AN OVERVIEW OF CARBON DOTS SYNTHESIS, PROPERTIES, AND APPLICATIONS TOWARDS ENERGY AND ENVIRONMENTAL REMEDIATION

Abstract

This book chapter captured the importance of existing and emerging carbon dots (CDs) based materials that are inexpensive and vigorously used towards environmental remediation-based applications. This chapter can summarize the photocatalytic degradation of organophosphates by CDs-based composites and hybrid materials synthesis, characterization, and applications towards photocatalytic degradation of organophosphates. Indeed, this chapter would bounce the future insights for the researchers working on the photocatalytic degradation of organophosphates. This survey could scrutinize the fascinating photocatalytic features of CDs that can aid in investigating their interaction with other environmental pollutants. This chapter has benefited materials scientists, chemists, biologists, and clinicians.

Keywords: Carbon dots; synthesis and properties; photocatalytic degradation; atmospheric pollutants; environmental remediation.

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I. INTRODUCTION

Environmental protection is anticipated to benefit considerably from nanotechnology [1]. Multitudinous nanomaterials have been systematically analyzed over the last twenty years for environmental remediations due to their potential characteristics of properties [2]. Nanomaterials with diverse uses in environmental decontamination, pollutant monitoring, and energy invention include transition metal oxides, sulfides, nitrides, phosphide, carbon-based 2D materials, and metal-organic frameworks [3-6]. Researchers and scientists are fascinated by carbon nanostructures [8-9]. Carbon-based nanomaterials, such as fullerene, pristine graphene, graphene oxide (GO), carbon nanotubes (CNT), and reduced graphene oxide (RGO) exhibit exceptional water stability, high specific surface areas, and substantial pore volumes. As a result, they are frequently employed in various environmental applications, including sensing, adsorptive contamination removal, photo-catalytic degradation, energy storage and conversion [10-13]. The carbon nanostructures come in a variety of shapes, from zero-dimensional "Carbon Dots" (CDs), 1D CNT and nanowires, 2D graphene, and other materials [14]. In a study published in 2004, two significant impurities like, "short tubular carbon fragments" and "fluorescent carbon," were identified and examined while single-walled carbon nanotubes (SWCNTs) were being purified. This study is where the first reports of CDs appeared [15]. Further work in 2006 discovered that the surface functionalization of the fluorescent carbon impurities further improved their intriguing size-dependent emissive capabilities [16]. The CDs are spherical-shaped nanoparticles under 10 nm that frequently have surface-functionalized carbon cores with sp^2 and sp^3 hybridized carbon entities [17]. An example of a low-dimensional system like this would exhibit quantum confinement and unique qualities like a more significant band gap, photostability, biocompatibility, better water solubility, and non-toxicity [18]. This book chapter explains the potential utilization of CDs in environmental remediation and pollution control technologies (Figure 1).

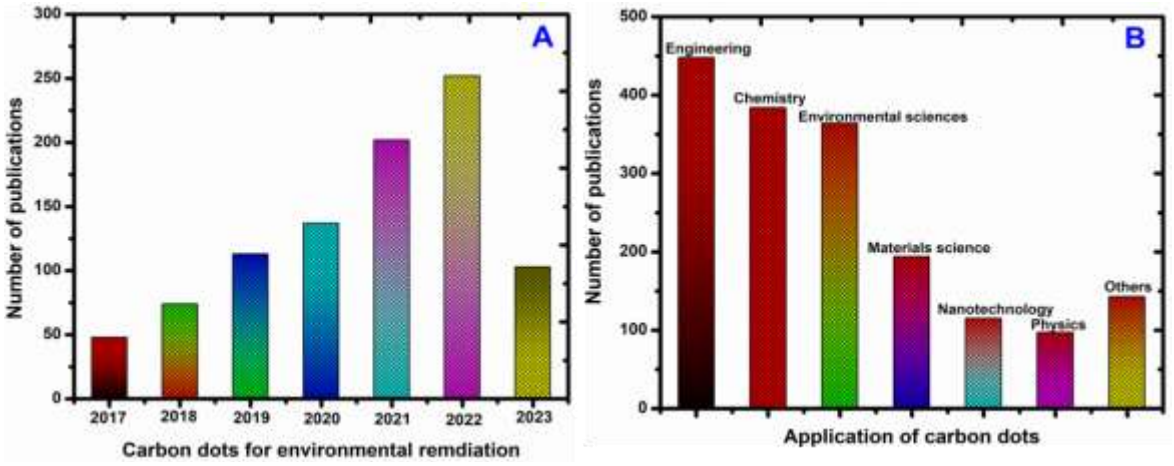

Figure 1: (A) Number of articles reported on "Carbon Dots for Environmental Remediation" from 2017 to 2023, (B) Number of articles reported on different fields for "Carbon Dots for Environmental Remediation" according to a Web of Science database search up to August-2023.

