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RESEARCH ARTICLE

A Review on Synthesis and Physicochemical Properties-Photocatalytic Activity Relationships of Carbon Quantum Dots Graphitic Carbon Nitride in Reduction of Carbon Dioxide

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Abstract Carbon dioxide (CO_2) is a major greenhouse gas present in over half of the Earth's atmosphere. Elevated CO_2 emissions in the atmosphere have become a global warming issue due to the excessive use of fossil fuels by human activities. Converting CO_2 into a useful compound is crucial since CO_2 exists in the environment and must be reduced. The use of semiconductor materials in photocatalysis is the best solution to degrade and potentially convert CO_2 into a useful energy source. Recently, research on graphitic carbon nitride (g-C_3N_4) has developed interest due to its phenomenal properties, such as effective charge separation and charge carrier lifetime, electron-hole recombination, and high surface area. CQDs/g-C_3N_4 has recently emerged as a novel technology due to its excellent physical and chemical properties, especially in the reduction of CO_2. Thus, this review outlines the recent modification of graphitic carbon nitride (g-C_3N_4) by carbon quantum dots (CQDs), which include the synthesis of CQDs/g-C_3N_4 for CO_2 reduction. Lastly, the review discusses physicochemical properties-photocatalytic activity relationship of CQDs/g-C_3N_4 in the photocatalytic reduction of CO_2. This review provides a wide range of perspectives and a guideline for designing the more effective CQDs/ g-C_3N_4 for photocatalytic reduction of CO_2.

Keywords: Carbon quantum dots, graphitic carbon nitride, physicochemical properties, photocatalytic activity, relationship, reduction carbon dioxide.

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Introduction

Carbon dioxide (CO_2) is a major greenhouse gas that causes environmental pollution, global warming, and climate change, and has increased due to global industrialization [1]. Human activities, such as the extensive use of fossil fuels (coal, gas, oil, wood, and other organic materials) and other greenhouse

gases, also contribute to the increase in CO_2 levels. CO_2 gas, which is present in more than half of the Earth's atmosphere causes food shortages, forest fires, declining animal populations, and environmental damage [2–7]. Even more devastating are the natural disasters brought on by global warming, including the rise in sea level, heat waves, storms and floods, and other catastrophes [3, 4, 8].

CO_2 emissions in Malaysia have increased significantly since 1978 [9]. In December 2021, eight states in Malaysia were affected by three (3) days of nonstop and intense rainfall that was unprecedented in scale. The Malaysian economy lost an estimated Ringgit Malaysia Fifteen Billion, nearly 70,000 people were affected, and most tragically, 54 people died and 2 went missing. According to experts, climate change caused by increasing carbon emissions is one of the main factors behind the flood. It is therefore crucial that those responsible for solving this growing global problem take the necessary remedial action, such as passing laws to combat climate change. In Malaysia, the Environmental Quality Act 1974 ("EQA 1974") is the main law that regulates the protection and conservation of the environment. Malaysia has also enacted several regulations that govern carbon emissions in Malaysia, most notably the Environmental Quality (Clean Air) Regulations 2014 ("Clean Air Regulations"), which direct that an owner or occupier of land involved in an activity or industry of power stations, waste fuel plants, asphalt mixing plants and others must incorporate strategies to reduce the emission of air pollutants into the atmosphere. In addition, Malaysia has enacted regulations to limit the emission of pollutants from various types of vehicles, including motorbikes and vehicles with petrol and diesel engines. The said regulations provide that the engine of such vehicles must not emit more pollutants than the limit specified in the regulations. According to the regulations, the engines of such vehicles must not emit more pollutants than the permissible limit [10].

An attractive solution for the effective use of CO_2 is to convert it into high-value products. Moreover, it is difficult to convert the stable CO_2 molecule into other useful compounds at moderate conditions. Recent advances in photocatalysis technology have made the conversion of CO_2 to be a promising application by reducing CO_2 to useful synthetic fuels by exposing it to solar light. Formaldehyde (HCHO), ethanol (C_2H_5OH), and methanol (CH_3OH) are some of the important compounds that can be produced from the chemical conversion of CO_2 [11–13]. Several photocatalyst materials that have been currently investigated for CO_2 reduction are TiO_2, CdS, g-C_3N_4, ZnO, Zn_2GeO_4, $ZnFe_2O_4$, Bi_2WO_6, $BiVO_4$, and BiOCl [6, 14].

