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Graphene nanocrystals in CO₂ photoreduction with H₂O for fuel production

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Graphene nanocrystals can utilize solar light and are valuable in cases where electricity is lacking due to their chemical stability during the photocatalytic process, low cost and non-toxicity. However, because of the large band gap, ultraviolet light irradiation can barely excite graphene, which limits its application in the environment. CO₂ photoreduction through the visible light-responsive photocatalytic performance of graphene nanocrystals has recently been the focus of research in nanoscience due to the ability to convert pollutants into CO₂ and H₂O for environmental applications such as energy, environmental purification and wastewater treatment. This paper highlights the present improvements in CO₂ photoreduction with H₂O through the visible light-responsive photocatalytic performance of graphene nanocrystals via the development of structural modification strategies, solar harvesting, methods of synthesis and solar light catalytic mechanisms.

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Introduction

Recently, activities such as transportation, industrial processes, and heating, among other main uses, have led to the consumption of large quantities of energy. This present situation is mainly centered on the substantial utilization of fossil fuels, including oil and natural gas, not only for transportation

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but also for the production of electricity and heat. Considering the limited resources of fossil fuels, it is clear that at the high current consumption rate, these resources will become depleted, making the present energy source scheme unsustainable.

Besides sustainability, a second driving force to develop alternative energy sources is climate change specifically atmospheric pollution due to greenhouse gases. CO₂ accumulation has become a global crisis as it is the major product of fossil fuel combustion. It has been predicted that by 2050, the CO₂ concentration in the atmosphere will reach over 500 ppm, which is nearly double the concentration present prior to the industrial revolution.¹

CO₂ is reduced with H₂O to form useful products such as carbon monoxide (CO), formate, methanol, ethanol, or hydrocarbons. These molecules are converted or used directly as sustainable alternatives to fossil fuels for energy storage.¹³⁹ CO₂ photoreduction, particularly with H₂O, is one promising solution compared to other methods, such as chemical, electrochemical and biological methods.¹⁴⁰

Solar energy can be readily gathered, transformed and kept in the form of heat, which can either be distributed to residences or further converted into electricity as well as into other forms of energy.⁶ The most innovative investigated technologies concerning solar photon capture may be those *via* photocatalysis, as described by Edmond Becquerel in 1839.⁶

Fujishima and Honda revealed the exceptional knowledge about the photochemical splitting of water into hydrogen and oxygen in the presence of TiO₂ in 1972; since then, research interest has been focused on heterogeneous photocatalysis.^{4–6} The increase in the rate of a photoreaction in the presence of a catalyst is described as photocatalysis. Photocatalytic reactions are best known to be carried out in media such as gas phases, pure organic liquid phases or aqueous solutions. Also, most photocatalytic reduction reactions involving photons and a catalyst are often identified as the best in controlling organic

wastewater, solar energy utilization, and environmental treatment applications.^{5,6}

Graphitic nanoparticles have become the prime candidates for CO₂ reduction with H₂O photocatalysis.⁷ Graphitic nanoparticles are visible light-responsive materials with outstanding band gaps, and the energy levels of CB and VB are optimally located with respect to the normal hydrogen electrode.⁷ In addition, these materials have the ability to resist heat as well as strongly acidic and strongly alkaline solutions.

Due to the outstanding properties of these nanoparticles, the use of these promising materials in water splitting, CO₂ photoreduction with H₂O, organic contaminant purification, catalytic organic synthesis, and fuel cells is more efficient and effective.⁷

This paper, however, highlights the capability and efficacy for the prospective applications of CO₂ photoreduction with H₂O through the visible light-responsive photocatalytic performance of graphene nanocrystals for energy and environmental treatment in order to design future implementations to solve the environmental problems related to fuel production. For this reason, these materials are recognized as attractive candidates for environmental uses such as purified fuel production and waste-water treatment.

Graphene

Graphene stands to be a promising 2D-carbon lattice in the field of material research due to its excellent chemical and physical properties.³⁹ A large surface area, unique thermal and chemical stabilities, excellent mechanical strength, and superior electrical conductivity make graphene a potential component in various fields such as solar cells.

In recent years, graphene materials with novel compositions and well-defined structures are of particular interest due to their composition-dependent electronic, optical and catalytic properties.^{23,24} They have been widely used as efficient heterogeneous or homogeneous catalysts for a broad range of inorganic and organic reactions.^{25,26}

Graphene is formed by the one-atom-thick planar sheets of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.^{27,33} The derivatives of graphene contain a large number of oxygen-containing functional groups, such as –COOH and –OH.^{28,29} Graphene is one of the best base materials to solid-load AgNPs. Graphene can fix other metals in their laminar structure so that these metals or nanomaterials can exhibit good dispersion and it additionally plays a stabilizing and protective role.^{30–32}

The use of graphene in phase change materials is more promising than other nanoparticles for enhancing the thermophysical properties of phase change materials.^{2,3,34,96,113,115–128} Graphene has the potential to outperform metal nanoparticles, carbon nanotubes, and other carbon allotropes as a filler in thermal management materials.³⁵ The addition of 4% graphene to 1-octadecanol and erythritol (Fig. 1) leads to 140% increase in thermal conductivity. These improvements are markedly superior to that for other nanofillers such as multiwall carbon nanotubes and silver nanowires.^{36,37}



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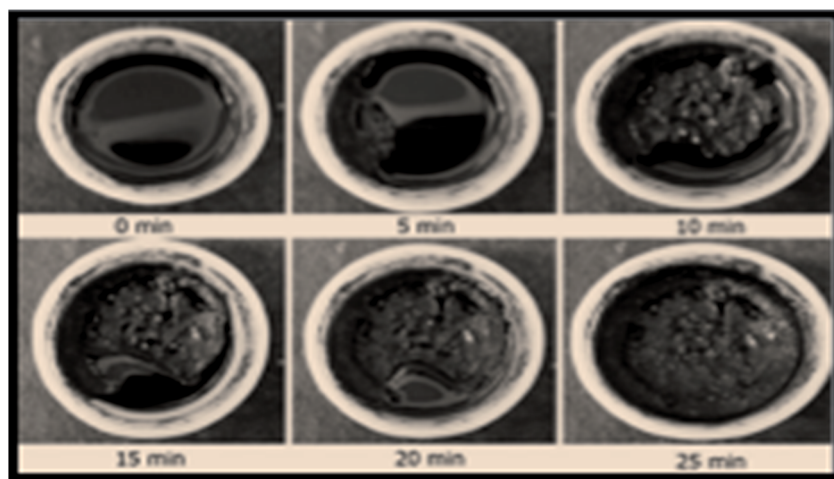


Fig. 1 Solidification of erythritol with 1% graphitic nanoparticles. Reproduced with permission from Mayilvelnathan *et al.*, 2019. Copyright 2019, Elsevier.