II. CARBON DOTS SYNTHESIS

Since Xu, et al, discovered CDs in 2004 [19], several techniques have been created to produce CDs. Top-down and bottom-up methods have both been used to manufacture carbon dots. CDs are formed when larger precursor molecules are broken down top-down. This strategy uses arc discharge, electrochemical processes, and laser ablation as techniques [20]. Contrarily, bottom-up strategies use simpler molecular precursors that are polymerized into CDs [21].

Some examples of bottom-up techniques are microwave and solvothermal synthesis, high thermal breakdown, and hydrothermal carbonization. Continuous and microfluidics-based techniques, such as low-temperature ceramic microreactors and continuous hydrothermal flow synthesis, have gained popularity recently because of improved heat transfer and reaction mixture homogenous distribution, which significantly cuts down on the amount of time needed, boosts yield, and makes them more suitable for industrial use [22-25].

1. **Top-Down Synthesis:** With the top-down method, more considerable carbon structure fragments like graphene, graphite, carbon nanotubes, and activated carbon are broken down using arc discharge, laser ablation, and electrochemical oxidation processes. Due to the simplicity of morphological control during this process, arc discharge has been widely employed for CD preparation.

   Another popular method for producing CDs is electrochemical oxidation, which has the benefits of being inexpensive, high-purity, high-yield, simple to adjust size, and repeatable [26]. The first report on an electrochemical method for CD production was made in 2007 by Zhou's group [27].

   Ming and colleagues recently developed a one-step electrochemical process that produced high-quality and pure CDs using only water as the electrolyte [28]. The CD synthesis process is cost-effective and ecologically benign thanks to this technique's excellent manufacturing efficiency. Chen et al. prepared CDs using easily accessible and inexpensive sucrose as a carbon source, which allowed them to considerably lower initial materials costs and increase the scale of CD production [29].

   Additionally, Sun et al. invented the process of creating CDs via graphite powder for laser ablation while employing argon as a carrier gas and water vapor as a shield [30]. These synthesis techniques have significantly aided in the production of CDs.

2. **Bottom-up Approach:** As an alternative to the above procedure, CDs can be produced by carbonizing the small molecules using hydrothermal techniques, microwave synthesis, calcination, or annealing [31]. Hydrothermal is a widely used because of the readily available, straightforward synthesis, ecologically friendly procedure, independence from high-cost instruments, and nontoxic route. The carbon sources can come from discarded peels, organic acids, sugars, or juice.

   Natural carbon sources are utilized in creating CDs more frequently than conventional sources due to their affordability, ecological friendliness, and recent growth

in availability [32–34]. Most hydrothermal techniques for CDs often call for a hydrothermal reactor to seal and react with the organic precursor under high pressures, for extended times, and at high temperatures.

Electromagnetic waves from 300 MHz to 300 GHz are defined as microwaves, and they have the power to disrupt the chemical bonds of the raw materials. The microwave approach can deliver uniform heating and efficiently shorten reaction times, resulting in uniform CD particle size distribution [35-36]. Recent research has shown that short external heat pulses can help to chemically oxidize and carbonize organic materials, converting them into CDs [37].

Because they utilize low-cost precursors, facile operation, rapid reaction times, and solvent-free processes, the hydrothermal and microwave synthesis methods are most frequently utilized in CD environmental applications. Usually, CDs synthesis can be considered via “top-down” and “bottom-up” approaches (Figure 2).