Graphitic carbon nitride (g-C_3N_4 or CN) is a metal-free semiconductor material that has attracted considerable interest and is widely used for the degradation of organic compounds. Since the first report by Wang *et al*. in 2009 [15] on the use of g-C_3N_4 as a visible light photocatalyst for water splitting, the photocatalytic activities of g-C_3N_4 have been investigated in more detail. However, g-C_3N_4 has disadvantages such as a high recombination rate of charge carriers, a small specific surface area, low visible-light absorption, and poor quantum efficiency. Therefore, the photocatalytic efficiency of g-C_3N_4 can be improved by nonmetal doping, a passivation layer and metal deposition, morphological control, formation of junctions, and modification with carbon nanodots such as carbon quantum dots (CQDs) [15].

CQDs are a novel class of carbon nanomaterials with a diameter of less than 10 nm. CQDs exhibit excellent features such as minimal toxicity and adequate biocompatibility, which may enable their use in bioimaging, biosensors, and drug administration. Additionally, the exceptional electrical characteristics of CQDs offer applications in optoelectronics, catalysis, and sensing. When paired with the g-C_3N_4, its role as electron acceptors or donors in redox processes makes it suited for photocatalytic applications [16–18].

CQDs/g-C_3N_4 is a metal-free photocatalyst that has drawn attention since Kang *et al.* released their work on stable visible-light water splitting using carbon nanodots and carbon nitride (C_3N_4). The study discovered that nanocomposites of CQDs and g-C_3N_4 are durable, cheap, and simple to fabricate. However, the inadequacies of g-C_3N_4 have prompted many researchers to manufacture it with CQDs. It has been widely employed in H_2 evolution, organic pollutant degradation, CO_2 reduction, and disinfection due to its superior quality photocatalytic performance. As a result, CQDs/g-C_3N_4 are the optimal partners. Additionally, by combining g-C_3N_4 with CQDs, it is possible to inhibit charge carrier recombination and stabilise the separation of electron-hole (e^--h^+) pairs and improving photocatalytic activity [3,15,19].

Thus, this review outlines the recent modification of g-C_3N_4 by CQDs, which include the synthesis of CQDs/g-C_3N_4 composites especially for photocatalytic reduction of CO_2. Furthermore, this review discusses the relationship between the physicochemical properties and photocatalytic activity of CQDs/g-C_3N_4 in the photocatalytic reduction of CO_2.

Fundamental Concepts of Semiconductor Photocatalysis

Photocatalysis is a green technology primarily created after the first paper on TiO_2 by Fujishima and Honda that described the production of H_2 water under sunlight irradiation. This technique has been recognized as an excellent application for the generation of energy and environmental remediation in recent years [20, 21]. The process of photocatalysis mimics photosynthesis and enables efficient energy conversion [22, 23]. In the presence of a semiconductor photocatalyst, photocatalysis is accomplished by absorbing and utilizing solar energy of ultraviolet, visible light, or visible light [23–25].

Various photocatalysts, such as TiO_2, CdS, g-C_3N_4, SnO_2, ZnO, etc., have been used for different applications, including energy production, organic synthesis, and environmental remediation. The ideal photocatalyst qualities should be chemical and biologically stable, active, inexpensive, non-poisonous, moderate operation, high efficiency, environmentally safe, and activated by visible and near-ultraviolet light [20, 21, 24]. Besides, the parameters for high photocatalytic activity include a narrow bandgap to capture an adequate amount of sunlight, an effective charge separation, and good adsorption sites and reaction centers on the catalyst surface [26–28].

General Mechanism of Photocatalysis

In the process of photocatalysis, electrons in the valence band (VB) are excited into the conduction band (CB), leaving positive holes in the VB, when light with photon energy absorbed by semiconductor catalyst (SC) have equal to or greater than the band gap energy (BG). The photoinduced free charge carriers of electron (e^-) and hole (h^+) must first diffuse into the active sites on the photocatalysts' surfaces before they can initiate redox reactions because these photocatalytic reactions occur at the surface of the photocatalysts [29]. Eqs. (1) and (2) describe the reactions that activate the semiconductors [30].

$$\mathrm{SC} + \mathrm{h}\nu \left(\geq \mathrm{E_{bg}}\right) \rightarrow \mathrm{h^+ e^-} \tag{1}$$

$$h^+ e^- \rightarrow {h^+}_{\mathrm{VB}} + {e^-}_{\mathrm{CB}} \tag{2}$$

Furthermore, these photoinduced charge carriers might go in many directions. The photogenerated electrons and holes may go and trap into the shallow and deep trapping sites. The electrons will recombine and produce thermal energy at the surface or bulk of the photocatalyst if they are unable to locate any trapped sites or if the semiconductor's energy band gap is very narrow. This charge carrier recombination is an undesirable process that takes place during the transfer of the absorbed energy as heat or photon emission and hinders the effectiveness of a photocatalytic process. The introduction of dopants is one method of reducing charge carrier recombination. The general mechanism of photocatalyst reactions is shown in Figure 1.

