion in NaOH solutions of different concentrations. The mixture was heated in an autoclave, and the resultant CDs were purified and freeze-dried, yielding 18-23%. The CDs' size, influenced by NaOH concentration, ranged from 1.9 nm to 5.8 nm. Larger CDs showed improved light absorption and narrower bandgaps, with CDs-A 0.25 (5.8 nm) having the highest light absorption and the narrowest bandgap (2.94 eV). Valence band XPS indicated consistent VB potentials across different sizes, and the calculated conduction band potentials confirmed the band structure. Photocatalytic hydrogen production was tested over 100 hours, showing stable H_2 evolution. CDs with larger sizes exhibited better photocatalytic performance, significantly enhanced by 3 wt.% Pt as a cocatalyst. The CDs-A 0.25 with the narrowest bandgap achieved the highest H_2 yield of 60.75 µmol H_2 g^{-1} h^{-1}, about 1.7 times higher than CDs-A 0.1.

Pt Single-atoms Supported Nitrogen-doped Carbon Dots system was developed by Titirici and coworkers.[25] In this work, they have developed a one-step photo-deposition process to fabricate platinum (Pt) single-atom catalysts (SACs) on nitrogen-doped carbon dots (NCDs). These Pt-NCDs were then hybridized with TiO_2 to enhance hydrogen generation activity and investigate the Pt/NCD/TiO_2 interface. NCDs were prepared via a one-step solvothermal carbonization process, as previously reported. The nitrogen content in NCDs (approximately 6%) includes pyridinic N, pyrrolic N, and amine groups, enhancing light absorption and charge carrier lifetime, beneficial for photocatalysis. The nitrogenated groups on NCDs act as active centers for adsorbing metal atoms, making them suitable for supporting metal species. The Pt-NCDs/TiO_2 sample was used as a visible-light-driven photocatalyst for hydrogen evolution reaction (HER). Immobilizing the photocatalytic system onto a mesoporous TiO_2 film facilitated scalability and recyclability. Thermogravimetric analysis determined the NCD loading to be 1.5 wt%, and ICP-MS confirmed a Pt loading of 0.20 wt%. Photocatalytic HER was evaluated using Na_2S-Na_2SO_3 as a sacrificial agent under visible light ($\lambda > 420$ nm). Pt-NCDs/TiO_2 demonstrated a hydrogen generation rate of 175.3 µmol $h^{-1}cm^{-2}$, significantly higher than NCDs/TiO_2 and pristine TiO_2. Pt-NCDs/TiO_2 had an H_2 evolution rate of 57.3 mmol h^{-1} $mgPt^{-1}$ and a turnover frequency (TOF) of 11171 h^{-1}, among the highest for metal-based cocatalysts. The enhanced performance is attributed to the synergy between NCDs and Pt SACs. The material showed excellent stability, with only a 4% reduction in hydrogen evolution rate after four cycles. Compared to Pt nanoparticles (Pt NPs) on TiO_2, Pt SACs exhibited higher atomic efficiency and better photocatalytic performance. DFT calculations suggested that Pt single atoms offer optimal hydrogen adsorption energy, enhancing photocatalytic activity. Time-correlated single photon counting (TCSPC) and photoluminescence (PL) decay measurements indicated ultrafast electron transfer from TiO_2 to Pt-NCDs, improving charge separation and photocatalytic efficiency. The proposed mechanism involves Pt-NCDs enhancing the photocatalytic activity of TiO_2 by creating an electron-rich environment and providing optimal adsorption sites for hydrogen reduction.

Mehta et al. has developed a gold-coated CQDs (Au@CQDs) core shell system to study photocatalytic behavior.[26] Photoluminescence analysis indicates that CQDs emit at 460 nm and red-shift at longer wavelengths. HRTEM images reveal spherical CQDs of 7 nm with a 0.22 nm d-spacing, and Au@CQDs with a 6 nm shell thickness. Under sunlight, both CQDs and Au@CQDs outperform other carbon materials in hydrogen production, with rates of 260 µmol and 280 µmol, respectively. The band gaps were calculated using tau plots, and the reduced band gap in Au@CQDs results from charge transfer between Au and CQDs. Photocatalytic water splitting experiments used methanol as a sacrificial mediator under sunlight, visible light, and UV light. Sunlight yielded the highest hydrogen production, with CQDs producing 240 µmol in 5 hours under visible light and 260 µmol under sunlight. Au@CQDs achieved 250 µmol under visible light and 280 µmol under sunlight, with solar-to-hydrogen efficiencies (STH) of 1.89% for Au@CQDs and 1.75% for CQDs. The enhanced activity of Au@CQDs is due to improved electron distribution, confirmed by photoelectrochemical studies showing higher current densities. Hydrogen production increases with sunlight flux, averaging 637 W/m² over 5 hours. The band gap energy of CQDs depends on size, with smaller CQDs having larger band gaps, supporting visible light emission. CQDs also act as electron buffers, reducing recombination rates and enhancing electron transport. A proposed mechanism involves visible-light absorption by Au nanoparticles, generating electrons transferred to CQDs' LUMO, facilitating efficient water splitting. CQDs and Au@CQDs are promising for utilizing the full spectrum of sunlight in photocatalysis.

