

# Chapter 6

## Polymeric Semiconductors as Efficient Photocatalysts for Water Purification and Solar Hydrogen Production



Sudesh Kumar, Raghava Reddy Kakarla, Ch. Venkata Reddy, Enamul Haque, Veera Sadhu, and S. Naveen

### Contents

6.1	Introduction .....	126
6.2	Photocatalysis .....	127
6.2.1	Basic Principles of Photocatalytic Reaction .....	128
6.2.2	Photocatalytic Properties .....	128
6.2.3	Photocatalytic Mechanism .....	129
6.3	Photocatalytic Functional Materials: Synthesis, Properties and Applications .....	130
6.3.1	Graphitic Carbon Nitride (g-C <sub>3</sub> N <sub>4</sub> ) .....	130
6.3.2	Metal-Organic Framework (MOF)-Based Photocatalysts .....	134
6.3.3	TiO <sub>2</sub> -Based Hybrid Photocatalysts .....	136
6.3.4	Graphene Oxide (GO)-Based Photocatalyst for Dye Degradation and H <sub>2</sub> Evolution .....	144
6.4	Conclusion .....	149
	References .....	151

---

S. Kumar

Department of Chemistry, Banasthali University, Banasthali Vidyapith, Vanasthali, Rajasthan, India

R. R. Kakarla (✉)

School of Chemical & Biomolecular Engineering, The University of Sydney, Sydney, NSW, Australia

C. V. Reddy (✉)

School of Mechanical Engineering, Yeungnam University, Gyeongsan, South Korea

E. Haque

School of Medicine and Centre for Molecular and Medical Research, Deakin University, Waurn Ponds, VIC, Australia

V. Sadhu (✉)

School of Physical Sciences, Banasthali University, Banasthali Vidyapith, Vanasthali, Rajasthan, India

S. Naveen

School of Basic Sciences, Jain University, Bangalore, India

© Springer Nature Switzerland AG 2019

Inamuddin et al. (eds.), *Nanophotocatalysis and Environmental Applications*, Environmental Chemistry for a Sustainable World 31, [https://doi.org/10.1007/978-3-030-04949-2\\_6](https://doi.org/10.1007/978-3-030-04949-2_6)

125

**Abstract** Environmental contamination is one of the serious issues to an environment and human health due to the contamination of a wide range of organic chemicals, industrial dyes and other hazardous substances in the drinking water, air and land. The innovation of the photocatalytic process has been presented to be the green and feasible method for the environmental decontamination.

Photocatalysis has a wide range of application such as wastewater treatment (organic dye degradation), disinfection, solar water splitting, CO<sub>2</sub> reduction and air purification. Many photocatalysts have been developed for the disintegration of water into CO<sub>2</sub>, H<sub>2</sub>O and other non-harmful substances. Compounds, with the help of O<sub>2</sub>, act as clean oxidants. Among various photocatalytic materials, the polymeric semiconducting photocatalysts show highly efficient photocatalytic performance for various photocatalytic applications. For example, oxygenated groups present on the surface of graphene oxide (GO) make it effective in the removal of pollutants such as phenol, chlorophenol and industrial dyes. In this chapter, we discussed various chemical methodologies, properties and photocatalytic applications of polymeric semiconductors (carbon nitride, C<sub>3</sub>N<sub>4</sub>), graphene and metal-organic framework (MOF)-based hybrid nanostructured photocatalysts for the water purification and the solar hydrogen production. Such efficient photocatalysts are expected to solve the issues of environmental remediation.

**Keywords** Graphene oxide · Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) · Metal-organic framework (MOF) · TiO<sub>2</sub> · Semiconductors · Functional heterostructured hybrid photocatalysts · Photocatalysis · Antibacterial activity · Photocatalysis fundamentals · Catalysts characterization · Photocatalysts kinetics · Photocatalytic mechanism · Environmental applications · Environmental decontamination · Organic dye degradation · Wastewater purification · Hydrogen evolution reactions · Solar hydrogen production

## 6.1 Introduction

A common problem spotted across the globe is environmental contamination. It's the burning issue which can't be over sighted. Among all the sort of environmental problems, the one striking at the top of the list is water pollution. Water pollution is probably the most important of the current issues, and the concern still continues for future also. The idea of using the water resources in a manner that it should fulfil our needs for the present inadequacy shouldn't be witnessed in future.