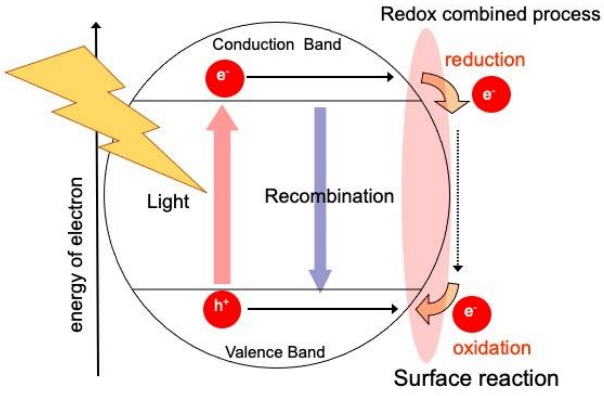

Figure 1. General mechanism of photocatalyst reactions

Mechanism of Photocatalytic Reduction of CO_2

CO_2 is a stable molecule with a linear structure and two double bonds between carbon and oxygen atoms that cannot be converted into value-added compounds without a catalyst or input energy. Aside from this, CO_2 becomes an inactive molecule due to the huge energy difference between LUMO (lowest unoccupied molecular orbital) and HOMO (highest unoccupied molecular orbital) and the large electron affinity of CO_2 [31]. Photocatalysis has been demonstrated to be an easy way of activating and converting CO_2 into valuable compounds. In nature, green plants convert CO_2 and water (H_2O) into carbohydrates and oxygen at room temperature during photosynthesis. Motivated by this natural process, several studies have been conducted to develop artificial or synthetic photocatalysts for the reduction of CO_2.

The production of fuels such as methane (CH_4), methanol (CH_3OH), and other energy-generating fuels is one way to reduce CO_2 using synthetic photocatalysts. It is not only to reduce CO_2 concentration but also to meet future energy demands. A reducing agent for providing hydrogen is required to get photocatalytic products. The primary reductants utilized to successfully reduce CO_2 are H_2O, H_2, CH_4, and CH_3OH [31]. According to the literature, photocatalytic CO_2 reduction follows several reaction pathways depending on the reducing agent.

The conversion of CO_2 to methanol has been extensively studied and has been shown to be effective, as the methanol is obtained immediately after the process. Electrons and holes are generated by the presence of the photocatalyst, g-C_3N_4, and irradiation with UV-Vis light as the light source. The electron is then stimulated from the valence band to the covalent band, where it reacts with the carbon dioxide molecule to produce methanol (CH_3OH). The oxygen gas produced by the holes that remain in the valence band leads to the oxidation of water molecules as a side effect of this reaction [30]. When water molecules are oxidized, four electrons, four protons, and dioxygen are produced.

In addition, CO_2 can be reduced to various products such as carbon monoxide (CO), methane (CH_4), formate, or other hydrocarbons at moderate potentials between from -0.2 V to -0.6 V versus the Normal Hydrogen Electrode (NHE). The reactions are listed here, together with their thermodynamic redox potentials [32–34].

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O,$$
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH,$$
$$CO_2 + 4H^+ + 4e^- \rightarrow HCOH + H_2O,$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O,$$
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\,H_2O,$$
$$2\,CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2\,H_2O,$$
$$2\,CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3\,H_2O.$$

The comparison of CO_2 photocatalytic reduction pathways between g-C_3N_4 and CQDs/g-C_3N_4 in the presence of H_2O has been shown in Figure 2. CO and CH_4 were efficiently produced under visible light due to modified photoreduction pathways and enhanced reaction kinetics.