Carbon dots/Nanoparticles systems:

Exploring broad-spectrum photocatalysts for photocatalytic reactions is crucial. Copper nanoparticles (Cu NPs) are used for hydrogen evolution due to their surface plasmon resonance (SPR) effect. To enhance their photocatalytic ability, Zeng and coworkers have modified Cu NPs with carbon quantum dots (CQDs).(27) The Cu/CQDs composites, prepared via in-situ photoreduction, showed a higher hydrogen evolution rate (64 mmol g^{-1} h^{-1} for 'sample **C**' with 15.6 wt% CQDs) than pure Cu NPs. CQDs trap electrons from Cu NPs, preventing electron-hole recombination. SEM, TEM, and HRTEM images revealed that Cu/CQDs particles were evenly distributed, but higher CQD content led to agglomeration, reducing charge transfer efficiency. Control experiments confirmed that hydrogen production required both Cu acetate and irradiation. Samples modified with CQDs showed increased H_2 evolution rates, with 'sample **C**' achieving the highest rate. However, excessive CQDs reduced photocatalytic ability due to agglomeration. Under visible light ($\lambda > 420$ nm), 'sample **C**' exhibited remarkable stability and little deactivation over 30 hours. XPS and XRD analysis showed no significant changes before and after testing, indicating stability. Long-wavelength experiments (700-900 nm) showed a decrease in photocatalytic ability but retained some activity due to the SPR effect. Transient photocurrent tests demonstrated that CQDs enhance electron-hole pair separation, prolonging electron lifetime and improving photocatalytic hydrogen evolution. The proposed mechanism involves Cu NPs generating electron-hole pairs upon light excitation, with CQDs facilitating electron transfer and storage, thereby enhancing photocatalytic activity.

Hydrogen gas is produced photocatalytically using 470 nm light, with PVP-coated carbon quantum dots (CQDs) as the photosensitizer and nickel nanoparticles (NiNPs) as the catalyst by Virca et al.(28) The effect of polyvinylpyrrolidone (PVP) on the CQD/NiNP composites' ability to catalyze proton reduction was studied. A maximum of 330 mmol H_2/g CQD is produced using 68 μg/mL of CQDs and 6 μg/mL of NiNPs, with activity lasting for 4 hours when 20 wt% PVP-coated CQDs are used, achieving a 6% H_2 production quantum yield. Higher PVP weight percentages decrease H_2 production rates but increase duration due to PVP's stabilizing effect, which also increases the fluorescence quantum yield of CQDs. Initial H_2 production rates were highest for uncoated CQDs but declined rapidly, whereas 20 wt% PVP-coated CQDs maintained a more consistent rate. Optimal H_2 production was achieved with 68 μg/mL CQDs and 24 μg/mL NiNPs, with deviations resulting in reduced H_2 output due to competition for electrons. The solution's pH also affected H_2 production, with optimal results at pH 4.71 using EDTA as a sacrificial electron donor (SED). Fluorescence quenching experiments indicated electron transfer from the SED to the photosensitizer and from the photosensitizer to the catalyst, supporting a mechanism involving both reductive and oxidative quenching pathways.