Composites of graphene

Graphene acts as a good electron acceptor and possesses transport properties. Metal/metal oxide–graphene composites absorb light on illumination and cause the photoexcitation of electrons. The excited electrons move from the valence band to the conduction band by electronic excitation between graphene and metal oxide. This process initiates the electron–hole pair charge separation between the metal oxide and graphene.^{43,96,101,112,148} Graphene is a potential electron acceptor and possesses a two-dimensional p-conjugation structure, which effectively suppresses the recombination of photogenerated e^- – h^+ pairs.⁴⁹

Jiang *et al.* synthesized a novel ternary SnO_2/Cu /graphene composite by a one-pot selective reduction method, in which $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was used as a reductant to realize a selective reduction fabrication process because its reduction strength falls in between these two components.⁴⁰ The process abandons complicated mechanical mixing (such as high-energy ball milling) and the possibility of destroying the integrity of the composite structure; it can also realize the uniform distribution of active substances and conductive components. In the as-prepared ternary graphene composite by Jiang and co-workers, the electrochemically active SnO_2 and inactive metallic Cu nanoparticles anchor tightly on flexible conductive graphene sheets and are located in close proximity to each other. Cu nanoparticles can promote the charge transfer kinetics of insulating SnO_2 at the interfaces, compress the volume stress as lithium ion insertion/deinsertion, and obstruct the aggregation of metallic Sn and Li_xSn alloys. Thus, improved reversibility of the conversion reaction from $\text{Sn}/\text{Li}_2\text{O}$ to SnO_2 is found in the $\text{SnO}_2/\text{Cu}/\text{GNS}$ composite (see Fig. 2). In summary, the results obtained from this study demonstrate that Cu nanoparticles are promising in promoting the reversibility of the conversion reaction and stabilizing the reversible capacity of SnO_2 –graphene-based composites.⁴⁰

Carbon allotropes such as 0D carbon dots, 1D carbon nanotubes and 2D graphene have attracted significant interest in many fields including catalysis, new device structures and solar energy harvesting.⁴¹ Particularly, the discovery of graphene has raised a wave of new research on a range of 2D materials, *e.g.*, phosphorene, transition metal dichalcogenides and hexagonal boron nitrides. Recently, graphdiyne (GDY) has emerged as a unique 2D carbon material and it consists of aromatic rings made by sp and sp^2 carbons and carbon–carbon triple bonds linked by an acetylenic linkage.

Motivated by the multiple merits of GDY, Xu and co-workers reported a GDY-decorated TiO_2 heterojunction prepared by the electrostatic-driven self-assembly of TiO_2 nanofibers and GDY nanosheets for light capturing CO_2 reduction. This work reveals that GDY can function as a highly effective co-catalyst for solar energy harvesting and may be used in other catalytic processes.⁴¹

The poor incorporation between graphene sheets and other nanoparticles has become a problem in the application of graphene-based composites.^{46–48} Graphene oxide was functionalized with triethylene tetramine (TETA) and then, reduced graphene oxide/Ag nanoparticle composites (rGO/Ag NPs) were prepared using TETA as the reductant *via* the hydrothermal method by Cheng *et al.* in 2019. rGO can be separated well by TETA and Ag NPs, and Ag NPs are dispersed on the surface of rGO and/or among the rGO sheets. Hence, the as-prepared rGO/Ag NP composites can be used as sensitive sensors for detecting traces of heavy metal ions except for certain deviations.

Han and co-workers modified a graphene foam electrode with Ag^{2+} NPs for detecting Hg using cyclic voltammetry (CV), and the limitation and sensitivity were $0.11 \mu\text{M}$ and $8.0 \mu\text{A} \mu\text{M}^{-1}$, respectively.⁴³ In addition, the composites containing graphene and Ag NPs can be explored for use as glucose and quercetin sensors.^{44,45}



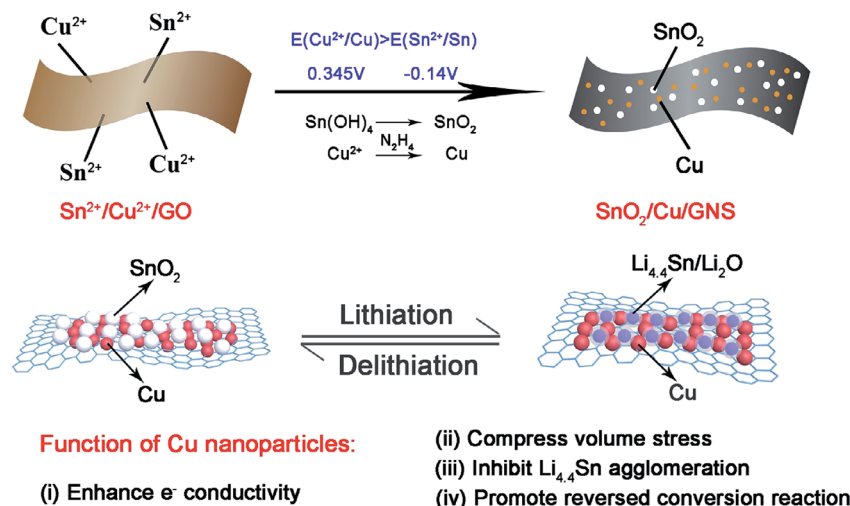


Fig. 2 Schematic illustration of the selective reduction fabrication of $\text{SnO}_2/\text{Cu}/\text{GNS}$ composite; structure evolution and functions of Cu nanoparticles during lithiation and delithiation processes. Reproduced with permission from Jiang *et al.*, 2019. Copyright 2019, Elsevier.

