

Chapter 13

**GRAPHENE-BASED NANOCOMPOSITE MATERIALS
FOR THE PHOTOREDUCTION OF CARBON DIOXIDE
INTO VALUABLE ORGANIC COMPOUNDS**

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ABSTRACT

Photocatalytic reduction of carbon dioxide (CO₂) into hydrocarbon fuels such as methane, methanol, etc is an attractive strategy for simultaneously harvesting solar energy and capturing CO₂, which is a major cause for global warming. Recently, graphene-based nanocomposites due to their large surface area, high conductivity, ease of functionalization and low cost have emerged as efficient photocatalysts for the reduction of CO₂ to hydrocarbons. Furthermore, graphene oxide (or reduced graphene oxide) can be coupled with various semiconductors to form graphene oxide (graphene)-semiconductor nanocomposites, which act as high-performance visible light active photoredox catalysts owing to their enhanced quantum efficiency. In this chapter, we will summarize the various graphene/semiconductor/homogeneous catalyst nanocomposites used as high performance visible light active photocatalysts for the reduction of CO₂ to high value chemicals such as methane, methanol, etc.

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INTRODUCTION

Manmade emissions of carbon dioxide (CO_2) have increased its atmospheric concentration from around 258 ppm in 1958 to 398 ppm in 2013 [1-6]. This CO_2 can be used as carbon feedstock for the production of valuable chemicals such as dimethyl carbonate, polycarbonates, carbamates, etc. [7-12]. But synthesis of such compounds is not viable because of conversion of thermodynamically more stable CO_2 molecule into less stable molecule is an energy intensive step [13-16]. Thus, the development of visible light—particularly solar assisted—conversion of CO_2 to high energy materials, has attracted increasing attention from the scientific community due to its great potential of fulfilling our future energy demands and getting rid from increasing global warming. Photochemical conversion of CO_2 to value added products is a most challenging task, because of the high reduction potential of CO_2 , multiple electron transfer pathway and need of a highly efficient robust catalyst that can derive electrons for CO_2 reduction by water splitting under visible light irradiation [17-21]. Many types of semiconductor photocatalysts such as TiO_2 [22, 23], ZnO [24, 25], BiVO_4 [26], InVO_4 [27, 28] and combinations [29-32] thereof have been widely studied for this purpose. By far the most researched photocatalytic material is anatase TiO_2 because of its low cost, high thermodynamic stability, strong oxidizing power and relative nontoxicity. However, the rapid recombination of electrons and holes is one of the main limitations for using TiO_2 as a high performance photoactive catalyst for practical applications [33]. Moreover, its wide band gap of 3.2 eV limits its application to the ultraviolet (UV) region. Or only a small fraction ($\approx 5\%$) of the total solar spectrum reaches the earth's surface. In order to utilize irradiation from sunlight or from artificial room light sources, the development of visible light-active TiO_2 is essentially necessary.

In order to improve the photocatalytic performance of semiconductor-based photocatalysts such as TiO_2 , a variety of strategies such as doping with various metals like Cu [34-39], Ag [40, 41], Ru [42], etc. and nonmetal N [43, 44], C [45], iodine [46], etc. have been investigated. Semiconductor doping with these elements not only slows down the rate of electron and hole recombination, but also lowers the band gap position by orbital overlapping. However, the conversion efficiencies are quite low far from the acceptable levels. Another approach to increase the absorption pattern of semiconductor type photocatalyst is the dye sensitization [47-51]. In this approach, any organic or inorganic dye (in solution or immobilized) is used as a visible light absorber which transfers the excited electrons to the semiconductor. This strategy, although advantageous as it provides visible light promoted CO_2 reduction, has major limitations which include the degradation of the dye by photogenerated oxidizing holes and leaching of photosensitizer. Recently, the coupling of semiconductor photocatalysts with carbonaceous nanomaterials has gained considerable interest due to their unique and controllable structural and electrical properties, which has proven to be beneficial for enhancing the photocatalytic activities. Among the carbon nanostructures (e.g., C_{60} , carbon nanotubes, and graphene), graphene offers new opportunities in photovoltaic conversion and photocatalysis through formation of hybrid structures with a variety of nanomaterials [52-56]. For example, when combined with TiO_2 graphene acts as an electron trap, which promotes electron-hole separation and facilitates interfacial electron transfer (Figure 1) [57, 58]. Graphene, a one-atom-thick sp^2 -hybridized carbon sheet, has

attracted a great deal of scientific interest since its discovery by Geim and co-workers [59-64].

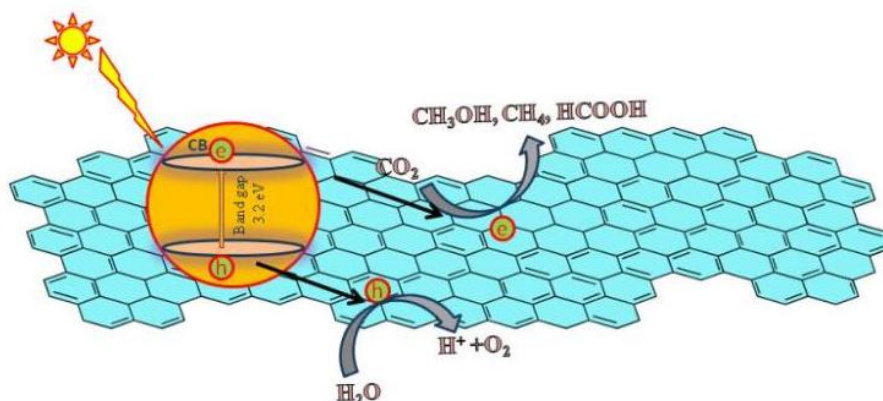


Figure 1. Mechanistic pathway of CO₂ reduction on graphene-TiO₂ nanocomposite.

Owing to its unique properties such as high mobility of charge carriers ($250,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [65-67], thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$) [68, 69], mechanical strength (1060 GPa) [70] and high specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [71, 72], graphene grasps a huge potential for various applications including electronic devices, solar energy conversion, supercapacitors, sensors, catalysis and particularly for the preparation of composite materials [73, 74]. Furthermore, graphene has an extensive two-dimensional π - π conjugation structure, which endows it with excellent conductivity of electrons. Several methods for the synthesis of graphene sheets are available namely micromechanical exfoliation, chemical vapour deposition (CVD), epitaxial growth, longitudinal unzipping of carbon nanotubes, direct sonication, chemical and thermal reduction/exfoliation as well as solution-based approaches [75, 76]. However, graphene synthesis faces a problem that is common to many novel materials: the absence of process for production in high yields (gram scale) [77, 78].