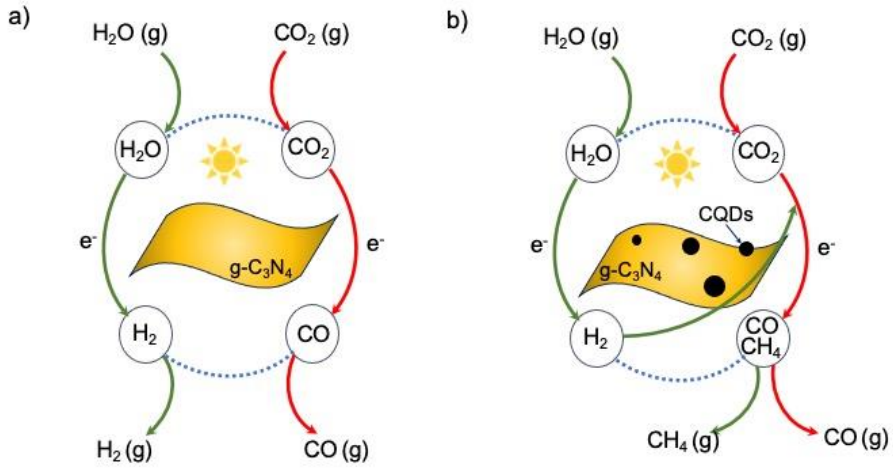

Figure 2. Comparison of CO_2 photocatalytic reduction pathways between a) g-C_3N_4, and b) CQDs/g-C_3N_4 in the presence of H_2O

The photoreduction of CO_2 is a five-step process that involves light absorption, charge separation, CO_2 adsorption, CO_2 reduction, and product desorption. First, a photocatalyst converts light to helpful energy, promoting CO_2 reduction. The second phase involves the excitation of electrons from the valence band to the conduction band, which occurs when photocatalysts absorb light with an energy larger than or equal to their band gap, creating gaps in the VB. Following, while the holes are oxidized to release water or sacrificial agents, the generated electrons will migrate to the photocatalyst's active sites and initiate a surface reduction reaction with the absorption of CO_2 to form extra useable material. Finally, the desorption process happens [35].

Until recently, the photocatalytic reduction of CO_2 with various semiconductors and in the presence of various reductants has been studied, such as WO_3, TiO_2, ZnO, CdS, GaP, and SiC. In this review, we discuss graphitic carbon nitride as a photocatalyst for the reduction of CO_2.

Graphitic Carbon Nitride as a Promising Photocatalyst

The graphitic carbon nitride (g-C_3N_4) polymer is 2D structure composed of carbon, nitrogen, and a trace of hydrogen impurity. It has a tri-s-triazine structure, as illustrated in Figure 3. The surface of g-CNs, like the other carbon-based materials, exhibits an electron-rich properties and multiple changed surface modified functionalities [36].

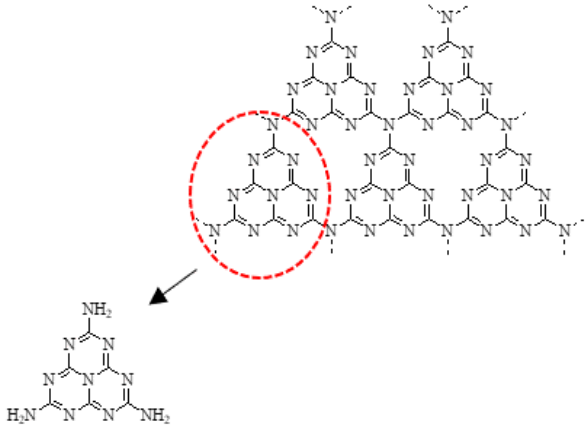

Figure 3. g-C_3N_4 structure: tri-s-triazine

In 1834, Liebig and Berzelius invented the term g-C_3N_4 as a melon after synthesising a polymer containing a carbon nitride (C_3N_4) derivative. Numerous allotropes of C_3N_4 with different properties have been identified, including alpha-C_3N_4, cubic-C_3N_4, beta-C_3N_4, pseudocubic C_3N_4, and g-C_3N_4. The most stable was determined to be g-C_3N_4 [3,37]. In 2006, the g-C_3N_4 heterogeneous photocatalyst was introduced. The g-C_3N_4 differs from other allotropes by a bandgap of 2.7 eV and a visible light emission range of 400–475 nm. Due to the g-C_3N_4 exhibiting a steady fluorescence and a broad excitation wavelength can be employed as a biomarker in living organisms [15, 19, 36–43].

g-C_3N_4 is gaining considerable attention due to its abundance, ease of synthesis, eco-friendly, low cost, readily available precursors, flexible electronic structure, and intriguing optical properties. Additionally, this metal-free semiconductor photocatalyst exhibits excellent chemical and thermal stability and an efficient conjugate structure employed as a stable catalytic scaffold [4, 44, 45]. Additionally, the broad porous g-C_3N_4 surface benefits photocatalytic CO_2 reduction by increasing the number of functional sites and the degree of CO_2 adsorption [5].