Synthesis of graphene

The interesting etiological and electronic nature of graphene makes it possible to develop a method to deposit layers of graphitic nanoparticles in a controlled manner; hence, graphene can be obtained. Considerably, the benchmark particle for comparison is bulk graphene. Graphitic materials are mostly bulk resources with small surface areas when they are prepared or synthesized by the direct condensation of organic precursors.

The mineralization of mesoporous structures and the increase in the specific surface area help in fine-tuning the physicochemical properties, which then increases the photocatalytic performance of graphene.¹² The nano-casting/replication of mesoporous silica matrices is the first method used to prepare graphite materials, such as carbon nitride ($\text{g-C}_3\text{N}_4$), which are famous for their cohort of the corresponding carbon nanostructures.^{10,11} Great efforts were then devoted to discover more innovative schemes for graphene modification, which was inspired by the hard template method. Liu and Cohen then discovered the soft template technique,⁸ and other graphene modification schemes such as acidic solution impregnation, ultrasonic dispersion, and chemical functionalization^{8,9} were also discovered. These methods described above are good signs of the principle of modifying the surface chemical properties and texture of graphene alone with its electronic potentials.

Thermal treatments such as physical vapor deposition (PVD),¹³ chemical vapor deposition,¹⁴ solvo-thermal method¹⁵ and solid-state reaction¹⁵ are used for their approachable processing steps and these serve as the basic techniques for graphene synthesis. Thermal oxidation exfoliation, ultra-sonic exfoliation and chemical exfoliation are well-known as the major exfoliation methods used for preparing graphitic nanomaterials.

The synthesis of AgRh bimetallic nanoparticles (AgRh BNPs) stabilized by graphene quantum dots (GQDs) and their

exceptional catalytic activity in the reduction of 4-nitrophenol, 2,4-dinitrophenol and 4-nitrobenzene diazonium tetrafluoroborate and generation of hydroxyl radicals was studied. The fabrication of the AgRh BNP nanocomposites was achieved by mixing GQDs and sodium borohydride, followed by the addition of simple commercial Ag and Rh salts at 0 °C in water.¹⁶ AgRh BNPs exhibited exceptional catalytic functions due to the positive synergistic effect between the Ag and Rh atoms on GQDs,^{21,22} and their catalytic activity was better than those of both monometallic counterparts. This graphene exhibited outstanding generation of hydroxyl radicals^{17–20} and further oxidized MB to MB-OH *via* some positive synergistic effects between the Ag and Rh atoms on GQDs than those of other BNPs and pure Ag or Rh NPs (Fig. 3).

Ioni and co-workers presented a new approach for the preparation of graphene with noble metal nanoparticles on its surface using supercritical 2-propanol as a reducing agent for Pd or Pt graphene oxide nanocomposites. The prepared nanocomposites were characterized by X-ray diffraction analyses (XRD) and transmission electron microscopy (TEM). XRD reveals the face-centered cubic structure of Pd and Pt in the nanocomposites, and TEM images show the good spatial distribution of metal nanoparticles on layered graphene sheets.³⁹

Photocatalysis

Studies define photocatalysis as one of the utmost environmental cleansing routines due to its potential to degrade refractory organic particles thoroughly by the use of sunlight or any visible light and its benefits of inferior energy utilization, no ancillary contamination, user-friendliness, *etc.* Graphene, as one of the best earliest established photocatalysts, has been well studied by scientists.^{111,112,114,115} Also, researchers have developed many other promising catalysts, such as nanocrystal particles, since the advancement of photocatalysis.^{116–121}

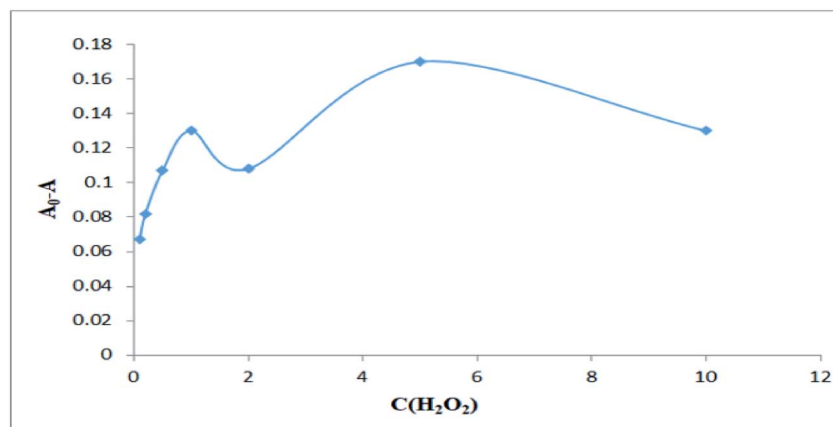


Fig. 3 Effect of H₂O₂ on the generation of hydroxyl radicals from samples containing 3 mL of 1.5×10^{-4} mmol 4, 3.375×10^{-5} mmol methylene blue and H₂O₂ at different concentrations. Reproduced with permission from Li *et al.*, 2019. Copyright 2019, Royal Society of Chemistry.

Notably, there are many classes of reactions involved in the photocatalysis phenomenon by the use of a catalyst initiated by light (see Fig. 5), such as the breakdown of organic complexes into biologically reactive water and carbon dioxide, leading to the attractive features of surfaces enclosed with a photocatalyst as these protect against the coatings of fouling matter.