The idea of how to wisely use the available should pop up the head. It's not only the inadequacy of water resources that should concern but also the consequences of consumption of polluted water. With the increasing advancements in technology and changing lifestyles, our natural resources are getting exploited and overconsumed. Water is indispensable for both living and existence. Data states that 88% of the

annual diarrheal occurrence is due to the unsafe water and improper hygiene (Bivins et al. 2017). The cause for this diarrheal outbreak is chiefly the human activity or the polluted water.

Water pollution could be classified under two headings:

1. *Point source*: In point source pollution, there is the direct emission of effluents and contaminants into the water bodies. The discharge could be regulated.
2. *Non-point source*: The pollutants are indirectly discharged into water bodies, and it can't be controlled.

The development of clean environment free from any fossil is very important. Thus, it's essential to think about such technologies which make water resources pollution free.

## 6.2 Photocatalysis

The catalyst could be defined as a substance which changes the rate of a reaction without being itself involved in the reaction. In other words, the catalyst is the substance which lowers the free activation energy of any reaction (Dasireddy and Likozar 2017). When any reaction is accelerated in the presence of a catalyst, then such reaction is called photocatalysis (Hathway et al. 2009). Photocatalysis is established on the ability of photocatalyst to both adsorb reactant and absorb photon, respectively (Job and Kang 2013).

Photocatalytic innovation has been exhibited to be one of the “green” and practicable systems for the natural remediation. Along these lines, ecological photocatalytic processes, including sanitization of water and air, risky environmental waste remediation, water refinement, freshening up, self-cleaning and antibacterial activity, have caused increasingly consideration as of late. Although, inferable from the low photocatalytic effectiveness and the utilization of light are still exceptionally constrained. Consequently, more examinations are required from the perspective of functional utilize.

The favourable activities including natural tainting, self-clean structures, freshening up, against the bacterial activity, antifogging settling cleaning activity. Moreover, nitrogen oxides (NO<sub>x</sub>) are noticeable all around, and it is important to remove such harmful air pollutants by oxidizing NO<sub>x</sub> to nitrates using photocatalysts. As indicated by the overview directed by the research organization, the market of photograph catalysis with respect to the issues of condition increment ceaselessly.

Both the mechanical and financial significance of photocatalysis have expanded extensively over the past decade. An assortment of utilizations extending from antifogging, self-cleaning surfaces via air and water filtration processes and sun-powered actuated hydrogen creation has been produced, and huge numbers of these have advanced into business items. Photocatalysts stimulate or quicken

compound responses coming about, for instance, in a disintegration of natural particles. Because of their expansive surface zone, nanosized particles demonstrate an essentially improved reactivity contrasted with bigger particles or mass material (Chen et al. 2000).

Keeping in mind the end goal to address this critical issue, broad research is in progress to create progressed scientific, physicochemical and biochemical techniques for the portrayal and disposal of risky concoction mixes from contaminated water, air and soil. Semiconductor-based photocatalysis is planned to be both enhancing and reciprocal to a portion of the more traditional methodologies for the pulverization or change of perilous substance squanders, e.g. high-temperature burning, altered enacted slop assimilation, anaerobic absorption and regular physicochemical treatment.

### **6.2.1 Basic Principles of Photocatalytic Reaction**

The word photocatalysis is a combination of photo and catalysis words, in which photo means the light and catalysis defines the process where the substance participates in the rate of a reaction without bringing about any change in its own composition and rate of reaction. Photocatalysis is a process where either direct irradiation or irradiation by catalyst accelerates the reaction.