The g-C_3N_4 is a yellow-coloured doping medium that supports in the reduction of nonmetal polymeric layered materials. It has a p-type bandgap energy. It is a stacked 2D layered structure with more active sites for targeted Van der Waals forces, where nitrogen heteroatom compounds in a single layer have been replaced in graphite nanosheets and creating sp2 hybridisation between carbon and nitrogen atoms. Numerous unique g-C_3N_4 forms have been synthesised, including one-dimensional nanorods, two-dimensional nanosheets, and three-dimensional hierarchical structures [42].

In 2009, the first study on the use of g-C_3N_4 in photocatalytic wastewater splitting under visible light illumination was published. g-C_3N_4 has recently attracted considerable interest in photooxidation

reactions, dye degradation, alcohol oxidation, hydrogen generation, O_2, H_2 generating potentials, and CO_2 reduction processes. As a result, it draws the scientific community's attention to the need for additional research on g-C_3N_4 [4, 45].

However, catalytic processes of g-C_3N_4 have several disadvantages, including low quantum efficiency, a narrow surface area, and accelerated recombination of generated e^-–h^+. Additionally, g-C_3N_4 absorbs very little visible light and has a low electrical conductivity due to its greater bandgap. Nevertheless, previous research has demonstrated that the structure of g-C_3N_4 may be chemically changed and doped with other semiconductors to inhibit e^-–h^+ recombination and increase the photocatalytic effectiveness of g-C_3N_4 composites [14, 39, 41, 44].

Carbon Quantum Dots/Graphitic Carbon Nitride Composites

According to the Web of Science, the statistics for the keywords "g-C_3N_4", "graphitic carbon nitride," "quantum dots," "CQDs," and "GQDs" in terms of the number of papers, articles, journals, and books relevant to CQDs/g-C_3N_4 photocatalysts increased annually from 2010 to 2019 [15]. However, there is no comprehensive list of CQD/g-C_3N_4 based photocatalysts especially for the photoreduction of CO_2.

Carbon Quantum Dots (CQDs)

Carbon dots (CDs) can be categorised into three types: graphene quantum dots (GQDs), polymer dots (PDs), and carbon nanodots (CNs) or carbon quantum dots (CQDs). GQDs contain graphene layers and functional groups on their edges, while PDs with polymer crosslinking or grafting. CNs or CQDs are CDs with amorphous or nanocrystalline centres [46, 47].

CQDs have drawn more interest than traditional semiconductor quantum dots (QDs) [15]. QDs are 3D semiconductor nanocrystalline with a size of less than 10nm [34]**.** They exhibit high absorption of light and a wide surface area due to the practical quantum size effect of QDs, enabling them to be employed as active sites in photocatalysis. QDs have been used in various domains, including material science, luminous devices, magnetism, catalysis, and biomedicine [48]**.**

CQDs were reported for the first time in 2004 during the purification of carbon nanotubes [49]. On the other hand, CQDs have generated considerable interest in recent years due to their unique physical, chemical, optical, and surface features. As a carbon-based material, CQDs are abundant, inexpensive, possess unique electron transfer characteristics, and have a wide surface area, which enables CQDs to perform exceptionally well in electrochemical reactions [50–54]. Additionally, CQDs have extremely adjustable electrical and photoluminescence capabilities due to the quantum confinement effect, with a high degree of surface functionalization adjustment efficiency. [44, 55]. The photon emission CQDs are water-soluble, non-reactive chemically, and have low toxicity. CQDs can potentially operate as electron acceptors or donors [11, 15]. CQDs are nanoparticles with a size below 10 nm [42, 49]

Moreover, oxygenated functional groups such as hydroxyl, carbonyl (C=O), epoxides, and amino are present on the surface of CQDs [18, 42, 49]. The oxygenated functional group enables CQDs to interact with inorganic, organic, polymeric, and biological materials, resulting in enhanced adsorption, surface passivation, and accessible surface modification [42,49]. These large surface functional groups provide additional flexibility and effective locations for formulating multicomponent and high-level performance actions on complicated materials [56].

CQDs are commonly used in fluorescence or chemiluminescence (CL), and detection applications. The CL technique does not require stimulation, and the luminescence is related to the electromagnetic radiation created during the chemical reaction process. CQDs may also be employed as oxidants, emitting species, energy acceptors in chemical processes, catalysis, or other applications [44, 46]. Different organic carbon sources are currently being used to make highly luminous CQDs for detection due to their distinct features [57].