Lei et al. have developed semiconductor based systems with cadmium sulfide (CdS) and graphene quantum dots (GQDs) for photocatalytic hydrogen evolution reaction.(29) These CdS/GQDs nanohybrids, synthesized via a one-step hydrothermal method, form a "dot-on-particle" structure with GQDs on CdS nanoparticles. While GQDs do not alter the crystallite structure of CdS, they enhance light absorption beyond CdS's band edge. Under visible light (≥ 420 nm), the CdS/GQDs nanohybrids achieved an H_2 production rate of 95.4 μmol·h^{-1}, 2.7 times higher than pure CdS, with an apparent quantum efficiency (AQE) of 4.2% at 420 nm. The photocatalytic performance is predominantly due to the efficient electron transfer and charge separation facilitated by the graphene-like nature of GQDs, acting as electron acceptors rather than photosensitizers. The optimal GQDs content was found to be 1.0 wt %. Photocatalytic stability was tested over 36 hours with intermittent evacuation every 12 hours. Both CG0 and CG1.0 showed a slow decrease in activity over time, with CG1.0 maintaining higher activity than CG0. The activity drop for CG0 was attributed to photocorrosion from inefficient hole consumption by the sacrificial reagent. For CG1.0, weakened chemical interaction between CdS and GQDs due to photoxidative reactions contributed to the decrease. In control experiments, GQDs alone showed no photocatalytic activity, and physically mixed CdS and GQDs had lower performance than the chemically coupled nanohybrids, highlighting the importance of their interaction. Photocurrent response, photoluminescence, and electrochemical impedance measurements supported these findings.

Other system:

To create novel CQDs/H-γ-TaON hollow urchin heterostructures, a feasible and straightforward process was developed by Hou and coworkers.(30) First, fluorine-containing Ta_2O_5 hollow urchins were prepared via in situ hydrothermal treatment, followed by thermal nitridation to obtain γ-TaON hollow urchins. Hydrogenation produced H-γ-TaON hollow urchins under heat treatment with hydrogen and argon gases. Finally, the CQDs/H-γ-TaON heterojunctions were formed using an oil bath reflux process. The CQDs/H-γ-TaON heterostructures exhibited superior photocatalytic performance in hydrogen production from water splitting, achieving a rate of about 495 mmol/h, higher than γ-TaON (395 mmol/h) and H-γ-TaON (415 mmol/h). An apparent quantum efficiency of 12.2% under 420 nm light was achieved, significantly surpassing conventional TaON. This enhanced performance is attributed to the efficient light harvesting by H-γ-TaON

urchins and the improved charge separation provided by the heterostructure, which suppresses electron-hole recombination. The stability of these photocatalysts was confirmed through five consecutive test cycles, showing no significant reduction in photocatalytic activity. XRD analyses demonstrated the high durability of the CQDs/H-γ-TaON sample, with no substantial changes in phase and chemical structure after repeated cycles. The CQDs enhance the photocatalytic process by acting as electron collectors and transporters, preventing electron-hole recombination, and absorbing longer wavelengths to emit shorter wavelengths, which excites H-γ-TaON and improves NIR photocatalytic properties. The synergistic effect of hydrogen treatment and CQD decoration enhances practical photocatalytic applications.

IV. Standalone Carbon Dots

The study of carbon dots as the lone material for photocatalytic hydrogen generation is not very extensive. For the last 10 years few studies have been done to understand the potential of carbon dots as both photosensitizer and photocatalyst simultaneously.

Zhu group has synthesized carbon nanodots via a simple ultrasonic hydrothermal process from multi-wall carbon nanotubes.(31) They have found that carbon nanodots (CNDs), without modification or cocatalysts, can efficiently drive photocatalytic hydrogen generation. Using methanol as a sacrificial donor, the hydrogen generation rate of CNDs reaches 3615.3 mmol g^{-1} h^{-1}, which is 34.8 times higher than that of the commercial Degussa P25 photocatalyst. CNDs maintain stability, with negligible change in hydrogen generation rate after four testing cycles. In pure water, the hydrogen production rate of CNDs is 423.7 mmol g^{-1} h^{-1}, confirmed by gas chromatography. Photocatalytic activity without CNDs or light results in no hydrogen production, indicating the necessity of both for the reaction. CNDs show a direct bandgap transition with an energy gap of 4.88 eV. Their conduction band (CB) is at -0.906 eV (versus NHE), suitable for hydrogen evolution. CNDs generate significant photocurrents under UV irradiation, aligning with photocatalytic results. The low photoluminescence (PL) quantum yield of CNDs (2.42%) also supports these results indicating a low recombination rate of photo-induced electron–hole pairs, which contributes to the high photocatalytic activity, as most photo-generated electrons in CNDs participate in photocatalysis.