Studies have shown that nanocrystal graphene has more high-quality photocatalytic potential than many promising nanoparticles under light irradiation.^{118,134} The widespread

application of nanocrystal graphene has been hampered due to its low separation efficiency of photo-excited electrons and holes. There have been many schemes to overcome these defects, such as forming a heterojunction structure *via* coupling with other semiconductors,^{120,121} doping with non-metals^{121,122} and depositing noble metals.^{122–124} These mechanisms can bring about high photocatalytic functioning. It is generally known that photocatalytic reactions usually take place on the surface of photocatalysts (Fig. 4). Subsequently, the surface environments of photocatalysts are fundamental to advance the photocatalytic activity for the calcination of organic pollutants. Inorganic oxyanions, for instance, phosphates, oxides, and metals have been used to modify photocatalysts and improve their performance.

The photocatalytic properties of graphene embedded in paints or concrete or positioned at the trivial of the particle can impact the high quality of these sustainable products.^{135–138} Photocatalysis is designed to harvest visible light by photocatalysts to drive chemical conversion.^{38,42}

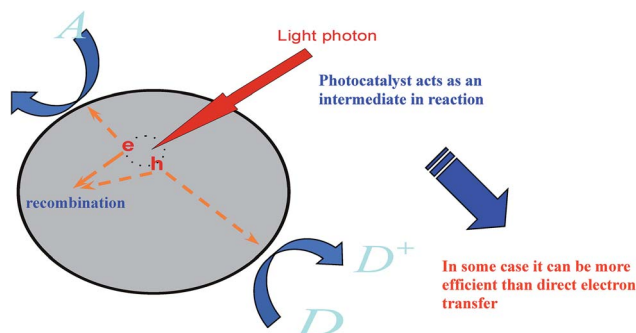


Fig. 4 Scheme of redox reactions driven by light in a photocatalyst.

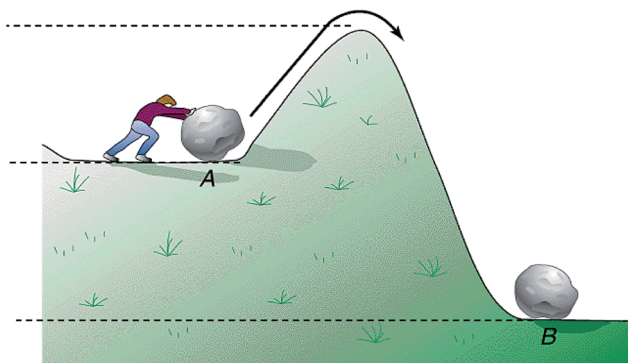


Fig. 5 Activation of energy of photons by the catalyst in the presence of light.

Mechanisms of photocatalysis

Gas and liquid phase photocatalysis

Numerous studies have revealed the efficacy of photocatalysis in gas and liquid phase remediation. Mostly, the catalytic route can be categorized into five distinct stages (Fig. 6): allocation of the reactants in the gas or liquid phase to the surface, adsorption of at least one of the reactants, reaction in the adsorbed phase, desorption of the product(s), and removal of the products from the interface region.

The third step is where photocatalytic nature of the graphene plays major role, despite, all the steps are usually found in heterogeneous processes. The nanocrystal graphene is excited with a photon carrying energy equal or in excess of its band gap, producing an electron-hole pair related to the photoinduced electron transfer, and the absorption of light stimulates one electron into the conduction band. Graphene may transfer its electron to any adsorbed electron acceptor (thereby promoting its



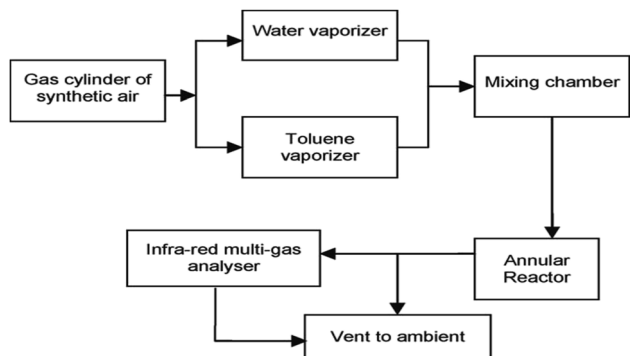


Fig. 6 Flow diagram of photocatalytic reaction system set-up. Reproduced with permission from Adormaa *et al.*, 2018. Copyright 2018, Royal Society of Chemistry.

reduction), while the hole (or the electron vacancy) may accept an electron from an adsorbed donor (promoting its oxidation).

Basic principle of photocatalytic CO₂ reduction

The basic principle of CO₂ reduction with H₂O photocatalysis occurs when the energy of the photons is enough to promote the electrons (see Fig. 5) in the valence band to jump to the conduction band. This occurs in three steps: (a) photon absorption and electron-hole pair generation,

(b) charge separation and migration to surface reaction sites or to recombination sites, and

(c) surface chemical reactions at the active sites containing donor oxidants at the valence-band holes and acceptor reductants at the electron center (Fig. 7). Numerous defects associated with these photocatalytic principles have been identified by researchers. During photocatalysis, cation radicals¹²⁶ can be produced by injecting charges from an excited molecule into the conduction band of graphene (Fig. 4 and 5).

Irradiation is usually the initial process of CO₂ reduction with H₂O photocatalysis; thus, the excitation of electrons by photons at the ground state is the prerequisite. Periodically, the photoexcitation of electrons at the ground state also occurs in most of the materials adsorbed on the surface of graphene,^{127,128} for instance, the reaction occurring in dye-sensitized solar cells.^{129,131} Different pathways are mainly experienced by the

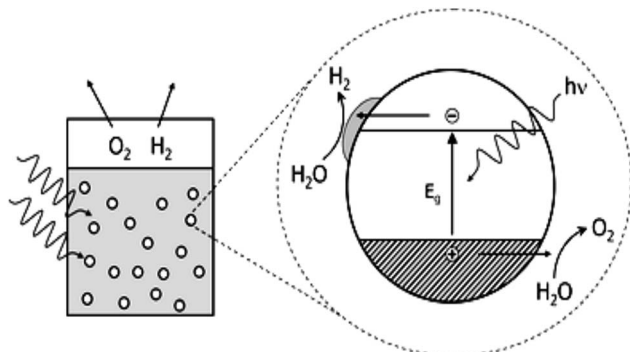


Fig. 7 Photoredox catalysis by a photocatalyst. The oxidation steps are portrayed on the right; the reduction steps are shown on the left.