Thus, doping heteroatoms such as nitrogen, sulfur, phosphorus, and boron with CQDs can improve electrocatalytic characteristics by increasing electron transport via inner contacts. Additionally, the contacts' strong crossing point may allow electron transfer within the intermolecular, which is critical for performance improvement. In recent years, CQDs have included fuel cells, rechargeable metal-air batteries, and water splitting with increased electrocatalytic efficiency. However, most CQD research focuses on improving their photocatalytic and biosensing characteristics [55]. In addition, their size impact and fluorescence qualities contribute to their photocatalytic efficiency. As a result, the best photocatalytic properties can be achieved [44].

CQDs can be synthesized using the top-down and bottom-up approaches. The top-down approach is used for larger carbon particles (carbon nanotubes, carbon fibers, graphite rods, carbon ash, and activated carbon), broken down into smaller bits via photoablation, electrochemical oxidation, and ultrasonic synthesis. Bottom-up synthesis of CQDs from molecular precursors such as glycerol, citric acid, amino acids, and natural materials using microwave, thermolysis, and chemical heat (coffee grounds, soy milk, soybeans, grass, eggs, pomelo peel, honey) [16, 46, 57].

The top-down and bottom-up synthesis requires the selection of the appropriate precursors, solvent, optimal temperature, and response time. Therefore, it is essential to affect the chemical composition, mass, and quantum yield of the CQDs. However, the lengthy and challenging procedure establishes routes during the nucleation and growth stages. Thus, developing a controlled CQDs preparation with the appropriate chemical arrangement, high-level emission capability, and outstanding quantum yield has been difficult [46]. Besides the previously described synthesis methods, hydrothermal carbonization (HTC) at elevated temperature and pressure has been praised as the most promising synthesis technique due to its high quantum performance, low cost, sustainable natural environment, and no toxicity.

Synthesis of Carbon Quantum Dots/Graphitic Carbon Nitride for Photocatalytic Reduction of Carbon Dioxide

There are numerous methods for the synthesis of CQD/g-C_3N_4 have been established. The first approach is hydrothermal synthesis. This method is usually carried out at a temperature of 120℃. Due to the low temperature requirements for the reaction, the hydrothermal approach is considered the most commonly used synthesis method [15]. The following method is thermal polymerization. In this approach, monomeric precursors are converted to polymers at elevated temperatures, which can enhance the interaction between CQDs and g-C_3N_4 via hydrogen bonds formed between precursors. Then there is the calcination method. This method is generally carried out at 550 ℃ under ambient conditions. Then, there is the solvothermal approach. In this method, heat is used and then solvents such as methanol and ethanol are added. This technique has the advantages of mild reaction conditions, high consistency, efficiency, and easy control. Finally, the method of impregnation. The most commonly used precursors in this process are cyanamide, citric acid, and ethylenimine.

Although the synthesis of CQD/g-C_3N_4 is numerously listed, the synthesis of CQD/g-C_3N_4 specifically used for the photocatalytic reduction of CO_2 is still limited. Some modifications made up so that the morphology of the CQD g-C_3N_4 might correspond to that specific application. The crystallized non-polar CQDs, which were previously prepared by a hydrothermal method, showed a good distribution of CQDs without aggregation on the surface of g-C_3N_4. The non-polar CQDs have a size of 2.5 nm, and g-C_3N_4 exhibits a mesoporous structure with a high surface area [58]. In another report, carbon nanodots (CND) and carbon nitride (CN) are synthesized via the approach of opposite electrostatic charges. The negatively charged CND and positively charged protonated-CN nanosheets are hybridized through hydrothermal treatment to produce 0D or 2D CND/pCN. These heterostructure materials also exhibit a uniform distribution of CND in size of 4.4. nm and strong bonding towards the surface of p-CN nanosheets [33]. The relation of the synthesised methods to morphology is further proved by the synthesis of carbon dots/carbon nitride (CD/CN) [59]. The CD/CN is synthesized in two methods. One is the microwave, and the other is the sonification method. The diameter of the microwave-CD is in 2–10 nm, whereas the diameter of sonification-CD is larger, around 15-20 nm. The small size of the microwave-CD is clearly distributed on the CN matrix, showing a strong interaction between the CD/CN phases. On the other hand, the large size of the sonification-CD is hardly observed through HRTEM because it is not well crystallized, relatively opposite to the morphology of microwave-CD. These morphology differences significantly showed in the properties of the CD/CN in which microwave-CD/CN exhibited better properties because it prolongs the lifetime of electrons and prevents rapid electrons recombination. The different selection of synthesised methods will consequently affect the morphology of the materials. The morphology CQDs must be uniformly distributed on the surface of g-C_3N_4 with good intact to ensure a smooth migration of electrons within the heterostructures.