The photocatalytic reaction could be classified into two categories:

1. *Environment purification*: The reactions occurring under this category are followed by decreasing in Gibbs free energy and are further categories as a lower-state reaction.
2. *High energy conversions*: These are led by a large positive change in the values of Gibbs free energy (Chen and Wang 2012).

The band gap is the difference of energy between conduction band valence bands. It's important to name the knowledge of band gap while studying semiconductor photocatalysis. When semiconductor absorbs photon energy greater than those of band gap, then the valence band electrons excite to the conduction band and leave behind a hole in valence band. These photoexcited electrons have the potential to reduce the substances, whereas the holes of valence band have the potential to oxidize substances (Man et al. 2017). One of most important and efficient technologies for the remediation of the environment is photocatalysis. It's listed in one of the green environmental remediation techniques.

### **6.2.2 Photocatalytic Properties**

Photocatalysis is an emerging advancement that allows a wide range of uses, including degradation of organics dyes, antibacterial activity and production of

fuel splitting of water and carbon dioxide degradation. Numerous inorganic semiconducting materials have been considered as photocatalysts, and the flexibility of these materials have grown in the current years. By understanding the properties of various photochemical materials and their exhibition of reaction forms, it is necessary to plan their combinations.

The main places of interest of the photocatalytic framework are:

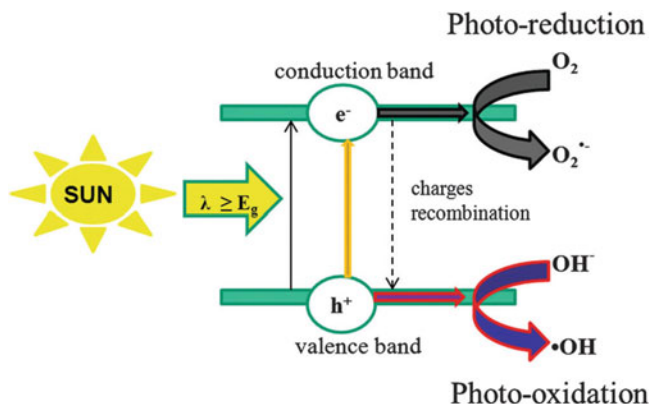
- (i) Desired band gap
- (ii) Appropriate morphological structures
- (iii) Large surface area
- (iv) Dependability
- (v) Reusability

Semiconducting metal oxides, for instance, oxides of vanadium (V), chromium (Cr), titanium (Ti), tin (Sn), zinc (Zn), tungsten (WO) and cerium (Ce) having above-mentioned characteristics, take after comparable photocatalytic procedures, for example, light ingestion, which incites an accuse division procedure of the arrangement of positive openings that can oxidize natural substrates. Among these semiconducting metal oxides ( $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$  and  $\text{CeO}_2$ ), which are plenteous in nature, have been broadly utilized as the photocatalysts, especially as the heterogeneous photocatalytic materials for very long time. This is due to their unique properties of biocompatibility, extraordinary strength in a variety of conditions and ability to generate the charge transporters when it permits with a measure of light vitality. The positive mix of electronic structure, the properties of charge transport and light absorption and energized functioning period of metal oxides have made it workable for their application as efficient photocatalysts.

Graphene oxide (GO) is a functional form of graphene sheet consist of rich oxygenated groups on their surface. The basal plane of GO is covalently attached by hydroxyl (OH) and epoxy groups, while carboxyl (-COOH) groups are originated at the edges of GO nanosheets. These -OH functional groups make of GO a hydrophilic nature and improve the dispersion in aqueous systems. The band gap of GO can be controlled by modifying the oxidation rate (Kim et al. 2003a). The good dispersion in water and its controllable band gap values motivate to explore this low-cost potential material for the applications in the research area of photocatalysis.