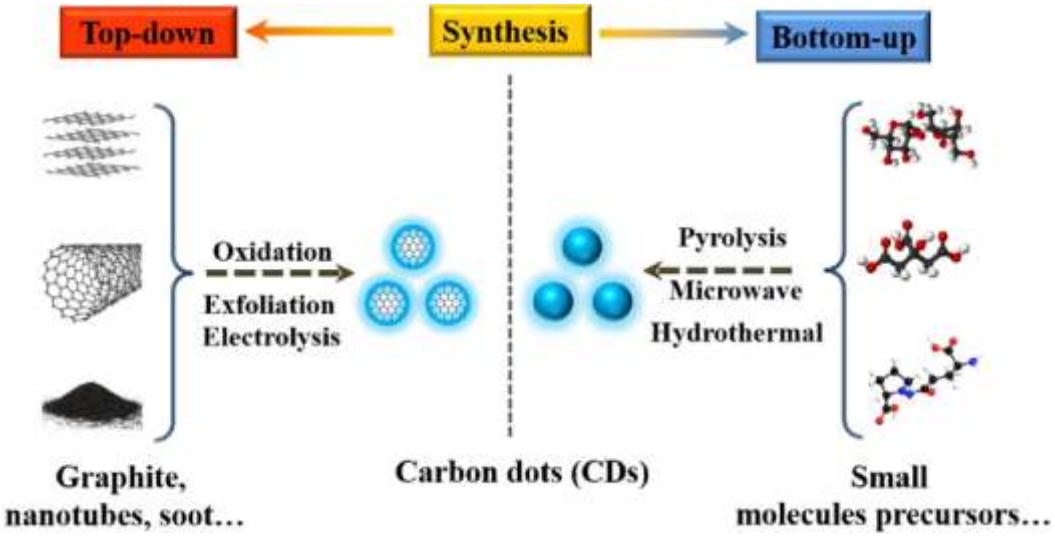

Figure 2: Carbon Dots Synthesis Methods (adapted from Ref. 7)

III. CARBON DOT PROPERTIES

CDs possess a broad range of physical and chemical characteristics attributed to the diversity of precursors and synthetic approaches. Similar characteristics shared by several CDs include their solubility in water, environmental friendliness, lack of toxicity, tunable fluorescence, and excellent stability [38-39]. This section discusses CDs' physical, chemical, and optical properties in greater detail.

1. **Physicochemical Properties:** An intriguing class of carbon nanoparticles through a typical size of 10 nm is known as CDs [38,40]. CDs demonstrate the quantum confinement effect due to the oxygenated functional groups on their surfaces changing surface constructions and the size of the particles [41-42].

Additionally, CDs are better at moving charges (excellent at trapping and moving electrons), which can effectively prevent charge recombination created by light [43-44]. The increased charge transport is partly due to the size-dependent visual properties of CDs, where the distance among small charge carriers and typically fewer than the diffusion carrier length [45].

Since photocatalysis occurs at edges more frequently than at basal planes, CDs' edge-rich properties benefit this reaction. Therefore, destroying organic contaminants using photocatalysis is a fantastic alternative for CDs. Additionally, CDs' particular chemical inertness and exceptional water stability make them suitable for application in nanotechnology and sensor production.

2. **Optical Properties:** Overall, CDs demonstrate solid optical absorption in the UV region, with a tail that reaches into the visible region and absorption that concentrates between 260 and 320 nm [46]. The chemical groups found on CDs may influence the UV-visible regions' absorption. The observed variations in the absorption spectra data imply that diverse hybrid derivatives have different compositions or structures, at least in part.

   The fluorescence emission properties of excitation-dependent are present in the bulk of previously characterized CDs, and CDs get redder as the excitation wavelength increases [47]. On the other hand, some research has covered the excitation-independent CDs emission spectrum. As an illustration, Liu et al. reported creating fresh CDs using potassium persulfate and acrylamide as a precursor.

   Intriguingly, the independence of CDs from excitation was demonstrated by the fact that the fluorescence emission peak at 434 nm barely changed when the excitation wavelength was changed within the 280-390 nm range. CDs' quantum size impact was thought to be related to this phenomenon [48].

   Understanding the mechanics underlying the fluorescence of CDs is essential for controlling their fluorescence and other physicochemical properties and expanding their range of applications. The fluorescence mechanism has thus been the focus of in-depth study.

3. **Upconversion Photoluminescence:** CDs' characteristic upconversion photoluminescence (UCPL) has been extensively applied for bioimaging and photocatalysis. The UCPL process, which concurrently absorbs several photons and generates fluorescence through a smaller wavelength over the excitation basis, produces the anti-stokes emission [49-50].