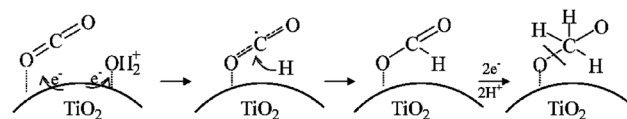


Fig. 8 Mechanism of the photoreduction of CO₂ with H₂O to a methoxyl radical on TiO₂ in the presence of water during the photocatalytic reaction. Reproduced with permission Adormaa *et al.*, 2018. Copyright 2018, Royal Society of Chemistry.

charge carriers. Most individual graphene materials are primarily used for water splitting and oxidation/reduction (Fig. 8) in both suspension and electrode systems.^{132,133}

CO₂ reduction with H₂O

Recently, the increased population as well as industrialization has been detrimental to the environment including the atmosphere.^{74,130} Recent increase in CO₂ has remained to be a major issue on this planet.^{75,76} CO₂ produced with H₂O from burning fuels from the domestic to industrial level has contributed significantly to the atmospheric air pollution, resulting in the current global warming the world is experiencing.^{77–79,82} There has been an introduction of alternative advanced strategies to cut down the production of CO₂. The SDG 7 has been identified for clean and renewable energy as one of the best mechanisms to reduce the production of CO₂ with H₂O in the atmosphere.^{80,81} However, due to the increasing demand of fuel and production on the industrial scale, the contribution of CO₂ is still high. Technologies have been developed to reduce the amount of produced CO₂. Among others, the photocatalytic reaction is one of the best technologies for CO₂ reduction (Fig. 9).⁸³

Zhou and co-workers described the facile *in situ* synthesis of a graphene (g-C₃N₄)-N-TiO₂ heterojunction as a competent photocatalyst for the selective photoreduction of CO₂ with H₂O

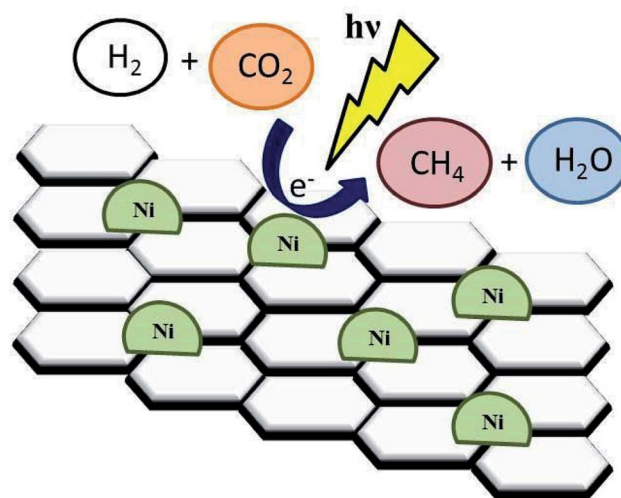


Fig. 9 Illustration of the photoreduction of CO₂ with H₂O to CO. Reproduced with permission from Mateo *et al.*, 2017. Copyright 2017, Elsevier.

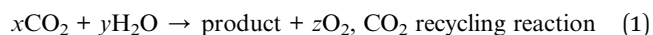
to CO. The composites of graphene, *i.e.*, carbon nitride and nitrogen-doped titanium dioxide composites (g-C₃N₄-N-TiO₂) were *in situ* synthesized by the thermal treatment of well-mixed urea and Ti(OH)₄ in an alumina crucible with a cover at different mass ratios. These results prove that graphene has high photocatalytic CO₂ reduction with H₂O as compared to its precursors.⁸⁴

Photo-assisted CO₂ reduction with H₂O by H₂ has been repeatedly described using fabrics covering noble or analytical metals, such as Pd, Ru and In.^{86–91} It was found that H₂O formed in the photocatalytic reaction of NiO/Ni nanoparticles (NPs) supported on defective graphene *via* photo-assisted CO₂ reduction with H₂ has a negative influence on the photocatalytic activity and studies further confirmed that H₂O desorption is one of the reasons why the system requires heating.⁸⁵ Therefore, it is anticipated that a promising function of temperature in the system can be to promote H₂O desorption from the photocatalyst surface, providing an opportunity for H₂ and CO₂ activation.^{72,85}

Strategies for the photoreduction of CO₂ with H₂O

CO₂ is the most oxidized form of carbon together with carbonate minerals with a formal oxidation state of +4. As a result, the conversion of CO₂ into a more energetic product involves the transfer of electrons to carbon, reducing its oxidation state. The family of reactions by which CO₂ is converted to a more reduced product is most often called CO₂ hydrogenation for thermally driven processes involving the reaction with hydrogen (H₂) or CO₂ fixation in natural photosynthesis and bioinspired catalysis.¹⁴¹

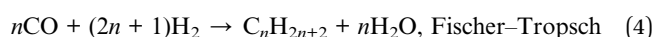
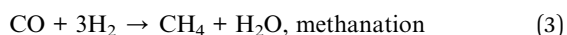
The ultimate source of electrons and protons for the reduction of CO₂ must be water (H₂O) as the combustion of a hydrogenated carbon product releases H₂O. CO₂ reduction/hydrogenation/fixation thus follows the following overall formula:



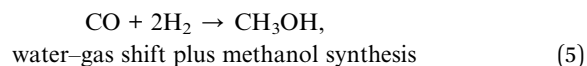
There are pathways in the traditional chemical industry, all thermally activated, that can be used for CO₂ hydrogenation using H₂ as the reductant.^{142,143} CO₂ can be reduced to carbon monoxide (CO) by the reverse water gas shift reaction:



If excess H₂ is used and the water is condensed out, the product gas is a mixture of H₂ and CO, which is called synthesis gas or syngas. Syngas can be used as the precursor to methane on a Ni catalyst,¹⁴⁴ multi-carbon hydrocarbons on an Fe or Co catalyst,¹⁴⁵ or methanol on a Cu/ZnO catalyst;^{146,147} these reactions are called methanation, the Fischer–Tropsch reaction, and methanol synthesis, respectively.