### 6.2.3 Photocatalytic Mechanism

At the point when a given photocatalyst is illuminated by the light of energy more prominent than the band hole energy of the photocatalytic material, the charge partition happens. At that point, using the electrons and openings produced by the charge division, the photocatalyst stimulates an oxidation-decrease response. Specifically,  $\text{TiO}_2$ , with generally expansive band hole energy of 3.0–3.2 eV, can



**Fig. 6.1** Photocatalytic activation of a semiconductor and primary reactions occurring on its surface. (Reproduction from Colmenares and Luque 2014, Royal Society of Chemistry)

accomplish an effective oxidation-lessening response with the bright beams introduce in our living condition (Szabó et al. 2006).

The effect of the photocatalyst concentration was investigated on the evolution of hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) from water ( $H_2O$ ) under illumination of the light. No photocatalytic material for the part of water has yet been marketed due to a need in proficiency, high generation cost and so forth. In any case, the advance accomplished in the photocatalytic material to date depends on the consequences of these investigations. Different photocatalytic materials for the water disintegration have been revealed and created, a significant number of which use  $TiO_2$  and the cases of which contain  $TiO_2$  particles conveying a metal, for example, platinum or rhodium or an oxide, for example,  $RuO_2$ . The general photocatalytic mechanism of a semiconductor and primary reactions take place on its surface are illustrated in Fig. 6.1.

## 6.3 Photocatalytic Functional Materials: Synthesis, Properties and Applications

### 6.3.1 Graphitic Carbon Nitride ( $g-C_3N_4$ )

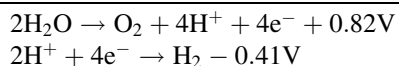
#### 6.3.1.1 Synthesis of Polymeric $g-C_3N_4$

A carbene is found to be a thermal robust compound which is non-volatile up to  $600^\circ C$ . It possesses one of the highest thermal stability for an organic compound. The thermal stability possessed by this molecule is higher than the entire thermal stable polymer, for example, aromatic polyamides. The thermal stability of polymeric graphite shows variations on the basis of different methods of synthesis and other parameters. The variation observed may be caused by the difference in the

condensation method (Komatsu and Nakamura 2001; Yan et al. 2009; Miller et al. 2002; Gillan 2000). The optimum Van Der Waal interaction between each layer of carbon nitride allows it to be soluble in almost all the samples such as water THF, DMF, alcohol, toluene, etc. Assessment of optical properties could be done by UV-Vis absorption and photoluminescence. Some theoretical calculation explained carbon nitride as a semiconductor. The carbon nitride obtained after self-condensation are macro powders with the small surface area.

### 6.3.1.2 Photocatalytic Mechanism of g-C<sub>3</sub>N<sub>4</sub>

The current studies on photocatalysis are primarily focused on the development of the materials having small band gap and desirable positions of band gap for the splitting of water (Gillan 2000). Maximum of the semiconductors are chiefly inorganic metal centred, consisting of metal oxides, sulphides and nitrides (Liang et al. 2017). The metal-based semiconductors are found in nature and in enzyme and act as active sites for photocatalytic degradation of contaminants present in the water. The g-C<sub>3</sub>N<sub>4</sub> possesses all the electronic properties suitable for the heterogeneous photocatalyst. This molecule also possesses a band gap of 2.7 eV which further corresponds to the band gap of 460 nm. The energy required for the production of H<sub>2</sub> from H<sub>2</sub>O can be calculated as follows:



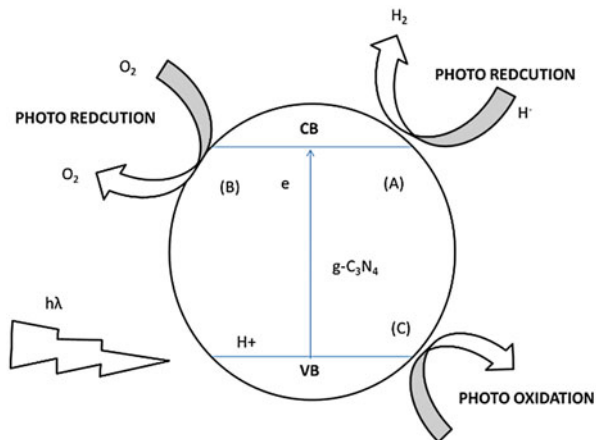
The photo water splitting in presence of photocatalyst, it's important to have a larger band gap. The band gap must be the photo-generated hole that should have enough oxidation strength to oxidize the water to oxygen. The photo-generated electron has sufficient reduction potential to reduce H<sub>2</sub>O to H<sub>2</sub> as shown in Fig. 6.2. The visible-light-driven photocatalytic process undergoes three strategies such as (A) H<sub>2</sub> generation from water, (B) photochemical initiation of O<sub>2</sub> and (C) photo-oxidation of organic contaminants present in wastewater.