   Cao et al. found the significant two-photon fluorescence from near-infrared stimulation by laser ablation [51]. It recommended NIR photoluminescent built of dopamine and o-phenylenediamine that displayed two-photon emission utilizing an 800 nm femtosecond pulse laser [52].

   Since they can be combined with widespread band semiconductors to increase the absorption range of CDs and to be used as spectral converters in photocatalysis.

4. **Photoinduced Charge Migration:** The distribution of graphitized-conjugated areas in CDs guarantees good electrical conductivity. Consequently, CDs have emerged as a growing star emphasizing charge transfer capability, such as in photocatalysis or optoelectronics [53-54].

   Steady-state of time-resolved spectroscopy showed that this fluorescence quenching was caused by charge transportation in the excited state. Furthermore, CDs act as supramolecular frameworks by their building blocks with customized electronic properties to further investigate charge movement performance as electron-donor or acceptor [55-56].

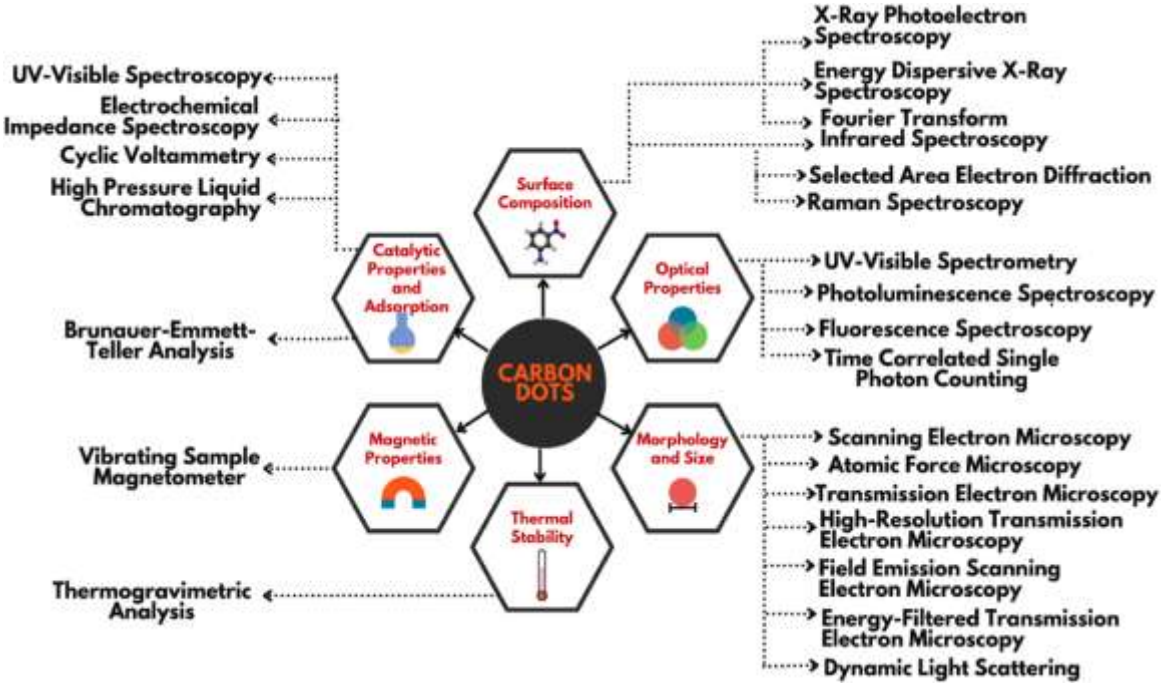

Figure 3: A Flow Chart on Numerous Properties of Carbon Dots (adapted from Ref. 8)

IV. CDS FOR ENVIRONMENTAL REMEDIATION

Although membrane separation and adsorption can eliminate inorganic or organic contaminants from water, they cannot entirely decompose the contaminants; this could necessitate additional disposal. Environmental contaminants may completely degrade or become mineralized with photocatalytic treatment.