The exceptional properties of graphene have generated huge interest for the synthesis of graphene-semiconductor nanocomposite materials. The principal driving force for the growing research trends in the field of graphene-semiconductor nanohybrids is the formation of nanocomposite materials of superior properties, resulting from the combination of the properties of graphene and semiconductors. In this context, extensive work has been carried out on the preparation of graphene-TiO₂ composite and its application in various fields such as photocatalytic bactericide [79, 80], hydrogen evolution [81-83], dye-sensitized solar cell [84, 85]. The nanohybrids of graphene/graphene oxide with TiO₂ and other doped/nondoped semiconductors were also reported for the photocatalytic dye degradation: Cu-TiO₂/grapheme [86, 87], P-25/grapheme [88, 89], functionalized graphene sheets/ZnO nanocomposites [90], N-doped graphene/ZnSe nanocomposite [91], graphene oxide wrapped Ag/AgX nanocomposites [92], graphene/Bi₂WO₆ nanocomposite [93], Nd/TiO₂ modified with grapheme [94], for water splitting: ternary polyaniline-graphene-TiO₂ [95], N-doped Sr₂Ta₂O₇ coupled with graphene sheets [96], and for organic pollutant degradation: TiO₂/graphene nanocomposites [97, 98]. Nevertheless, there is a limited number of reports on the use of graphene-based TiO₂ (and other semiconductors) nanocomposites for photocatalytic CO₂ conversion into high value chemicals (Figure 1). Tu et al., [99] reported on robust hollow

spheres consisting of molecular-scale alternating titania ($\text{Ti}_{0.91}\text{O}_2$) nanosheets and graphene (G) nanosheets prepared by a layer-by-layer assembly technique with polymer beads as sacrificial templates under microwave irradiation.

The use of microwave technique helps in removing the template and simultaneously reduces graphene oxide into graphene.

The developed photocatalyst was subsequently used for photocatalytic conversion of CO_2 into renewable fuels (CO and CH_4) in the presence of water vapour. The formation rates of CO and CH_4 over the as-prepared G- $\text{Ti}_{0.91}\text{O}_2$ hollow spheres were found to be 8.91 and 1.14 $\text{mmol g}^{-1} \text{h}^{-1}$, respectively. The total conversion of CO_2 over G- $\text{Ti}_{0.91}\text{O}_2$ hollow spheres was found to be five-times higher than blank $\text{Ti}_{0.91}\text{O}_2$ hollow spheres and nine-times higher than commercial P-25. The superior photoactivity of G- $\text{Ti}_{0.91}\text{O}_2$ hollow spheres can be attributed to the ultrathin nature of $\text{Ti}_{0.91}\text{O}_2$ nanosheets, allowing charge carriers to move rapidly onto the surface to participate in the photoreduction process. In addition, the sufficiently compact stacking of ultrathin $\text{Ti}_{0.91}\text{O}_2$ nanosheets with G nanosheets allowed the photo-generated electron to transfer fast from the titania nanosheets to G to enhance lifetime of the charge carriers; the hollow structure probably acted as a photon trap-well to allow the multiscattering of incident light for the enhancement of light absorption.

Very recently, Zhou et al., [100] described another TiO_2 -graphene (G) hybrid nanocomposite, prepared by an *in situ* reduction-hydrolysis technique in a binary ethylenediamine (En)- H_2O solvent. The reduction of graphene oxide (GO) into graphene (G) by En and the formation of TiO_2 nanoparticles loaded onto graphene through chemical bonds (Ti-O-C bond) was achieved simultaneously. Due to the reducing role of En, abundant Ti^{3+} is formed on the surface of the TiO_2 in the obtained G- TiO_2 nano hybrids. The synthesized G- TiO_2 nanocomposite exhibited higher photoactivity (8 $\text{mmol g}^{-1} \text{h}^{-1}$ CH_4 and 16.8 $\text{mmol g}^{-1} \text{h}^{-1}$ C_2H_6) in comparison with the blank TiO_2 sample (10.1 $\text{mmol g}^{-1} \text{h}^{-1}$ CH_4 and 7.2 $\text{mmol g}^{-1} \text{h}^{-1}$ C_2H_6) and commercial P-25 (0.69 $\text{mmol g}^{-1} \text{h}^{-1}$ CH_4 , and minor CO 0.16 $\text{mmol g}^{-1} \text{h}^{-1}$, C_2H_6 is absent). The enhanced photocatalytic performance of the G- TiO_2 nanocomposite was probably due to the synergistic effect of the introduction of graphene and the presence of surface Ti^{3+} sites. Particularly, the yield of C_2H_6 was found to be increased with the content of incorporated graphene.

Graphene not only facilitates the transportation of electrons, but in some studies it was found that graphene can elevate the position of the semiconductor's conduction band. For example, tungsten trioxide (WO_3) is a visible light active semiconductor due to its narrow band gap of 2.7 eV. However, the low position of its conduction band (lower than -0.1 V vs. NHE, pH = 7) has limited its application for reduction of CO_2 to hydrocarbons. Wang et al., [101] have shown that nanocomposite of WO_3 with graphene synthesized using *in situ* hydrothermal method can elevate the position of conduction band of WO_3 . By using this hybrid system, 0.89 $\mu\text{mol g}^{-1} \text{cat}$ CH_4 was obtained after 8 h visible light illumination. XPS VB spectra recorded on WO_3 and WO_3 -graphene nanocomposite allowed to determine the position of the VB band edge. It was found that WO_3 has a deeper VB maximum of 0.37 eV than WO_3 -graphene nanocomposite, suggesting a stronger oxidation power of holes photogenerated in the WO_3 VB. A correlation of this value with the CB minimum indicated its higher value by -0.24 V than CO_2/CH_4 redox potential.

Apart from TiO_2 /graphene and WO_3 /graphene composites, graphene oxide (GO) was also found to be a promising photocatalyst for the catalytic conversion of CO_2 to methanol (MeOH). GO can be easily synthesized through extensive oxidation of natural graphite [102].

GO contains functional oxygen groups (hydroxyl, epoxy, carbonyl and carboxyl) and sp^3 carbon, responsible for its variable properties from pristine graphene. Although the chemistry is still under debate, these oxygen-containing groups provide graphene with hydrophilic character and chemical reactivity [103, 104]. In contrast to graphene, GO is insulating in nature due to presence of oxygen carrying functionalities on its surface.

The presence of these oxy-containing groups generates lots of sp^3 hybridized carbons and simultaneously disrupts the conjugated sp^2 carbons π - π network. However, the controlled reduction of GO by removing most of the oxygen-containing groups can transform it into semiconductor of appropriate band gap [105, 106].