Nabid et al. has studied the fabrication and characterization of boron and nitrogen co-doped carbon-based dots (B, N co-doped CDs) used as catalysts for hydrogen generation from the hydrolysis of sodium borohydride ($NaBH_4$).(32) The carbon dots are prepared by dissolving citric acid, dicyandiamide, and boric acid in water, followed by heating in a Teflon-lined autoclave at 160°C for 4 hours. The resulting product was purified using ethanol and centrifugation. XPS and FT-IR analyses confirmed successful doping of the CDs. Hydrogen generation experiments revealed that the amount of catalyst and reaction temperature significantly influenced the hydrogen production rate. At room temperature, 0.007 g of the catalyst generated approximately 91 mL H_2 in 225 minutes, while increasing the temperature to 40°C produced around 106 mL H_2 in 100 minutes. The catalyst's effectiveness was also tested with other hydrogen sources, such as formic acid, glycerol, and hydrous hydrazine, showing excellent activity. The co-doping of nitrogen and boron improved the catalytic performance compared to single-doped CDs, attributed to the synergistic effects of the heteroatoms. A proposed mechanism suggests that the B, N co-doped CDs facilitate the combination of protic hydrogen from water and hydridic hydrogen from $NaBH_4$ to form H_2. Reusability tests demonstrated that the catalyst maintained significant activity over five cycles, with a slight decrease in hydrogen generation rate from 74.6 to 64.8 mL min^{-1} g^{-1}_{cat}. This study highlights the potential of B, N co-doped CDs as efficient, metal-free catalysts for hydrogen generation.

These studies have opened the focus of the researchers towards understanding and modifying the properties of carbon dots for better photocatalytic behavior. Doping, surface functionalization are some of the approaches have been considered by the researchers.

Teng group have synthesized Surface-intact nitrogen-doped graphene oxide quantum dots (iNGO-QDs), composed of C, H, O, and N, by thermally treating graphene oxide sheets in NH_3 followed by ultrasonic exfoliation.(33) The as synthesized particles are found to be 2 to 6 nm in size with about 3 graphitic layers. XPS analysis reveals nitrogen atoms in iNGO-QDs are pyridine-like (398.4 eV), pyrrolic-like (399.1 eV), and quaternary (400.7 eV) forms, with most nitrogen replacing graphitic carbon to form pyridine-like and quaternary functionalities. The nitrogen doping repairs vacancy defects in GO, creating p- and n-type domains in the QDs. Photocatalytic performance analysis showed that iNGO-QDs, in a gas-enclosed system with visible light (420–800 nm), have four times higher H_2 production activity than iGO-QDs, attributed to defect elimination and n-type domain embedding. Pt deposition significantly increases photocatalytic activity, with 3 wt% Pt proving optimal. Over 6 days, the iNGO-QDs with 3 wt% Pt produced ca. 2.2 mmol H_2, demonstrating stable photocatalytic reaction with a high turnover (t). The rate of H_2 production was 4.9 μmol h^{-1}, corresponding to an AQY of 12.8%, superior to many other photocatalysts.

More detail effect of nitrogen doping is studied by Tsai et al.(34) They have examined the photoelectrochemical (PEC) properties and photocatalytic activity of nitrogen-doped graphene quantum dots (N-

GQDs) for solar water splitting. To prepare the N-GQDs, a graphene oxide (GO) dispersion was mixed with varying amounts of urea (0.5-8 g), sonicated, and subjected to hydrothermal treatment at 180°C for 12 hours. After filtration and purification, the N-GQDs were obtained. Five different N-GQDs samples were prepared (0.5N-GQDs to 8N-GQDs), along with non-doped GQDs for comparison. Transmission electron microscopy (TEM) revealed that both pristine GQDs and N-GQDs had similar diameters (approximately 6.6 nm) and were highly crystalline with an interlayer spacing of 0.21 nm. Among the N-GQDs, the 2N-GQDs (2 g urea) had the highest nitrogen content (6.85 wt%), with pyrrolic and pyridinic-N dominating at low urea amounts and quaternary-N increasing with higher urea amounts. The optical properties of the samples were analyzed using UV-visible absorption and photoluminescence (PL) spectroscopy. Along with 330 nm (π- π^* transition) and 350-400 nm (n- π^* transition) absorption edges N-GQDs exhibited additional absorption at 450-500 nm due to the C-N bonds. The 2N-GQDs showed the highest PEC activity and photocurrent generation, correlating with the largest PL carrier lifetime at 525 nm, indicating that nitrogen-related electronic states significantly enhanced PEC performance. As photocatalysts for hydrogen production, both pristine GQDs and 2N-GQDs were active, with 2N-GQDs achieving twice the activity of pristine GQDs. The solar-to-hydrogen (STH) efficiency for pristine GQDs and 2N-GQDs was 0.012% and 0.035%, respectively, demonstrating the potential of N-GQDs for solar hydrogen production applications.