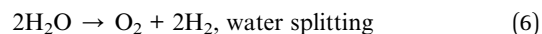


The role of CO is to react with the water released by CO₂ hydrogenation and generate more CO₂ molecules *via* the water–gas shift reaction (reverse of reaction (2)). The net reaction is as follows:

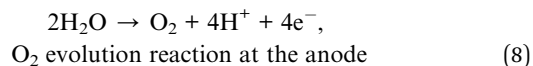
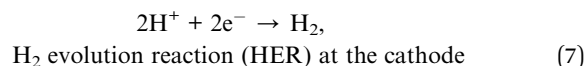


All of these processes run at high pressures and temperatures; for example, ~100 bar and 250 °C are typical conditions for methanol synthesis, which is the mildest of the three reactions.¹⁴²

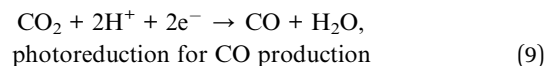
In order for CO₂ hydrogenation by the above-mentioned reactions to be a renewable process, hydrogen must come from water splitting using renewable energy: (4) in methanol synthesis, some CO molecules are required in the syngas stream because CO₂ is actually the immediate reactant,



such that the combined reaction is in the form of reaction (1) mentioned above. Water splitting would be driven photochemically using electrical energy from renewable sources such as wind and solar¹²⁰ according to the following half-reactions:



An alternative to CO production by the reverse water–gas shift reaction (reaction (2)) is the photoreduction of CO₂ with H₂O to CO:



Photocatalytic reduction of CO₂ to methanol (methanol oxidation reaction)

The photocatalytic conversion of CO₂ with H₂O into fuels such as methanol and formic acid by graphene and graphene oxides based on light irradiation at a specific coverage could decrease the amount of CO₂ in the environment and meet the increasing demands for energy.^{93–95} Honda *et al.* stated for the first time that the photocatalytic reduction of CO₂ with H₂O into valuable chemicals can be achieved using various semiconductor-based catalytic materials.⁶⁹ The conversion of CO₂ by photocatalysis and artificial photosynthesis as well as electrochemical, chemical and biological approaches can not only alleviate the increasing levels of CO₂ in the environment but also provide alternative fuels and valuable chemicals.^{97–100}

Gusain and co-workers prepared reduced graphene oxide (rGO)–copper oxide nanocomposites *via* the covalent grafting of CuO nanorods on the rGO skeleton. This study explored the potential of the rGO–CuO nanocomposites for the reduction of CO₂ into methanol under visible light irradiation. The pristine CuO nanorods demonstrated very low photocatalytic activity



due to the fast recombination of charge carriers and yielded $175 \mu\text{mol g}^{-1}$ methanol although rGO-Cu₂O and rGO-CuO revealed considerably better photocatalytic activities and yielded five ($862 \mu\text{mol g}^{-1}$) and seven ($1228 \mu\text{mol g}^{-1}$) times as much methanol, respectively. The superior photocatalytic activity of CuO in the rGO-CuO nanocomposites was credited to the slow recombination of charge carriers and the efficient transfer of photogenerated electrons through the rGO skeleton. This study further excludes the use of a scavenging donor.⁹²

Recently, it was revealed that an rGO coating significantly increases the activity of Cu₂O for CO₂ photoreduction to CO, which is nearly six times higher than that for the optimized Cu₂O.¹⁰² This was attributed to the slower electron-hole recombination, efficient charge transfer and protective function of rGO. Herein, CuO (Cu²⁺) nanorods grafted on rGO showed better photocatalytic activities than the rGO-Cu₂O (Cu¹⁺) nanocomposite.

Also, a facile combined method, sonothermal-hydrothermal method, was used to construct titanium dioxide (TiO₂) nanoparticles on the surface of reduced graphene oxide (rGO) to form nanocomposites. There was improved photocatalytic CO₂ reduction to methanol by the composites under UVA and visible irradiation, which suggested the modification in the band gap of the composite and the promotion of the separation of photogenerated carriers, yielding a methanol production rate of $2.33 \text{ mmol g}^{-1} \text{ h}^{-1}$ (ref. 103) (Fig. 10). From the study, it can be deduced that the photoreaction process occurs through the traditional mechanism of photogenerated electron transfer to rGO, while visible light CO₂ reduction proceeds as a result of the charge transfer photoexcitation that directly produces electrons in rGO and holes in TiO₂.

Among the various applications of graphene, such as photocatalytic CO₂ reduction,^{104,110} water splitting,¹⁰⁵ dye and organic pollutant degradation,^{106,107} lithium-ion batteries,¹⁰⁸ and antibacterial activity,¹⁰⁹ photocatalytic CO₂ reduction to valuable hydrocarbons *via* solar irradiation can serve as

a solution to the total dependence on fossil fuels with its concomitant global warming.

CO₂ methanation

CO₂ methanation is an exothermic reaction involving CO₂ as a substrate, which can be easily implemented in a thermal process to achieve maximum conversions and rates.^{67–71} Photo-assisted reactions are considered advantageous since they can be implemented in a range of temperatures, in which the thermal process does not happen or results in only low CO₂ conversions because of the low reaction rates.^{72,73} In exothermic reactions, in order to shift the equilibrium towards the products, low reaction temperatures but with suitable rates are more appropriate, which can be provided by the photo-assisted process. CO₂ methanation is one of the few exothermic reactions involving Ni/SiO₂-Al₂O₃ as a catalyst at temperatures above 400 °C to reach high conversions and rates. Therefore, it is well-defined that H₂O is a robust poison of photo-methanation and it is proposed that the role of temperature is to desorb this generated H₂O acting as a poison from the catalyst surface.