Recently, Hsu et al., [107] have conducted a systematic investigation of the photocatalytic CO_2 reduction on various GO samples synthesized under different conditions. They found that the GO, obtained by the modified Hummer's method [108] in the presence of excess $KMnO_4$ and excess H_3PO_4 to raise the level of oxidation, exhibited the highest photocatalytic efficiency among the studied samples. The photocatalytic conversion rate of CO_2 to methanol was found to be $0.172 \text{ mmol g}^{-1} \text{ cat h}^{-1}$ under simulated solar-light source irradiation for 4 h, which is six-fold higher than pure TiO_2 . They proposed a possible explanation that in the modified GO, the oxygenated functional groups provide a 2D network of sp^2 and sp^3 bonded atoms, leading to the presence of a finite band gap depending on the isolated sp^2 domains. During the photocatalytic reduction process, the modified GO with surplus oxygenated components is photoexcited to generate electron-hole pairs (e^-h^+), which then migrate to the GO surface to react with adsorbed reactants [109]. The reduction potential of an e^- in the GO conduction band (ca. -0.79 V vs. NHE) is lower than the potential of CO_2/CH_3OH (-0.38 V vs. NHE), while the oxidation potential of the h^+ in the GO valance band (ca. 4 V vs. NHE) is higher than the potential of H_2O/O_2 , H^+ ($E = 0.82 \text{ V vs. NHE}$). Therefore, the photogenerated electrons and holes on the irradiated GO can react with adsorbed CO_2 and H_2O to produce CH_3OH via a six-electron reaction.

Yadav et al., [110] reported the use of a novel graphene-based visible light active photocatalyst consisting of a covalently attached chromophore, such as multianthraquinone substituted porphyrin to GO coupled with the activity of an enzyme, formate dehydrogenase. In this system, under visible light irradiation, the chromophore is excited and transfers its electrons through GO to a rhodium complex in solution, which becomes reduced. The reduced rhodium complex then reduces the co-enzyme NAD^+ to NADH thus forming the photocatalysis cycle. Finally, NADH is consumed by the CO_2 substrate for its enzymatic (formate dehydrogenase) conversion to formic acid. The NAD^+ released from the enzyme can undergo photocatalysis cycle in the same way, leading to the photoregeneration of NADH. The higher conversion rate of CO_2 using this system indicates the potential use of enzyme incorporation into a photocatalytic system to enhance the catalytic activity of the graphene-based materials in CO_2 photoreduction systems.

An et al., [111] synthesized Cu_2O /reduced graphene oxide (rGO) composite using a facile one-step microwave-assisted chemical method and investigated its performance for the photoreduction of CO_2 . In this system, rGO acted not only as an ideal electron trap to hinder fast charge recombination, but also as a stabilizer to improve the stability of Cu_2O . The rGO coating dramatically increases Cu_2O activity for CO_2 photoreduction and provided a nearly six times higher activity than the optimized Cu_2O and 50 times higher activity than Cu_2O/RuO_x junction in the 20th hour. Furthermore, an apparent initial quantum yield of approximately 0.34% at 400 nm has been achieved by the Cu_2O /rGO junction for CO_2

photoreduction. The photocurrent of the junction is nearly double that of the blank Cu₂O photocathode. The improved activity together with the enhanced stability of Cu₂O is attributed to the efficient charge separation and transfer to rGO as well as the protection function of rGO. By coupling with rGO, the photoreduction activity of Cu₂O was enhanced by two times, with CO as the only reduction product.

The incorporation of rGO into Cu₂O further improves the photocatalyst stability remarkably, which shows a great potential for CO₂ conversion in a sustainable manner.

Tan et al., [112] investigated the photocatalytic activity of rGO-TiO₂ hybrid nanocrystals, synthesized through a simple solvothermal route, for the reduction of CO₂ to hydrocarbons. The prepared rGO/TiO₂ nanocomposites exhibited superior photocatalytic activity (0.135 μmol g⁻¹ cat h⁻¹) in the reduction of CO₂ over graphite oxide and pure anatase. The intimate contact between TiO₂ and rGO was proposed to accelerate the transfer of photogenerated electrons on TiO₂ to rGO, leading to an effective charge anti-recombination and thus enhancing the photocatalytic activity. Furthermore, rGO/TiO₂ nanocomposite photocatalysts were found to be active even under the irradiation of low-power energy saving light bulbs, which renders the entire process economically and practically feasible. In another work [113], a composite of solvent exfoliated graphene (SEG) synthesized by ultrasonication in *N,N*-dimethyl formamide (DMF) and TiO₂ (P-25) in the form of film made by using ethyl cellulose as a stabilizing and film forming polymer was used for the photoreduction of CO₂ to methane.

The as obtained SEG (0.27%)-TiO₂ gave 8.3 μmol h⁻¹ m⁻² methane under UV light irradiation that was 4.5 times higher than bare TiO₂. Further it was demonstrated that less defective SEG composite with TiO₂ possessed higher photocatalytic activity than more defective rGO composite with TiO₂, for the reduction of CO₂ to CH₄, with up to a 7-fold improvement as compared to pure TiO₂ under visible illumination.

As described above a number of improved semiconductor-graphene (graphene oxide) nanocomposites have been developed as potential catalysts for the photoreduction of CO₂, but their quantum yields and selectivities of products are still far from the acceptable level for practical applications. Thus, considerable efforts are being paid towards using transition metal complexes as visible light active photoredox catalysts for CO₂ reduction [114-118]. Such catalysts can have multiple and accessible redox states that have been shown to promote multiple electron transfer (MET) reactivity.

Furthermore, the formal reduction potentials can be systematically tuned through ligand modification to better match the potential required for CO₂ reduction. A number of transition metal based molecular complexes such as ruthenium(II) polypyridine carbonyl complex [119-122], cobalt(II) trisbipyridine [123], cobalt(III) macrocycles [124] rhenium [125, 126] and iridium complex [127, 128] with a photosensitizer have been developed as efficient photocatalytic systems to reduce CO₂ with relatively high quantum yield and high selectivity of products. Rhenium(I) complex and Re(bpy)(CO)₂X₂ (X = Cl, Br, I) were found to be superior catalysts for CO₂ reduction reaction. It was demonstrated that if the halogens were replaced by phosphene-based ligands then the yield of product was increased manifold [129]. This was attributed to the overlap between phosphorous and metal orbital. However, in some instances, a weak absorption in the visible region makes the utility of these complexes limited. This limitation can be overcome by using high nuclearity transition metal complexes having more than one metal unit joint together in a single complex [130-133]. Furthermore, supporting a soluble metal complex onto an inorganic solid matrix is one of the promising

approaches to combine the advantages of both homogeneous catalyst such as high reactivity, selectivity with heterogeneous one such ease of separation from products, lack of corrosiveness, and robustness for operation at high temperatures. In this context, a number of homogeneous photoredox complexes have been immobilized onto various supports such as TiO₂, organic polymers, ion exchange resins, etc. [134-136].