Xu and his cowarkers on the other hand, synthesized amino groups conjugated water-soluble carbon quantum dots (CQDs) prepared via a simple hydrothermal method form citric acid and urea.(35) Experiments with 50 mg of amino-conjugated CQDs in 100 mL aqueous solution showed negligible H_2 production without sacrificial reagents due to rapid recombination of electrons and holes. However, adding 0.5 M Na_2SO_3 and 0.43 M Na_2S significantly enhanced H_2 production, achieving an average rate of 27.31 $\mu mol\ h^{-1}$. This improvement is attributed to the suppression of electron-hole recombination. Bare CQDs without amino groups showed negligible H_2 evolution, highlighting the crucial role of amino groups in passivating surface traps, expanding optical absorption, and facilitating photoelectron transfer.

The amino-conjugated CQDs demonstrated stable photocatalytic activity over four cycles, suggesting their potential as a durable photocatalyst for continuous H_2 production. The solar-to-hydrogen (STH) efficiency was calculated to be 0.36%, with a peak efficiency of 0.62% for 80 mg of CQDs. The quantum efficiency (QE) of H_2 evolution varied with incident light wavelength, aligning with the UV-vis absorption spectrum of the CQDs.

The above studies have confirmed that the incorporation of nitrogen in the carbon dots has the massive impact on the photocatalytic hydrogen production.

For understanding the specific position or functionalities of nitrogen in carbon dots toward photocatalytic hydrogen production, Bhattacharyya et al. have investigated the incorporation of nitrogen in carbon dots (CDs) and how it affects their photocatalytic and photo-emissive properties by monitoring photoluminescence quantum yield (PL QY) and hydrogen generation efficiency.(36) CDs were synthesized from citric acid and varying amounts of branched polyethyleneimine (BPEI) using a microwave-assisted pyrolysis technique. By varying the BPEI content, the nitrogen content in the CDs ranged from 2.5% to 35%. Photocatalytic activity was assessed by measuring H_2 generation under xenon lamp illumination, with methanol added as a hole scavenger. The H_2 production rate increased linearly over 24 hours, with the highest rate of 18.7 $\mu mol\ g^{-1}\ h^{-1}$ observed for CDs with the highest BPEI content (CD2). The production rate corresponded strongly with the absorption spectrum, peaking around 360 nm. The CDs remained stable and retained their photocatalytic properties during the experiments. Results showed that PL QY peaked at an intermediate BPEI level, while hydrogen generation efficiency increased for both low and high BPEI levels. This anti-correlation was explained by the different roles of graphitic, pyridinic, and pyrrolic nitrogen atoms in CDs. Graphitic nitrogen was linked to higher PL QY due to its compatibility with sp^2-hybridized aromatic domains, enhancing radiative lifetimes and reducing non-radiative recombination. Higher BPEI levels led to more nitrogen atoms at the edges of aromatic domains, increasing non-radiative recombination but also improving photocatalytic efficiency due to better charge separation and transfer. Interestingly, the CDs exhibited their highest H_2 generation efficiency under near-neutral pH conditions (7.5–8.5), making them suitable for practical applications. The H_2 generation proceeded even without additional hole scavengers, suggesting that the amine groups in the sp^3-hybridized matrix may act as internal hole scavengers. The X-ray photoelectron spectroscopy (XPS) results revealed that the trend in PL QY matched the carbon content of the aromatic domains and the graphitic nitrogen content. Graphitic nitrogen, compatible with sp^2-hybridized polycyclic hydrocarbons, increases the radiative lifetime of the aromatic domains and reduces non-radiative recombination. For higher BPEI concentrations, nitrogen atoms were predominantly found at the edges of aromatic domains in pyrrolic and pyridinic positions. This decreased the rigidity of the structures, increased non-radiative recombination, and facilitated energy/charge transfer to exterior defect sites. The presence of pyrrolic nitrogen, with its high electron affinity, enabled efficient interfacial electron transfer processes crucial for photocatalytic activity. Graphitic and pyrrolic nitrogen acted synergistically, with graphitic nitrogen serving as an electron transfer

mediator and pyrrolic nitrogen providing catalytically active sites. Unreacted amine groups from the precursor functioned as hole traps, aiding charge separation and transfer, which is often a limiting step in photocatalytic hydrogen generation.