It is obvious from Fig. 11 that the specific initial rate of CH₄ formation is contingent on the irradiation power, suggesting that under the current conditions, CO₂ methanation is a photo-assisted process.⁶⁷

Recently, developing the photocatalytic activity of predictable semiconductors has attracted many researchers' attention and it has been stated that graphene as a useful additive can be provided to promote the photocatalytic activity. From the experiments of Karach *et al.*, 2018, it has been established that Rh₂O₃/Rh NPs maintained on rGO can be an excellent photocatalyst for the methanation of CO₂ at temperatures around 175 °C, achieving a specific CH₄ formation rate of $814.38 \mu\text{mol g}_{\text{Rh}}^{-1} \text{ h}^{-1}$, which is approximately double that of the estimated rate for Rh NPs supported on high-surface-area silica-alumina with a discernible quantum efficiency of 2.55%. It seemed that the photoinduced electron transfer from excited Rh₂O₃/Rh NPs to graphene sheets is responsible for the positive impact of graphene.

Photoelectrochemical CO₂ reduction

Photoelectrochemical (PEC) CO₂ reduction with H₂O has been an innovation for artificial photosynthesis, which provides an effective route to relieve the environmental issues and energy crisis. Therefore, the development of effective catalytic materials with low energy consumption, controllable product selectivity and high quantum efficiency is an urgent concern for the PEC CO₂ reduction with H₂O.^{51–53}

Graphene has been given considerable attention in many prospects of material science, such as solar cells,^{54,55} supercapacitors,^{56–58} and fuel cells.^{59,60} Due to the large specific surface area, chemical durability and excellent charge carrier mobility, graphene has become one of the most ideal carrier materials and electron collectors to promote the separation and transfer of photoinduced charge carriers.^{61,62} Also, graphene has been brought into focus in their optoelectronic applications due

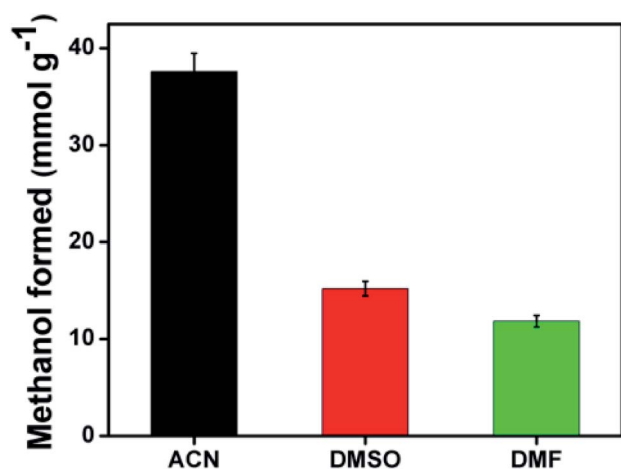


Fig. 10 Influence of the reaction medium for the production of methanol from CO₂ reduction under visible light by 5.0rGO-TiO₂ for a period of 16 h. Reproduced with permission from Mungse *et al.*, 2015. Copyright 2015, Royal Society of Chemistry.