However, in some instances, the non-covalent attachment of the metal complex to support materials leads to the leaching of the active species during the reaction. Graphene/graphene oxide have been acknowledged to be ideal supporting materials for the attachment of homogenous redox metal complexes not only due to their high surface area and presence of various oxygen-containing functional groups, but work synergistically with metal complexes to provide better photocatalytic activity [137-140].

In a study by Zhu et al., [141] Ru(dcbpy)₃ complex was immobilized to rGO *via* non covalent interaction and then platinum nanoparticles (co-catalyst) were deposited on the surface of rGO. This hybrid system was found to be much more active for hydrogen evolution reaction in comparison to Ru(dcbpy)₃-sensitized Pt composites and rGO/Pt nanocomposites under visible light. Here, it is important to mention that photoexcited electrons flow from Ru(dcbpy)₃ to rGO to Pt because of low lying Fermi level of rGO and lower work function of Pt nanoparticles. Although, a number of homogeneous complexes such as zinc phthalocyanine, iron phthalocyanine, porphyrine, ruthenium complexes and organic dyes have been immobilized to GO/rGO for various applications, a very few reports are known on the photocatalytic CO₂ reduction.

Very recently, Kumar et al., [142] reported a novel GO tethered Co(II) phthalocyanine complex (CoPc-GO), prepared by a stepwise procedure, as an efficient, cost effective and recyclable photocatalyst for the reduction of CO₂. The covalent attachment of the CoPc to the GO support not only enhances the stability of the developed heterogeneous catalyst, but also prevents the leaching of the active metal from the support. The beauty of the method was that CoPc was also decorated on the basal plane of GO so a higher loading of CoPc was achieved in comparison to conventional methods where only edge groups were used (Figure 2) [143]. The prepared catalyst was used for the photocatalytic reduction of CO₂ by using water as a solvent and triethylamine as sacrificial donor.

Methanol was obtained as the major reaction product along with the formation of minor amount of CO (0.82%). It was found that GO-grafted CoPc exhibited higher photocatalytic activity than homogeneous CoPc as well as GO and showed good recoverability without significant leaching during the reaction. The yield of methanol after 48 h of reaction by using GO-CoPc catalyst in the presence of sacrificial donor triethylamine was found to be 3781.8881 μmol g⁻¹ cat and the conversion rate was found to be 78.7893 μmol g⁻¹ cat h⁻¹.

After the photoreduction experiment, the catalyst was easily recovered by filtration and reused for the subsequent recycling experiment without significant change in the catalytic efficiency.

In another report by Kumar et al., [144] ruthenium trinuclear polyazine complex was immobilized onto GO support through complexation using phenanthroline ligands (GO-phen) as coupling moieties (Ru-phen-GO). The three ruthenium units were joined through bipyrimidine bridging ligand and works like antenna [145, 146].

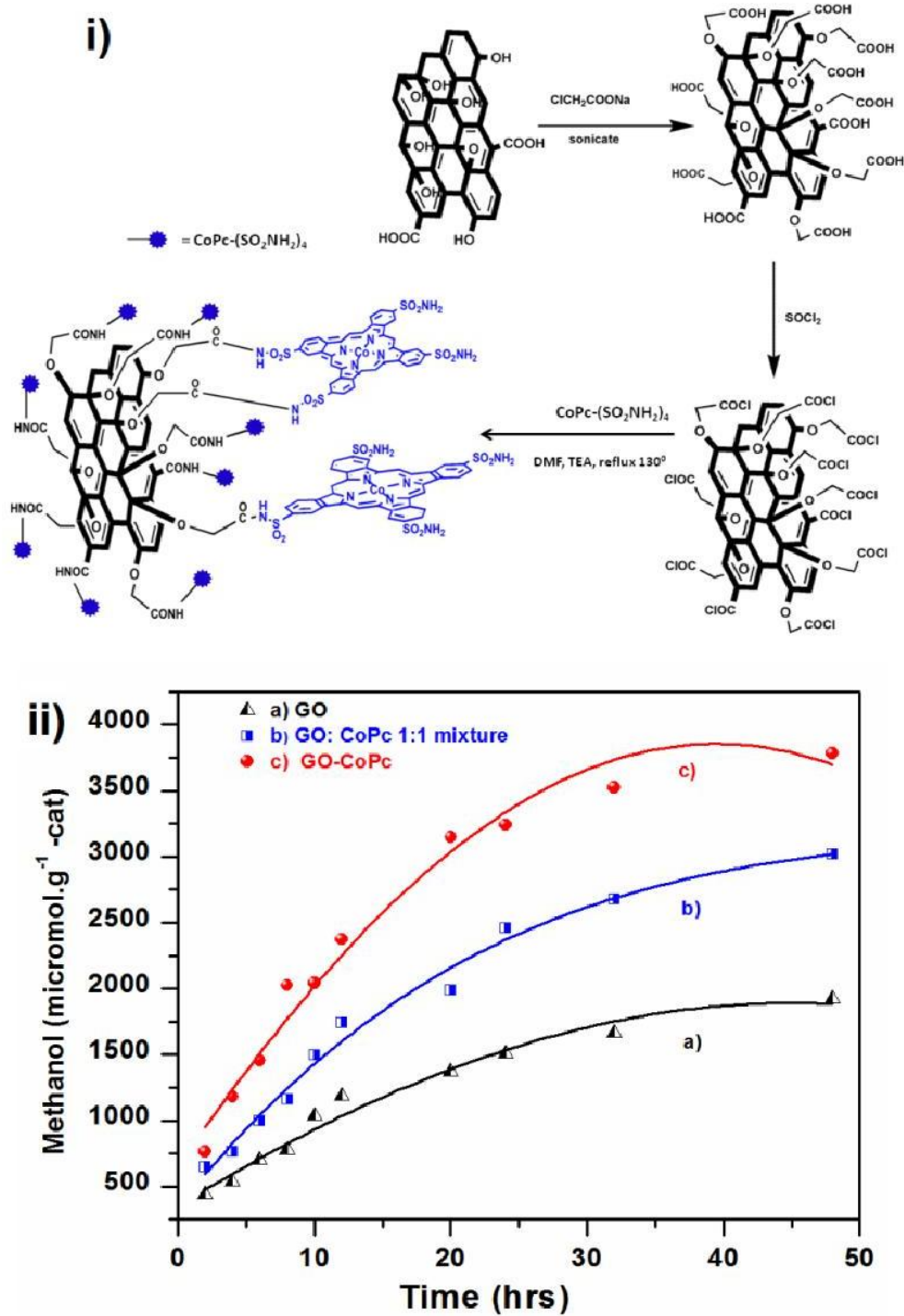


Figure 2. i) General synthetic scheme for the synthesis of CoPc-GO; ii) Methanol formation rate by using CoPc-GO catalyst.