The position of band gap must be such that photo-generated hole is strengthened enough to oxidize water to oxygen; later this photo-generated electron reduces water to H<sub>2</sub>, i.e. the HOMO and LUMO engulfs redox potential of water. This type of engulfing is rarely observed in organic semiconductors, for example, if the semiconductor is stable against water and oxygen, it would be a case of photocorrosion (Wang et al. 2012).

### 6.3.1.3 Photodegradation of Chemical Pollutants Using g-C<sub>3</sub>N<sub>4</sub>

The organic pollutants are oxidized into CO<sub>2</sub>, water and other non-harmful compounds with the aid of oxygen. O<sub>2</sub> act as a clean oxidant. The above-mentioned

**Fig. 6.2** Three strategies to realize visible light-induced photocatalysis. (Reprinted with permission from Wang et al. 2012, copyright (2009) American Chemical Society)



approach is considered as a natural and effective way to remove organic pollutants rapidly. Methyl orange was being degraded using  $g\text{-C}_3\text{N}_4$  as metal-free photocatalyst (Yan et al. 2009). The studies revealed that the reduction process for degradation of MO over  $g\text{-C}_3\text{N}_4$  was initiated by photogeneration of electrons. Doping of  $g\text{-C}_3\text{N}_4$  with boron could improve dye absorption and light absorption. To activate  $\text{H}_2\text{O}$  under visible-light radiation, carbon nitride has been applied as metal photocatalyst. The catalyst was reusable even after activation of water, which ensures clean environment from organic pollutants.

### 6.3.1.4 Graphene Oxide-Based Hybrid Photocatalysts

To enhance the implementation of photocatalytic semiconductor materials, few steps should be kept in mind. One of the mixtures of promising semiconducting materials is with 3D graphene. Graphene has the capability to act as an electron acceptor. Instead of knowing the fact that titanium supported semiconductors hold more value than the graphene-based conductors for the removal of toxins from natural sources. There exist many semiconductors which have been joined to the graphene network with a specific termination objective to watch the adjustment of its impact on the evacuation of natural poisons from the water.

Cuprous oxide ( $\text{Cu}_2\text{O}$ ) exists as one of the potential semiconductors to get combined with the graphene. The outcomes demonstrated a critical increment of the photocatalytic movement of the  $\text{Cu}_2\text{O}/\text{rGO}$  nanocomposites with regard to nanosize  $\text{Cu}_2\text{O}$ . Such hybrid nanostructured catalysts enhance the absorbance of light and expand the light retention and exchange of photo-generated electrons of  $\text{Cu}_2\text{O}$  to reduced graphene oxide (rGO). This leads to the improvement of charge partition of hybrid catalyst, and it was determined by the photoluminescence spectra.

GO is the most functional form of possessing oxygenated groups. GO is surrounded by epoxy and hydroxyl groups at the basal plane. GO appear as a



hydrophilic material due to the presence of oxygenated groups (Ramirz et al. 2015). The oxidation level can be modified by adjusting the band gap. The above-mentioned properties, i.e. tunable band gap and dispersion in water, encourage exploring the application in the photocatalytic area. 3.26 eV was the calculated band gap of GO. Some of the aromatic compounds such as phenol and chlorophenol were easily removed from water with the help of GO as a photocatalyst.