One of the best photocatalytic hydrogen production activities using only carbon dots was achieved by Jana et al.(37) They have synthesized pCNDs (photoluminescent carbon nanodots) from citric acid and urea using 5 minutes of microwave irradiation. The resulting pCNDs underwent photo-oxidation under white light in the presence of oxygen, producing oCND-1 and oCND-2. This transformation was monitored through changes in their absorption spectra and isosbestic points. The fluorescence of these materials changed, with quantum yields decreasing in the order pCNDs > oCND-1 > oCND-2, which correlates with an increase in their catalytic hydrogen evolution reaction (HER) activity. Photo-oxidation did not significantly alter the size or morphology of the CNDs, but X-ray diffraction and Raman spectroscopy showed increased ordering in oCNDs compared to pCNDs. Optimal HER activity was achieved with 0.015 mg of catalyst in a 10 vol% TEOA solution at pH 8.5. oCND-2 was the most efficient HER catalyst, achieving a maximum turnover frequency (TOF) of 15.15 mmol(H_2) g(oCND-2)$^{-1}$ h^{-1} after 1 hour of illumination. In seawater, the catalytic activity increased to 19.70 mmol(H_2) g(oCND-2)$^{-1}$ h^{-1}, attributed to differences in ionic strength affecting electron transfer rates. Photo-oxidation mechanisms were explored by studying HPPT (4-hydroxy-1H-pyrrolo-[3,4-c] pyridine-1,3,6(2H,5H)-trione) and CZA (citrazinic acid), the molecular fluorophores in pCNDs. CZA undergoes two clean transformations under light, involving dimerization and trimerization, leading to oCND-1 and oCND-2, respectively. These transformations were accelerated in the presence of HPPT, suggesting significant electronic interactions between the fluorophores and the carbon matrix. The catalytic cycle for HER involves light absorption, generating excited *CNDs that react with TEOA. Time-resolved spectroscopy (fsTAS and nsTAS) revealed the dynamics of these excited states and the electron transfer steps. The study supports a model where CND-bound hydrogen radicals are formed, which then produce hydrogen gas.

Overall, the detailed mechanism and structural insights provided a comprehensive understanding of the photo-oxidation and catalytic properties of carbon dot materials, highlighting their potential for efficient photocatalytic HER applications. The aforementioned research clearly points us in the direction of deeper structural analysis and modification to produce more hydrogen.

V. Conclusion

Photocatalytic hydrogen production utilizing carbon dots (CDs) holds immense promise due to their exceptional optical and electronic properties, including broad-spectrum light absorption, upconverted photoluminescence, and superior electron transfer capabilities. These features, combined with their tunable surface chemistry, high photostability, and low toxicity, position CDs as compelling candidates for sustainable energy solutions. One side, CDs enhance the performance of semiconductor photocatalysts by improving charge separation and migration efficiency, acting as effective photosensitizers. On the other hand, in can behave as standalone material for effective hydrogen production.

Despite these advantages, several challenges must be addressed to fully harness the potential of CDs in photocatalytic hydrogen production. Precise control over CD size and surface properties is crucial for optimizing their photophysical characteristics. Additionally, scalable synthesis methods that preserve the desirable properties of CDs while enabling large-scale production are essential. Enhancing the long-term photostability of CDs and gaining a deeper understanding of their excited state dynamics are also key areas for improvement.

Recent advancements, such as nitrogen doping and the development of novel synthetic procedures, have significantly boosted the photocatalytic rates of CD-based systems. Integrating CDs with other catalytic materials, including molecular and enzymatic catalysts, further broadens their applicability and efficiency.

To propel the field forward, future research should focus on a deeper understanding of the structure-property relationships in CDs, refining synthetic techniques to produce well-defined CD materials, and developing robust and efficient catalytic systems. Exploring the covalent immobilization of catalytic species on CDs and integrating CDs into photoelectrochemical cells are promising strategies for enhancing their practical utility. With continued innovation and research, CDs hold great potential for advancing efficient and sustainable hydrogen production technologies.

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