The developed photocatalyst was used for the photocatalytic reduction of CO_2 to methanol by using 20 watt white cold LED flood light in dimethyl formamide/water mixture containing triethylamine as a reductive quencher. After 48 h illumination, the yield of methanol was found to be $3977.57 \pm 5.60 \mu\text{mol g}^{-1} \text{cat}$ (Figure 3). The developed photocatalyst exhibited higher photocatalytic activity than GO: $2201.40 \pm 8.76 \mu\text{mol g}^{-1} \text{cat}$ (Figure 3). After the reaction, the catalyst was easily recovered and reused for subsequent four runs without significant loss of catalytic activity and no leaching of the metal/ligand was detected during the reaction.

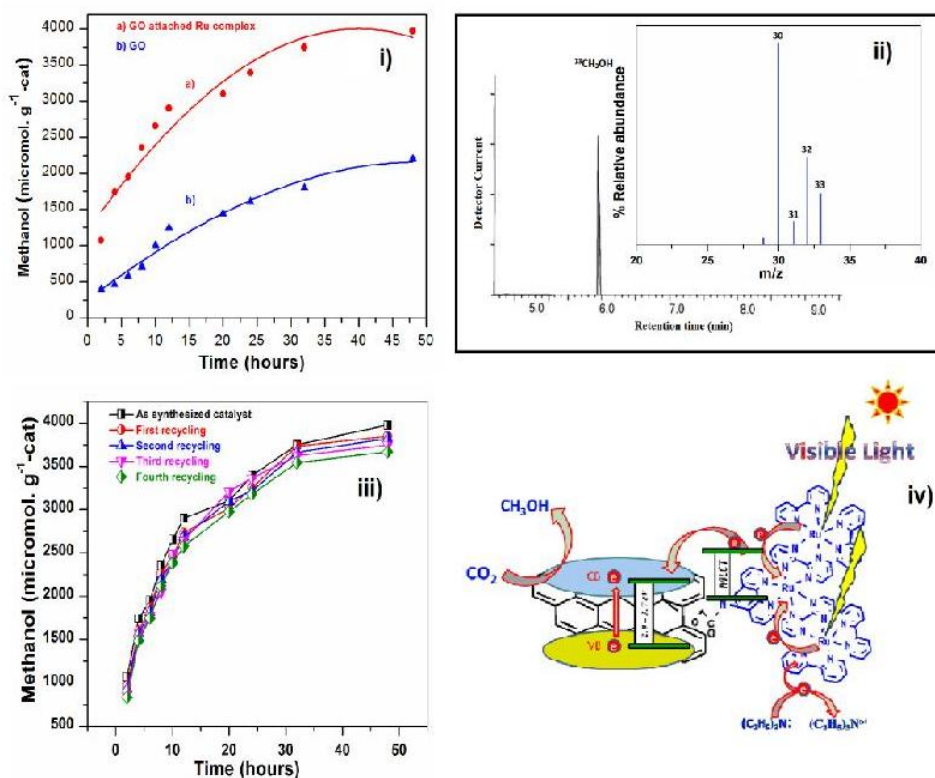


Figure 3. i) Methanol formation rate by using Ru-phen-GO catalyst; ii) GC-MS of product formed by using $^{13}\text{CO}_2$; iii) Recycling experiments; iv) Plausible reaction mechanism of the reaction.

CONCLUSION

In this chapter, we have attempted to review the prior art in the field of photoreduction of CO_2 using graphene-based nanocomposite materials as photoredox catalysts under visible light irradiation. We also covered its conversion to molecules that are precursors to or are directly usable as fuels.

In most studies, the enhanced photocatalytic performance of the nanocomposites was attributed to graphene playing the role as a medium for electron capturing/transporting. In case of graphene oxide/ TiO_2 nanocomposites, the photocatalytic enhancement can be brought

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up by: 1) increasing the amount of surface-adsorbed reactant species, 2) lowering the recombination rate of photogenerated electron-hole pairs, and 3) extending the light absorption range.

At this stage, it can be concluded from past work that graphene-based nanocomposites can be established as efficient heterogeneous catalysts to be applied as high performance photoactive catalytic materials for reduction of CO₂ to valuable products.

REFERENCES

- [1] Halmann, M. M., Steinberg, M. *Greenhouse Gas Carbon Dioxide Mitigation Science and Technology*, Lewis Publishers, Boca Raton, Florida. 1999.
- [2] Song, C. *Catal. Today* 2006, 115, 2–32.
- [3] Olah, G. A. *Angew. Chem. Int. Ed.* 2013, 52, 104–107.
- [4] Maginn, E. J. *J. Phys. Chem. Lett.* 2010, 1, 3478–3479.
- [5] Keeling, C. D.; Whorf, T. P. Atmospheric CO₂ records from sites in the SiO air sampling network, In: *Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center*, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN, US, 2005.
- [6] Solomon, S.; Quin, D.; Manning, M.; Marquis, M.; Averyt, K.; Tignor, M. M. B.; Miller, Jr. H. L.; Chen, Z. *The Physical Science Basis, Climate Change, 4th Assessment Report of the IPCC*; Cambridge University Press: Cambridge, UK, 2007.
- [7] Aresta, M.; Dibenedetto, A. *Dalton Trans.* 2007, 2975.
- [8] Aresta, M. *Carbon dioxide reduction and use as a chemical feedstock*, Tolman, W. B., Ed.; Wiley-VCH: Weinheim, Germany, 2006, 1–41.
- [9] Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. *Energy Environ. Sci.* 2010, 3, 43–81.
- [10] Omae, I. *Catal. Today* 2006, 115, 33–52.
- [11] Choi, J. C.; He, L. N.; Sakakura, T. *Green Chem.* 2002, 4, 230.
- [12] Xiaoding, X.; Moulijn, J. A. *Energy Fuels* 1996, 10, 305.
- [13] Zeverhoven, R.; Eloneva, S.; Teir, S. *Catal. Today* 2006, 115, 73.
- [14] Ferguson, J. E. *Carbon Dioxide. MacMillan Encyclopedia of Chemistry*, 1997, MacMillan References, New York, Vol. 1, 302–308.
- [15] Morris, A. J.; Meyer, G. J.; Fujita, E. *Acc. Chem. Res.* 2009, 42, 1983–1994.
- [16] Indrakanti, V. P.; Kubicki, J. D.; Schobert, H. H. *Energy Environ. Sci.* 2009, 2, 745–758.
- [17] Fujita, E. *Coord. Chem. Rev.* 1999, 185–186, 373–384.
- [18] Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* 2009, 38, 89–99.
- [19] Barber, J.; Tran, P. D. *J. R. Soc. Interface* 2013, 10, 20120984.
- [20] Roy, S. C.; Varghese, O. K.; Paulose, M.; Grimes, G. A. *ACS Nano* 2010, 4, 1259–1278.
- [21] Michl, J. *Nature Chem.*, 2011, 3, 268–269.
- [22] Habisreutinger, S. N.; Mende, L. S.; Stolarczyk, J. K. *Angew. Chem. Int. Ed.* 2013, 52, 7372–7408.
- [23] Tahir, M.; Amin, N. S. *Energy Conversion Management* 2013, 76, 194–214.