Previous study shows the fabricating g-C_3N_4 with CQDs improves its performance in CO_2 photoreduction when exposed to visible light. The selectivity of CO_2 reduction products of CQDs/g-C_3N_4 nanocomposite resulted in a 6-fold increase in CO, O_2, and CH_4 production [58] compared to the single g-C_3N_4, which generated CO and O_2 [3]. After the reaction, CO_2 molecules were transformed into another chemical containing functional group, such as methane (CH_4) or carboxylic acid (HCOOH) [60, 61].

Relationship between Physicochemical Properties and Photocatalytic Activity of CQDs/g-C_3N_4 for Photocatalytic Reduction of CO_2

Numerous developments producing a several kinds of CQDs/g-C_3N_4 have occurred in recent years. The synthesis method and photocatalytic activity results of CQDs/g-C_3N_4 and its relationship between the physicochemical properties and photocatalytic activity are summarised in Table 1. The study identified four significant relationships between the physicochemical properties and the photoreduction of CO_2: charge carrier separation, e^--h^+ recombination, surface area, and surface polarity.

Electron Hole Recombination

According to the previous study, the recombination of e^--h^+ will affect photocatalytic activity. The fabrication of g-C_3N_4 with CQDs alters and improves the defects by increasing the photocatalytic activity and light absorption range, preventing the recombination of e^--h^+, and improving the quantum efficiency of pure g-C_3N_4 [15, 18, 19]. Another intriguing experiment with a CQDs/g-C_3N_4 hybrid demonstrated a photodegradation rate three times higher than that of pure g-C_3N_4. Thus, the development of CQDs/g-C_3N_4 nanocomposite beat commercial photocatalysts in terms of capability [18]. Furthermore, CQDs/g-C_3N_4 have been shown to absorb UV light while producing visible photons that can be reabsorbed by the polymer molecules [62]. As a result, CQDs/g-C_3N_4 have been widely used in H_2 evolution, organic compound degradation, CO_2 elimination, and disinfection [15]. Ong *et al*. (2017) [33] synthesised metal-free 0D/2D carbon nanodot/g-C_3N_4 (CND/pCN) hybrid nanocomposites to inhibit e^--h^+ recombination. The CND/pCN combination produced the most extensive total evolutions of CH_4 (29.23 μmolgcatalyst^{-1}) and CO (58.82 μmolgcatalyst^{-1}), which were 3.6 and 2.28 fold higher than those generated with pCN, respectively.

Charge Carrier Separation

According to Li *et al*. (2019) [63] CQDs act as a co-catalyst by facilitating charge separation and transfer, raising the electron density near CO_2 adsorption sites. According to Wang *et al*. (2020) [59], the efficiency of the CD/CN is double that of the CN, indicating that charge carriers are separated more efficiently in CD/CN.

Table 1. Summary of CQDs/g-C_3N_4 for photocatalytic reduction of CO_2

No	Materials	Synthesis Methods	Reductant agents	Photocatalytic activity	Relationship	References
1	Non-polar CQDs/g-C_3N_4	Hydrothermal method	Water vapor	CQDs/g-C_3N_4 generates six times more CO and CH_4 compared to pristine g-C_3N_4 Product production rate (μmol g^{-1} h^{-1}): CO: 23.38 CH_4: 20.78	The addition of non-polar CQDs onto g-C_3N_4 decreases the surface polarity of CQDs/g-C_3N_4. This result enhanced adsorption of non-polar CO_2 and altering CO_2 photoreduction pathways for efficient generation of hydrocarbons.	[58]
2	N-doped C dot/CoAl-layered double hydroxide/g-C_3N_4 (NCD/LDH/CN) hybrid	Hydrothermal method	Water vapor	High stability and CH_4 production rate Product production rate (μmol g^{-1} h^{-1}): CH_4: 25.69	Suppress e^--h^+ recombination by accelerating charge transportation processes, which enhance the photoreduction of CO_2.	[64]
3	Carbon quantum dots/oxygen-atom-doped CN (CQD/OCN)	Hydrothermal method	Water vapour	CQD/OCN-25% exhibits the best performance, with CH_4 production is 14 times higher than pure CN.	CQDs facilitate charge separation and transfer, and thus increasing the electron density around the CO_2 adsorption sites.	[63]