They also used an efficient adsorbent for the environmental applications. Graphene oxide (GO) and reduced graphene oxide (rGO) were investigated as an adsorbent to think about the adsorption attributes of substantial metal mixes and natural from fluid arrangements. Specialists have tried a wide range of kinds of created adsorbents, for example, activated carbon (AC), polymeric materials, zeolites and hybrid nanomaterials, used as adsorbents for the expulsion of chemical pollutants or heavy metal ions from wastewater. Be that as it may, these adsorbents have been experiencing either low adsorption limits or low performances. Accordingly, incredible exertion has been done as of late to look for a novel class of adsorbents and grow new adsorbent systems.

The carbonaceous nanostructured materials are viable adsorbents to purify water from wastewater through removing the contaminants. Graphene nanosheets are hydrophobic, and, subsequently, stable scatterings in the polar solvents must be acquired with the expansion of appropriate surfactants. Graphene oxides displays oxygen-having useful gatherings, for example, epoxy and hydroxyl (generally situated on the base and best surfaces), and carbonyl (C=O) and carboxyl (-COOH) in the most part of the nanosheets edges, randomly appropriated in the structures graphene nanosheets. These utilitarian gatherings particularly increment the hydrophilic characteristics of GO, making it effortlessly well dispersed in the aqueous system and very stable for a long time under basic ecological conditions.

Rapid industrialization has led to increasing in the discharge of effluents (Castillo et al. 2017). Presence of heavy metals in the water poses threat to the health of the living forms and causes damage to the aquatic life. Metals mainly found in the industrial discharge are chromium, arsenic, zinc, nickel, cobalt, mercury and chromium. These metals are toxic even at the lowest concentrations (Chandana and Subrahmanyam 2017). Several chemical and physical methods have been involved to remove the organic contaminants and metals from the water. Some of the methods are:

- Filtration
- Precipitation
- Coagulation
- Adsorption
- Ion exchange
- Osmosis

These methods are not very efficient and economic. The one used mostly is adsorption, and the reason behind its wide use is its economic and efficient compared to the others. The other most important reason for its popularity is it does not generate any waste in the end.

## **6.3.2 Metal-Organic Framework (MOF)-Based Photocatalysts**

### **6.3.2.1 Principles**

In the late 1990s, the disclosure of another sort of permeable mixes has offered extraordinary consideration because of the potential these materials displayed in cutting-edge mechanical applications. These are named as permeable coordination polymers or metal-organic framework (MOF) structures. MOFs are notable to have vast surface regions due to ultrahigh porosity with the measure of their pores running from the smaller scale to mesoporous administration. The structures of MOFs are obtained from natural ligands (alluded to as linkers) and metal groups that act as the connectors.

The main secondary building unit (SBU) is the natural linker, which might be ditopic (having two sorts of coordinative functionalities), tritopic (three composers) or polytopic (more than three kinds). The second SBU is a metal molecule, a limited polyatomic inorganic group with at least two metal iotas, or a boundless inorganic unit, for example, an interminable occasional bar of metal particles. Metal-containing SBUs are produced in situ and can be predesigned because of the sensible decision of response conditions (dissolvable framework, temperature, molar focus, pH). The states of SBUs are characterized by their purposes of expansion (network with natural linker SBU) and can be shown as a polyhedron, polygon or interminable pole. To differentiate, natural linkers are performed to a custom shape. The tasteful science of MOFs relies upon a blend of given metal optional building unit with an assortment of natural SBUs.