- [24] Sakthivel, S.; Neppolian, B.; Shankar, M. V.; Arabindoo, B.; Palanichamy, M.; Murugesan, V. *Solar Energy Mater Solar Cells*, 2003, 77, 65–82.
- [25] Li, X.; Wang, Q.; Zhao, Y.; Wu, W.; Chen, J.; Meng, H. *J. Colloid Interface Sci.* 2013, 411, 69–75.
- [26] Liu, Y.; Huang, B.; Dai, Y.; Zhang, X.; Qin, X.; Jiang, M.; Whangbo, M.-H. *Catal. Commun.* 2009, 11, 210–213.
- [27] Wang, Z. Y.; Chou, H. C.; Wu, J. C. S.; Tsai, D. P.; Mul, G. *Appl. Catal. A* 2010, 380, 172–177.
- [28] Pan, P. W.; Chen, Y. W. *Catal. Commun.* 2007, 8, 1546–1549.
- [29] Naval, S.; Dhakshinamoorthy, A.; Ivaro, M.; Garcia, H. *ChemSusChem* 2013, 6, 562–577.
- [30] Cowan, A. J.; Durrant, J. R. *Chem. Soc. Rev.* 2013, 42, 2281–2293.
- [31] Benson, E. E.; Kubiak, C. P.; Sathruma, A. J.; Smieja, J. M. *Chem. Soc. Rev.* 2009, 38, 89–99.
- [32] Tran, P. D.; Wong, L. H.; Barber, J.; Loo, J. S. C. *Energy Environ. Sci.* 2012, 5, 5902–5918.
- [33] Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Anpo, M. *J. Phys. Chem. B* 1999, 103, 3120–3127.
- [34] Liu, L.; Gao, F.; Zhao, H.; Li, Y.; *Appl. Catal. B* 2013, 134–135, 349–358.
- [35] Slamet, H. W.; Nasution, E.; Purnama, S.; Kosela, J.; Gunlazuardi, J. *Catal. Commun.* 2005, 6, 313–319.
- [36] Li, Y.; Wang, W.-N.; Zhan, Z.; Woo, M.-H.; Wu, C.-Y.; Biswas, P. *Appl. Catal. B* 2010, 100, 386–392.
- [37] Izumi, Y. *Coord. Chem. Rev.* 2013, 257, 171–186.
- [38] Liu, S.; Guo, E.; Yin, L. *J. Mater. Chem.* 2012, 22, 5031–5041.
- [39] Yu, J.; Ran, J. *Energy Environ. Sci.* 2011, 4, 1364–1371.
- [40] Yanyuan, W.; Hanming, D. *Chin. J. Catal.* 2011, 32, 36–45.
- [41] Liu, L.; Pitts, D. T.; Zhao, H.; Zhao, C.; Li, Y. *Appl. Catal. A* 2013, 467, 474–482.
- [42] Sasirekha, N.; Basha, S. J. S.; Shanthi, K. *Appl. Catal. B* 2006, 62, 169–180.
- [43] Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* 2001, 293, 169–293.
- [44] Zhang, Q. W.; Wang, J.; Yin, S.; Sato, T.; Saito, F. *J. Am. Chem. Soc.* 2004, 126, 1161–1163.
- [45] Khan, S. U. M.; Al-Shahry, M.; Ingler, Jr. W. B. *Science* 2002, 297, 2243–2245.
- [46] Zhanga, Q.; Li, Y.; Ackermanb, E. A.; Josifovskac, M. G. Li, H. *Appl. Catal. A* 2011, 400, 195–202.
- [47] Sato, S.; Koike, K.; Inoue, H.; Ishitani, O. *Photochem. Photobiol. Sci.* 2007, 6, 454–461.
- [48] Fujita, E.; Milder, S. J.; Brunschwig, B. S. *Inorg. Chem.* 1992, 31, 2079–2085.
- [49] Lang, X.; Chen, X.; Zhao, J. *Chem. Soc. Rev.* 2014, 43, 473–486.
- [50] Suzuki, T. M.; Tanaka, H.; Morikawa, T.; Iwaki, M.; Sato, S.; Saeki, S.; Inoue, M.; Kajino, T.; Motohiro, T. *Chem. Commun.* 2011, 47, 8673–8675.
- [51] Sato, S.; Morikawa, T.; Saeki, S.; Kajino, T.; Motohiro, T. *Angew Chem. Int. Ed.*, 2010, 49, 5101–5105.
- [52] Leary, R.; Westwood, A. *Carbon* 2011, 49, 741–772.
- [53] Huang, X.; Qi, X.; Boey, F.; Zhang, H. *Chem. Soc. Rev.* 2012, 41, 666–686.
- [54] Dai, L.; Chang, D. W.; Baek, J. B.; Lu, W. *Small* 2012, 8, 1130–1166.