No	Materials	Synthesis Methods	Reductant agents	Photocatalytic activity	Relationship	References
4	Carbon nanodot-hybridized protonated g-C_3N_4 (CND/pCN)	Hydrothermal method	Water vapour	The CND/pCN-3 shows highest photocatalytic activity with the production rate of CH_4 and CO is 3.6 and 2.28 times higher, respectively, than pCN alone. Product evolution (μmol g^{-1} h^{-1}) CO: 58.82 CH_4: 29.23	The significantly increased photocatalytic activity of CND/pCN-3 compared to the pure CN due to the fast electron transfer from pCN to CNDs via well-formed heterointerface and reduction of the electron-hole recombination.	[33]
5	Carbon dots/carbon nitride (CD/CN)	Hydrothermal method	Water vapor	CD/CN reduce CO_2 to methanol	Carbon dots improved separation efficiency of photoexcited charge carriers	[59]
6	Carbon vacancy modified carbon quantum dots with carbon nitride (VCQDs/C_3N_4)	Hydrothermal method	Aqueous water	Better photoreduction activity of CO_2 for VCQDs/C_3N_4 compared to the CQDs/C_3N_4	The strong interaction between g-C_3N_4 and VCQDs and carbon vacancy in VCQDs can facilitate the migration of photogenerated electron and broaden the absorbance range of heterojunctions.	[65]
7	NiAl-LDH/g-C_3N_4/carbon quantum dots (LDH/CN/CQDs)	Hydrothermal method	Aqueous water	Highest CO production rate for the LDH/CN/CQDs-6 with the 26.8 and 20.9-fold higher than those of the pristine LDH, pure CN, respectively.	The highest CO evolution rate for the sample of LDH/CN/CQDs-6 compared to the other sample of LDH/CN/CQDs because of the larger surface area.	[66]

Surface Area

Previous study shows the increased surface area increases the number of active catalytic sites, which improves the efficacy of the photocatalyst. Liu *et al.* (2022) [66] shows the greatest CO evolution rate under visible light irradiation for the sample of LDH/CN/CQDs-6 compared to the other LDH/CN/CQDs because it has a larger special surface area and a suitable CQD content. This is 26.8 and 20.9 times greater than the pristine LDH, pure CN, and binary counterparts, respectively, and exceeds almost all reported LDH-based photocatalysts. The extensively dispersed CQDs in the LDH/CN heterojunction considerably boost the utilization efficiency of light energy and separation efficiency of photogenerated electron-hole pairs as unrestricted electron conduction bridges.

Surface Polarity

According to Feng *et al*. (2018) [58], using non-polar CQDs on the g-C_3N_4 increases the non-polar CO_2 adsorption and modifies CO_2 photoreduction pathways for efficient hydrocarbon synthesis. Compared to g-C_3N_4, which generated only CO and H_2 under the same conditions, CQDs/g-C_3N_4 could generate sixfold more CO and comparable quantities of CH_4 without generating detectable H_2. Appropriate surface modification of the catalyst is critical for optimizing CO_2 adsorption activation, lowering the reaction barrier for subsequent CO_2 photoreduction, and thereby optimizing photocatalytic performance. As a result, non-polar CQDs exhibit exceptional CO_2 photoreduction performance.

Morphology and Porosity

The synthesized CQDs are uniformly dispersed and exhibit good crystallization, as seen by the TEM image from a previous study [58]. The TEM image of pure g-C_3N_4 reveals a mesoporous structure, which denotes the presence of a large surface area [64].

Conclusion

This review provides the recent modification of graphitic carbon nitride (g-C_3N_4) by carbon quantum dots (CQDs), which includes the synthesis of CQDs/g-C_3N_4 for CO_2 reduction. The physicochemical properties of several carbon dots graphitic carbon nitride (CQDs/g-C_3N_4) photocatalysts have been investigated to determine their relationship. As a result, this review discussed four significant relationships between the physicochemical properties and the photoreduction of CO_2: e^--h^+ recombination, charge carrier separation, surface area, and surface polarity.

Increased surface area increases the number of active catalytic sites, which improves the efficacy of the photocatalyst. Furthermore, preventing e^--h^+ recombination and optimising charge carrier separation enhances the photocatalyst's ability to degrade CO_2. Finally, the non-polar CQDs on the g-C_3N_4 increase the non-polar CO_2 adsorption and modifies CO_2 photoreduction pathways for efficient photoreduction of CO_2.

This review gives a wide variety of viewpoints as well as a guideline for developing more effective CQDs/g-C_3N_4 for photocatalytic CO_2 reduction. The researchers must develop efficient methods for loading CQDs onto g-C_3N_4 and optimize the CQDs/g-C_3N_4 ratio to achieve maximum effectiveness in the photoreduction of CO_2, which will require unique insights to address energy and environmental problems.

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