The degradation by photocatalysis has emerged in appealing method for treating wastewater treatment [57-58]. Due to the following characteristics, CDs have a great deal of potential for use in the photocatalytic destruction of environmental pollutants

- CDs outperform conventional photocatalytic semiconductor materials (such as TiO_2, ZnO, and CdS) in terms of chemical stability, water solubility, affordability, and environmental friendliness;

- CDs have outstanding and adjustable optoelectronic and photoluminescent capabilities. In particular, wide bandgap semiconductors' sunlight absorption into the visible and near-infrared regions can be significantly increased by CDs' up-conversion photoluminescence;
- CDs can effectively distinguish electrons from holes and outstanding electron donors and acceptors. As a result, CDs can be utilized in the design of electron mediator, spectrum converter, solitary photocatalyst, photosensitizers, and catalytic centers [31, 38].

Table 1 provides an overview of current developments in bare CDs and CDs-based hybrid photocatalysts for the degradation of environmental pollutants.

Table 1: Recapitulation CDs-based Photocatalysts for Environmental Pollutant Degradation

Photocatalysts	Synthesis	Degraded pollutants	Ref.
CDs	Reflux	Methylene blue	[59]
N-CDs	Hydrothermal	2, 4-dichlorophenol	[60]
N-CDs	Ultrasonic	Rhodamine B	[61]
Au/CDs	Electro-chemical	Cyclohexane	[62]
Cu–N-CDs	Pyrolysis	1, 4-dihydro-2, 6-dimethylpyridine-3, 5-dicarboxylate	[63]
TiO_2/CDs	Calcination	Ciprofloxacin	[64]
TiO_2/CDs	Hydrothermal	Paraoxon pesticide	[65]
ZnO/CDs	Electrochemical Hydrothermal	Gas-phase benzene	[66]
Fe_2O_3/CDs	Electrochemical and Hydrothermal	Benzene and methanol	[67]
g-C_3N_4/S, N: CDs	Hydrothermal	Rhodamine B	[68]

1. **Photodegradation of Dyes:** Large-scale dye discharges into the aquatic environment, ubiquitous components in industrial effluent, may increase oxygen ingestion during natural humiliation and result in the widespread anoxic demise of organisms.

There has been much research done so far on the degradation of usual organic dyes like Methylene Blue (MB), Rhodamine B (RhB), and Methyl Orange (MO) using various CDs situated photocatalysts. Additionally, CDs can serve as an electron transfer conduit in a photocatalytic system between two photosensitive parts, allowing for an improved separation of photo-excited holes and electrons.

The plasmonic photocatalyst comprises CPDs/Ag/Ag_2O to improve photostability and electron-hole separation [69]. This ternary photocatalyst displays exceptional degrading efficiency across the spectrum, following the larger electron transfer capacity and upconversion characteristic of CPDs (**Figure 4A**).

Photodegradation of dyes can be evaluated by Feng et al. through CdS/CPDs/g-C_3N_4 (CSCCN) composites with Z-scheme transfer and vis-NIR light response (**Figure 4B**) [70].

Using the electron chemical impedance spectroscopy (EIS), photoluminescence (PL) spectra, and the transient photocurrent responses, CdS/g-C_3N_4 and CPDs/g-C_3N_4 indicating that carriers had longer lifetimes.