- [55] Yu, Y.; Yu, J. C.; Yu, J. G.; Kwok, Y. C.; Che, Y. K.; Zhao, J. C.; Ding, L.; Ge, W. K.; Wong, P. K. *Appl. Catal. A* 2005, 289, 186-196.
- [56] An, X.; Yu, J. C. *RSC Adv.* 2011, 1, 1426-1434.
- [57] Park, Y.; Kang, S. H.; Choi, W. *Phys. Chem. Chem. Phys.* 2011, 13, 9425-9431.
- [58] Gao, Y.; Pu, X.; Zhang, D.; Ding, G.; Shao, X.; Ma, J. *Carbon* 2012, 50, 4093-4101.
- [59] Geim, A. K.; Novoselov, K. S. *Nature Mater.* 2007, 6, 183-191.
- [60] Novoselov, K.; Geim, A.; Morozov, S.; Jiang, D.; Zhang, Y.; Dubonos, S.; Grigorieva, I.; Firsov, A. *Science* 2004, 306, 666-669.
- [61] Meyer, J. C.; Geim, A.; Katsnelson, M. Novoselov, K.; Booth, T.; Roth, S. *Nature* 2007, 446, 60-63.
- [62] Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. *Rev. Mod. Phys.* 2009, 81, 109-162.
- [63] Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S. *Prog. Mater. Sci.* 2011, 56, 1178-1271.
- [64] Rao, C. N. R.; Sood, A. K.; Subrahmanyam, K. S.; Govindaraj, A. *Angew. Chem. Int. Ed.* 2009, 48, 7752-7777.
- [65] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D. Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. *Nature* 2005, 438, 197-200.
- [66] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* 2004, 306, 666-669.
- [67] Du, X.; Skachko, I.; Barker, A.; Andrei, E. Y. *Nat. Nanotechnol.* 2008, 3, 491-495.
- [68] Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. *Nano Lett.* 2008, 8, 902-907.
- [69] Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E. P.; Nika, D. L.; Balandin, A. A.; Bao, W.; Miao, F.; Lau, C. N. *Appl. Phys. Lett.* 2008, 92, 151911-151913.
- [70] Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* 2008, 321, 385.
- [71] Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; Keffe, M. O'; Yaghi, O. M. *Nature* 2004, 427, 523-527.
- [72] Stoller, M. D.; Park, S.; Zhu, Y.; An, J.; Ruoff, R. S. *Nano Lett.* 2008, 8, 3498-3502.
- [73] Mas, A. A.; Wei, D. *Nanomaterials* 2013, 3, 325-356.
- [74] Biro, L. P.; Incze, P. N.; Lambin, P. *Nanoscale* 2012, 4, 1824-1839.
- [75] Eda, G.; Fanchini, G.; Chhowalla, M. *Nature Nanotechnol.* 2008, 3, 270-274.
- [76] Juang, Z. Y.; Wu, C. Y.; Lu, A. Y.; Su, C. Y.; Leou, K. C.; Chen, F. R.; Tsai, C. H. *Carbon* 2010, 48, 3169-3174.
- [77] Sharma, P.; Hussain, N.; Das, M. R.; Deshmukh, A. B.; Shelke, M. V.; Szunerits, S.; Boukherroub, R. *Handbook of Research on Nanoscience, Nanotechnology and Advanced Materials*; Ed. Mohamed Bououdina, M.; Davim, J. P., IGI Global; US, 2014, Chapter 10, pp. 196-225.
- [78] Das, M. R.; Sharma, P.; Borah, S. C.; Szunerits, S.; Boukherroub, R. *Innovative Graphene Technologies: Developments and Characterization*; Tiwari A. Rapra Publishers, US, 2013.
- [79] Akhavan, O.; Ghaderi, E. *J. Phys. Chem. C* 2009, 113, 20214-20220.
- [80] Akhavan, O.; Ghaderi, E. *Carbon* 2012, 50, 1853-1860.
- [81] Zhang, X.; Sun, Y.; Cui, X.; Jiang, Z. *Int. J. Hydrogen Energy* 2012, 37, 811-815.
- [82] Cheng, P.; Yang, Z.; Wang, H.; Cheng, W.; Chen, M.; Shangguan, W.; Ding, G. *Int. J. Hydrogen Energy* 2012, 37, 2224-2230.

Complimentary Contributor Copy

- [83] Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K. *Renew. Sust. Energy Rev.* 2007, 11, 401–425.
- [84] Yang, N. L.; Zhai, J.; Wang, D.; Chen, Y. S.; Jiang, L. *ACS Nano* 2010, 4, 887–894.
- [85] Sun, S. R.; Gao, L.; Liu, Y. Q. *Appl. Phys. Lett.* 2010, 96, 083113.
- [86] Xiang, Q.; Yu, J.; Jaroniec, M. *Chem. Soc. Rev.* 2012, 41, 782–796.
- [87] Liu, S.; Tian, J.; Wang, L.; Luo, Y.; Sun, X. *Catal. Sci. Technol.* 2012, 2, 339–344.
- [88] Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. *ACS Nano* 2010, 4, 380–386.
- [89] Zhang, Y.; Tang, Z. R.; Fu, X.; Xu, Y. J. *ACS Nano* 2010, 4, 7303–7314.
- [90] Yang, Y.; Ren, L.; Zhang, C.; Huang, S.; Liu, T. *ACS Appl. Mater. Interfaces* 2011, 3, 2779–2785.
- [91] Chen, P.; Xiao, T. Y.; Li, H. H.; Yang, J. J.; Wang, Z.; Yao, H. B.; Yu, S. H. *ACS Nano* 2012, 6, 712–719.
- [92] Zhu, M.; Chen, P.; Liu, M. *ACS Nano* 2011, 5, 4529–4536.
- [93] Gao, E.; Wang, W.; Shang, M.; Xu, J. *Phys. Chem. Chem. Phys.* 2011, 13, 2887–2893.
- [94] Khalida, N. R.; Ahmed, E.; Hong, Z.; Zhang, Y.; Ullah, M.; Ahmed, M. *Ceram. Int.* 2013, 39, 3569–3575.
- [95] Jing, L.; Yang, Z. Y.; Zhao, Y. F.; Zhang, Y. X.; Guo, X.; Yan, Y. M.; Sun, K. N. *J. Mater. Chem. A* 2014, 2, 1068–1075.
- [96] Mukherji, A.; Seger, B.; Lu, G. Q.; Wang, L. *ACS Nano* 2011, 5, 3483–3492.
- [97] Stengl, V.; Popelkova, D.; Vlacil, P. *J. Phys. Chem. C* 2011, 115, 25209–25218.
- [98] Jiang, G.; Lin, Z.; Chen, C.; Zhu, L.; Chang, Q.; Wang, N.; Wei, W.; Tang, H. *Carbon* 2011, 49, 2693–2701.
- [99] Tu, W.; Zhou, Y.; Liu, Q.; Tian, Z.; Gao, J.; Chen, X.; Zhang, H.; Liu, J.; Zou, Z. *Adv. Funct. Mater.* 2012, 22, 1215–1221.
- [100] Zhou, Y.; Bao, Q. L.; Tang, L. A. L.; Zhong, Y. L.; Loh, K. P. *Chem. Mater.* 2009, 21, 2950–2956.
- [101] Wang, P. Q.; Bai, Y.; Luo, P. Y.; Liu, J. Y. *Cat. Commun.* 2013, 38, 82–85.
- [102] Brodie, B. C. *Phil. Trans.* 1859, 149, 249–259.
- [103] Loh, K. P.; Bao, Q.; Ang, P. K.; Yang, J. *J. Mater. Chem.* 2010, 20, 2277–2289.
- [104] Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zboril, R.; Kim, K. S. *Chem. Rev.* 2012, 112, 6156–6214.
- [105] Loh, K. P.; Bao, Q.; Eda, G.; Chhowalla, M. *Nature Chem.* 2010, 2, 1015–1024.
- [106] Eda, G.; Mattevi, C.; Yamaguchi, H.; Kim, H.; Chhowalla, M. *J. Phys. Chem. C* 2009, 113, 15768–15771.
- [107] Hsu, H. C.; Shown, I.; Wei, H. Y.; Chang, Y. C.; Du, H. Y.; Lin, Y. G.; Tseng, C. A.; Wang, C. H.; Chen, L. C.; Lind, Y. C.; Chen, K. H. *Nanoscale* 2013, 5, 262–268.
- [108] Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* 1958, 80, 1339.
- [109] Eda, G.; Chhowalla, M. *Adv. Mater.* 2010, 22, 2392.
- [110] Yadav, R. K.; Baeg, J. O.; Oh, G. H.; Park, N.-J.; Kong, K.-J.; Kim, J.; Hwang, D. W.; Biswas, S. K. *J. Am. Chem. Soc.* 2012, 134, 11455–11461.
- [111] An, X.; Li, K.; Tang, J.; *ChemSusChem*. 2014, 7, 1086–1093.
- [112] Tan, L. L.; Ong, W. J.; Chai, S. P.; Mohamed, A. R. *Nanoscale Res. Lett.* 2013, 8, 465–474.
- [113] Liang, Y. T.; Vijayan, B. K.; Gray, K. A.; Hersam, M. C. *Nano Lett.* 2011, 11, 2865–2870.