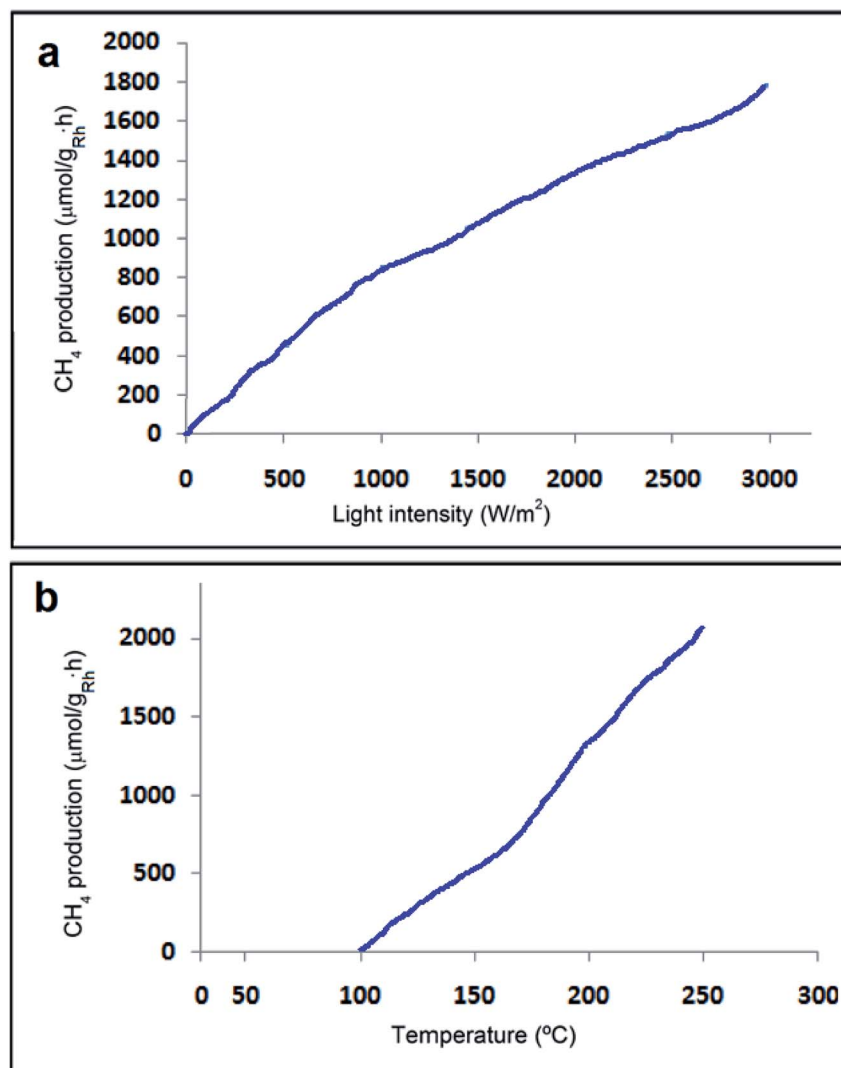


Fig. 11 Specific CH_4 formation rate of Rh (18)-G photocatalyst as a function of the light intensity (a) and temperature (b). The entire catalyst amount utilized in the light intensity experiment was 25 mg and 20 mg in the temperature experiment. Light intensity tests were carried out at a constant temperature of 175 $^{\circ}\text{C}$, while the light intensity in the temperature dependency experiments was 2541 W m^{-2} . $P_{\text{H}_2} = 1.00$ bar, $P_{\text{CO}_2} = 0.25$ bar in all cases. Reproduced with permission from Karach et al., 2018. Copyright 2018, Elsevier.

to the wide absorption range in the visible light region and long carrier diffusion length.^{63–65}

The proposed possible photoelectrochemical mechanism of a graphene hybrid to achieve CO_2 photoreduction with H_2O is shown in Fig. 12. Graphene hybrids are the subject for photoelectrochemical CO_2 reduction, from which the photoelectrons can be derived under solar-simulated light illumination. Graphene can be treated as a semiconductor due to the oxygen-containing groups on its surface.⁶⁶ The sp^2 carbon atoms function like a conduction band, while the sp^3 carbon atoms serve as the valence band. After introducing a small amount of graphene into the hybrid, in addition to slightly enhanced light absorption, graphene mainly functions as an electron transfer medium to separate photogenerated electron-hole pairs, thus improving photocurrent.

Wang and co-workers proposed that the *in situ* synthesized GO/MAPbBr₃ hybrid was more beneficial to

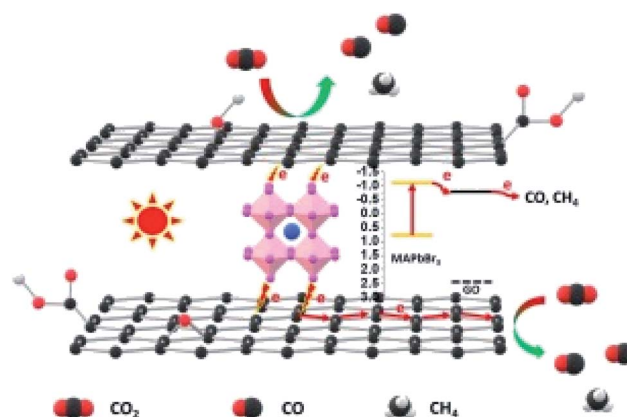


Fig. 12 Possible mechanistic pathway of photoelectrochemical CO_2 reduction. Reproduced with permission from Wang et al., 2018. Copyright 2018, Elsevier.

photoelectrochemical CO₂ reduction with H₂O than bare MAPbBr₃. The yield of CO for the MAPbBr₃ photoelectrochemical CO₂ reduction was 0.268 μmol cm⁻² h⁻¹. After the hybridization of MAPbBr₃ and GO, a significant improvement in the photoelectrochemical activity was obtained.⁵⁰

Future prospects and conclusion

From the discussion, the prospective investigations of CO₂ photoreduction with H₂O through the visible light reactive photocatalytic performance of graphene nanocrystals may consider both designing and producing more effectual nanostructures, for example, hollow spheres with a high surface area or nanoplates with a highly active surface and the degradation performance and mechanism of additional categories of pollutants, particularly for non-dyed pollutants, better CO₂ reduction with H₂O and hydrogen production.

Also, future prospects should consider developing nanocrystals that are responsive to morphology monitoring, evaluating the photocatalytic practicality and efficacy of traditional synthesis and preparative strategies of graphene nanocrystal compounds and then discovering the functions of distinct graphene nanoparticles in the context of viable fuel production and its effective application in solar energy utilization.

The photocatalytic reduction of CO₂ using H₂O is a perfect approach for clean fuel production, but it remains challenging to design an extremely well-organized photocatalytic system by tracking the charge flow in a facile manner. Distinctive investigations have demonstrated the high photocatalytic activity of graphene over pollutant carbon dioxide reduction. Among others, graphene in recent times has presented photocatalytic activity towards organic pollutants, hydrogen production and carbon dioxide reduction.

Graphene nanocrystals are mostly used as co-catalysts to help improve the separation and transfer efficacy of electron-hole pairs to enhance the photocatalytic performances of the catalysts. Chen *et al.* (Qin *et al.* 2018; Wang *et al.*, 2009) indicated that graphene nanocrystals coupled with nanoparticles, for instance, n-type graphitic carbon nitride, can usually form a p-n junction to promote charge separation and transfer for improved photocatalytic activity.

Graphene nanocrystals are very important in the management of the environment, especially those which are used in the photocatalytic processes. This was confirmed by (Deng *et al.* 2018; Lan *et al.*, 2015) in their research, where they indicated that noble metals incorporated with graphene catalysts have significant application prospects in the chemical production processes and environmental protection fields.

Lastly, this review on CO₂ photoreduction with H₂O through the visible light-responsive photocatalytic performance of graphene nanocrystals highlights the current state of knowledge on the photocatalytic activity of these nanocrystals from different aspects of their structural alterations, synthesis, and catalytic capabilities. This mini-review offers a thoughtful perspective of the diverse means of solar harvesting with graphene nanocrystals for better visible light-responsive CO₂ reduction activities. In light of this, further investigations are

also needed in order to construct a complete picture of the exceptional properties of CO₂ photoreduction with H₂O through the visible light-responsive photocatalytic performance of graphene nanocrystals.

Conflicts of interest

The authors declares that they have no conflict of interest.

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