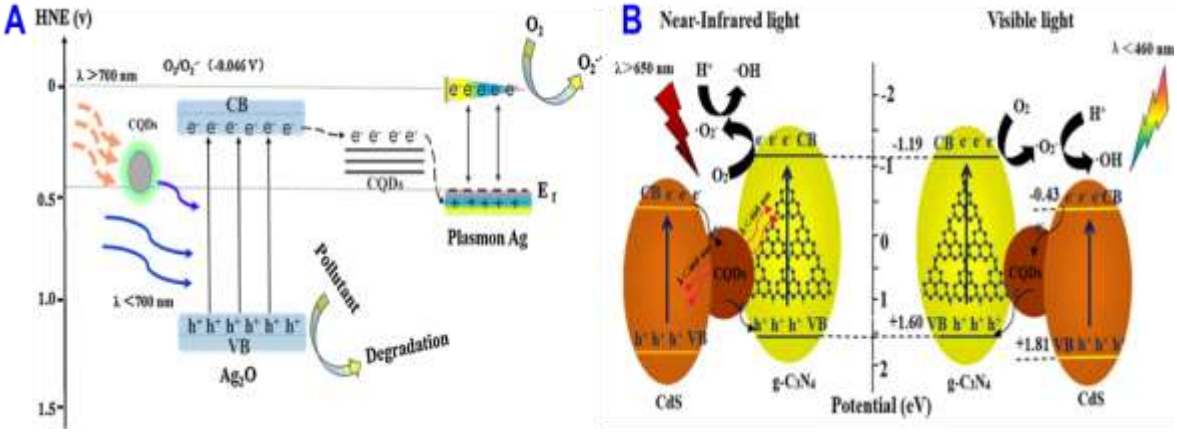

Figure 4: (A) A projected reaction mechanism for pollutant degradation on the nanocomposites of CQDs/Ag/Ag_2O and (B) Energy band diagram of CdS/CQDs/g-C_3N_4 through Z-scheme electron transfer (Adapted from Ref. 69 and 70)

2. **Photodegradation of Plastics:** Along with pollutants in the water, a significant issue in the realm of eco-sustainability is the conversion or degradation of hard plastic trash. The annual production of plastic worldwide has remained constant in recent years at thousands of countless tons [71].

Most plastics, however, cannot break down naturally, and their combustion or disposal in landfills may release large amounts of plastic particles and flue gas into the atmosphere, harming nearby wildlife [72]. Han et al. realized photocatalytic recycling of polyethylene terephthalate (PET) and polylactic acid (PLA) along with simultaneous H_2 generation [73].

Graphitic carbon nitride (GCN) powders are added to CPD solutions before hydrothermal processing to create this composite catalyst. During the above-mentioned process, photo-excited holes were continually disbursed, and the residual electrons powered the conversion of H_2O to H_2.

It has been demonstrated that adding CPDs to GCN can significantly increase the charge carrier lifetime and assist carrier partition by reducing fluorescence lifetime and PL intensity. A correct CPD doping ratio in GCN enables a decreased resistance and more extraordinary charge transfer capability, as shown by *i-t* plots and EIS analysis.

This research offers a revolutionary method for recycling plastic and photo-catalytically converting optical energy into H_2 fuels.

3. **Photocatalytic CO_2 Reduction:** The world's population growth and rapid industrial development have led to an enormous rise in energy demand. As the primary direct energy source at this time, fossil fuels as a significant growth in the atmospheric concentration of greenhouse gases, of which CO_2 is the most well-known.

The global ecological system is seriously threatened due to the greenhouse effect, global warming, and rising sea levels by the rapidly rising atmospheric CO_2 level [74]. To achieve CO_2 capture, it is required to investigate practical, effective, and environmentally beneficial solutions. An appealing and likely possibility is the photocatalytic conversion of CO_2 into valuable hydrocarbon fuels [75].

Theoretically, compared to the water reduction reaction, the multielectron and multi-proton reduction of CO_2 is often more advantageous because of its comparatively low thermodynamic barriers [76]. The crucial problem today is to attain highly peculiar target products due to the identical thermodynamical potentials for the reduction products CO_2 and H_2O [77].

Currently, CO_2 has been reported to be converted by CDs-based photocatalysts into CO, CH_3OH, CH_4, and -COOH acids. The first publication on photocatalytic CO_2 conversion using CDs-based catalysts mainly concentrated on processes that produced carboxylic acid. For photocatalytic CO_2 conversion, Sun, et al, reported the PEG functionalized CDs on the metal coating on the surface [78].

K. Wang and workers reported the CDs conscripted Cu/TiO_2 (Cu/TiO_2-C), a photo-thermal linked device was created [79]. Under UV light illumination at higher temperatures (>150 °C), CH_4 synthesis shows dramatic promotion but mediocre photo-promotion at ambient temperatures.