- [114] Takeda, H.; Koizumi, H.; Okamoto, K.; Ishitani, O. *Chem. Commun.* 2014, 50, 1491-1493.
- [115] Inagakia, A.; Akita, M. *Coord. Chem. Rev.* 2010, 254, 1220-1239.
- [116] Reithmeier, R.; Bruckmeier, C.; Rieger, B. *Catalysts* 2012, 2, 544-571.
- [117] Takeda, H.; Ishitani, O. *Coord. Chem. Rev.* 2010, 254, 346-354.
- [118] Cokoja, M.; Bruckmeier, C.; Rieger, B.; Kuhn, F.; Hermann, W. A. *Angew. Chem. Int. Ed.* 2011, 50, 8510-8537.
- [119] Planas, N.; Ono, T.; Vaquer, L.; Miro, P.; Buchholz, J. B.; Gagliardi, L.; Cramer, C. J.; Llobet, A. *Phys. Chem. Chem. Phys.* 2011, 13, 19480-19484.
- [120] Voyame, P.; Toghill, K. E.; Mendez, M. A.; Girault, H. H. *Inorg. Chem.* 2013, 52, 10949-10957.
- [121] Chen, Z.; Concepcion, J. J.; Brennaman, M. K.; Kang, P.; Norris, M. R.; Hoertz, P. G.; Meyer, T. J. *Proc. Nat. Acad. Sci.* 2012, 109, 15606-15611.
- [122] Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. *Proc. Nat. Acad. Sci.* 2012, 2012, 1-6.
- [123] Grodkowski, J.; Neta, P.; Fujita, E.; Mahammed, A.; Simkhovich, L.; Gross, Z. *J. Phys. Chem. A* 2002, 106, 4772-4778.
- [124] Ogata, T.; Yamamoto, Y.; Wada, Y.; Murakoshi, K.; Kusaba, M.; Nakashima, N.; Ishida, A.; Takamuku, S.; Yanagida, S. *J. Phys. Chem.* 1995, 99, 11916-11922.
- [125] Gholamkhash, B.; Mametsuka, H.; Koike, K.; Tanabe, T.; Furue, M.; Ishitani, O. *Inorg. Chem.* 2005, 44, 2326-2336.
- [126] Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. *Photochem. J. Photobiol. A* 1996, 96, 171-174.
- [127] Sato, S.; Morikawa, T.; Kajino, T.; Ishitani, O. *Angew. Chem. Int. Ed.* 2013, 52, 988-992.
- [128] Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* 2009, 131, 8730-8731.
- [129] Sato, S.; Koike, K.; Inoue, H.; Ishitani, O. *Photochem. Photobiol. Sci.* 2007, 6, 454-461.
- [130] Fujita, E.; Milder, S. J.; Brunschwig, B. S. *Inorg. Chem.* 1992, 31, 2079-2085.
- [131] Miao, R.; Mongelli, M. T.; Zigler, D. F.; Winkel, B. S. J.; Brewer, K. J. *Inorg. Chem.* 2006, 45, 10413-10415.
- [132] Miao, R.; Brewer, K. J. *Inorg. Chem. Commun.* 2007, 10, 307-312.
- [133] Windle, C. D.; Campian, M. V.; Klair, A. K. D.; Gibson, E. A.; Perutz, R. N.; Schneider, J. *Chem. Commun.* 2012, 48, 8189-8191.
- [134] Zhou, X. T.; Ji, H. B.; Huang, X. J. *Molecules*, 2012, 17, 1149-1158.
- [135] Sato, S.; Morikawa, T.; Saeki, S.; Kajino, T.; Motohiro, T. *Angew. Chem. Int. Ed.* 2010, 49, 5101-5105.
- [136] Hirose, T.; Maeno, Y.; Himed, Y. *J. Mol. Catal. A* 2003, 193, 27-32.
- [137] Ragoussi, M. E.; Malig, J.; Katsukis, G.; Butz, B.; Spiecker, E.; Torre, G. de la; Torres, T.; Guldi, D. M. *Angew. Chem. Int. Ed.* 2012, 51, 6421-6425.
- [138] Zhu, J.; Li, Y.; Chen, Y.; Wang, J.; Zhang, B.; Zhang, J.; Blau, W. J. *Carbon* 2011, 49, 1900-1905.
- [139] Mahyari, M.; Shaabani, A., *Appl. Catal. A* 2014, 469, 524-531.
- [140] Yu, Y.; Zhou, M.; Shen, W.; Zhang, H.; Cao, Q.; Cui, H. *Carbon* 2012, 50, 2539-2545.

Complimentary Contributor Copy

-
- [141] Zhu, M.; Dong, Y.; Xiao, B.; Du, Y.; Yang, P.; Wang, X. *J. Mater. Chem.* 2012, 22, 23773-23779.
- [142] Kumar, P.; Kumar, A.; Sreedhar, B.; Sain, B.; Ray, S. S.; Jain, S. L. *Chem. Eur. J.* 2014, 20, 6154-6161.
- [143] Sun, X.; Liu, Z.; Welsher, K.; Robinson, J. T.; Goodwin, A.; Zaric, S.; Dai, H. *Nano Res.* 2008, 1, 203-212.
- [144] Kumar, P.; Sain, B.; Jain, S. L. *J. Mater. Chem. A* 2014, 2, 11246-11253.
- [145] Fleming, C. N.; Maxwell, K. A.; Simone, J. M. D.; Meyer, T. J.; Papanikolas, J. M. *J. Am. Chem. Soc.* 2001, 123, 10336-10347.
- [146] Rybtchinski, B.; Sinks, L. E.; Wasielewski, M. R. *J. Am. Chem. Soc.* 2004, 126, 12268-12269.