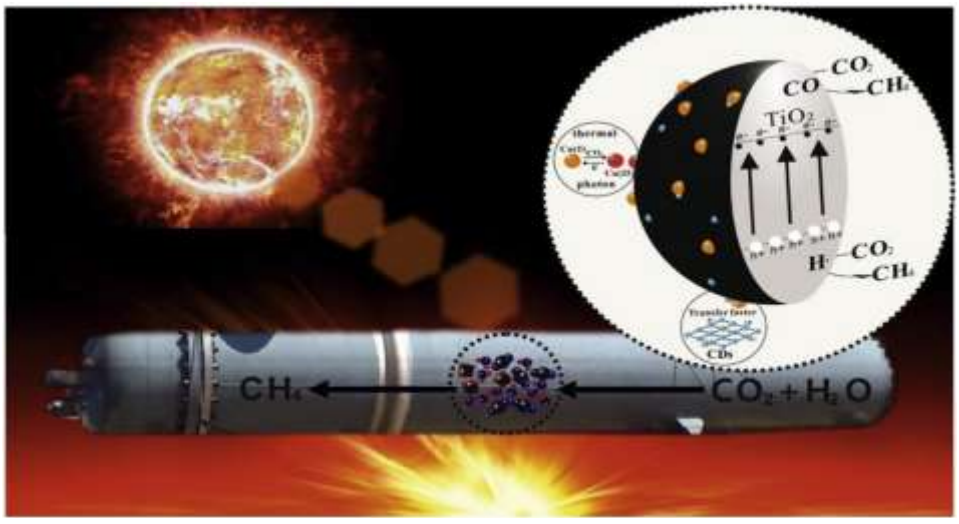

Figure 5: CO_2 methanation by H_2O over CDs drafted Cu/TiO_2 catalyst
(Adapted from ref. 79)

On the Cu/TiO_2 sample lacking CDs, the synergy effect of UV light and temperature does not exist. Here, Cu (II) is primarily abridged to Cu (0), but a weak

Cu(I)/Cu(II) cycle by H_2 pretreatment was visible after UV exposure. This study demonstrates that adding UV light makes it possible to construct the non-spontaneous processes to spontaneous reaction (**Figure 5**).

4. **Photocatalytic N_2 Fixation:** Despite making up to 78% of the atmosphere, nitrogen has a very high N-N bond energy, making it difficult to convert and utilize properly [80]. By combining atmospheric nitrogen with hydrogen at high pressure and temperature, while iron is present, Haber developed a way to make ammonia, and the Haber-Bosch process is still employed in the commercial strategy for nitrogen fixation today [81].

   Regrettably, the extreme situation will utilize many fossil fuels, and emissions of thousand tons of greenhouse annually. Moderate artificial nitrogen fixation techniques, including photocatalysis, are desperately needed for the environment's sake and long-term energy sustainability. Metallic semiconductors dominate the list of catalysts used in photocatalytic nitrogen fixation.

   The nitrogen atom's antibonding orbitals and cation sites of metals are likely to interact due to nitrogen atoms' positive electron affinities, N-N bonds activating and speeding up nitrogen fixation [82].

   Through a microwave-assisted technique, Khalilabad et al. added CPDs to g-C_3N_4 nanosheets (CN-NS) that were embellished with CdS NPs [83]. CPDs' upconversion photoluminescence assisted in converting long-wavelength light into short-wavelength light that CN-NS could directly absorb.

V. SUMMARY

The bottom-up, top-down, continuous preparation and characterization analytical methods utilized to ascertain the chemical, physical, and optical characteristics of CDs were all thoroughly described in this book chapter.

CDs have outstanding optical and photoelectric capabilities because of their distinct nanoscale structure and internal integration of graphitized sp^2 domains. Diverse fabrication techniques also provided several implements for CDs synthesis and subsequent modification.

The characteristics of UCPL and the capacity for photoinduced charge movement make CDs an effective wide-response photocatalyst. Additionally, photoinduced processes such as pollutant degradation, CO_2 conversion, and N_2 fixation on CDs-based hybrids or composites were thoroughly examined by concentrating on their activity, selectivity, and stability.

For instance, structural natures can be changed to increase the stability of CDs, such as by raising the carbon cores of the degree of graphitization. A high molecular state concentration in CDs makes it susceptible to photobleaching under photoexcitation, deactivating the CDs-based catalyst.

Additionally, greater graphitization gives better charge movement capabilities for CDs. In contrast, several functional groups incorporated on the surface of CDs can interact

with specific substrates, lowering the energy barrier and making it easier for CDs to operate as a photocatalyst in catalytic reactions.

Notably, these functional groups are advantageous for CDs when combined with other semiconductors as cocatalysts. Even if the development path is fraught with obstacles, it is hoped that CDs will open up more intriguing possibilities for environmental applications. As it develops and is integrated with other nanotechnology, future environmental science and engineering will be increasingly impacted by nanotechnology.

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