### **6.3.2.2 Photocatalytic Applications of MOFs**

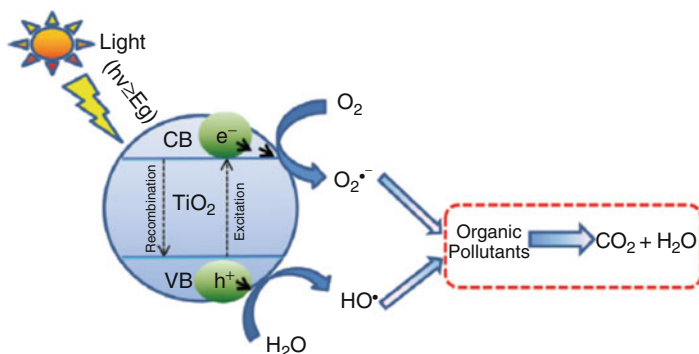
With consistently expanding requests of vitality and with petroleum products ending up perpetually lessened, sun-based vitality speaks to an alluring elective arrangement and an extensive group of research which portrays the outfitting and sequestering of vitality from the sun. A few ways to deal with change and store sunlight based vitality as concoction bonds have been proposed, including photochemical methodology, for example, the decrease of CO<sub>2</sub> and H<sub>2</sub>O part. The inalienable capacity of plants to trap daylight and change water and CO<sub>2</sub> to sugars (a procedure named photosynthesis) is the wellspring of much motivation for scientists in the field. The advancement of systems to encourage photochemical change has additionally been the subject of huge core interest. Nevertheless, certain materials showing the capacity to part water by outfitting UV light a few confinements on the utilization of the sun-powered range exist. It, in any case, stays of essential significance to plan a steady, capable and practical approach that can change over sun oriented vitality by benefiting from the most extreme sunlight based range.

The retention of light by certain photoactive natural particles makes them experience changes which typically can't be encouraged under standard thermally actuated conditions. Given that the extensive piece of the range isn't utilized by natural mixes, which just retain UV photons, their effectiveness is imperfect. Confinements identified with sun-powered range retention can be alleviated by the utilization of atomic colours which can retain low vitality photons, offering to ascend to new photocatalytic responses under the noticeable light. Three phases include the transformation of sun-powered vitality into helpful compound vitality: the age of charge-isolated energized states by utilizing a photosensitizer to assimilate daylight, the making of redox proportional and resulting exchange to receptive destinations and the nearness of oxidation and lessening half responses at reactant focuses. With the target of combining photosensitizer and reactant segments into covalent fortified dimers, supramolecular structures or polymers a few sorts of mixes have been produced; this approach has a high level of many-sided quality, be that as it may, in that the procedure is difficult and requires many advances, accordingly restricting its pertinence.

MOFs can work as photocatalysts for the fundamental reason that they consolidate photosensitizer and reactant usefulness inside one structure. The previously mentioned three phases of photocatalysis are in this way encouraged inside one strong compound. Through substitution of the standard photocatalyst which ordinarily incorporates substantial metals, photoactive MOFs can work as predominant photocatalysts by limiting sullyng and can promptly be recouped and reused because of their strong frame, subsequently giving financial advantages.

In the recent years, MOFs have been well researched for heterogeneous photocatalytic applications. The utilization of MOFs in the photocatalytically determined exploitation of natural poisons and NO<sub>x</sub>, antibacterial movement and age of sun-powered fills and photoelectrochemical (PEC) vitality features. Furthermore, there are a few announced MOFs that have additionally been utilized in the photocatalytic generation of high-esteem chemicals under mellow conditions. In these reports, the attainability of calibrating the MOF's vitality band structure and surface practical gathering was demonstrated. From the studies, MOFs now remain as an exceptional class of highly efficient photocatalysts due to their tunable characteristics (size, shape, morphology and porosity) compared with the conventional semiconductor photocatalysts.

There are a few incredible surveys that address the advances of MOFs in the photodegradation of natural toxins in wastewater, water part and photoreduction of CO<sub>2</sub>, where these materials' security and light retention properties are basically talked about. Although, these audits are constrained as far as outlining the plan rule/criteria and the photocatalytic working instrument, both of which are vital to the advancement of new MOF photocatalysts having attractive properties for acknowledgement in future reasonable applications.



**Fig. 6.3** Illustration of photocatalytic activity of TiO<sub>2</sub> photocatalyst. (Reprinted with permission from Samsudin et al. 2015, copyright (2015) Penerbit UKM publisher)

### 6.3.3 TiO<sub>2</sub>-Based Hybrid Photocatalysts

#### 6.3.3.1 Principles

In the framework of environmental issues such as water and air contamination, it is essential to talk about photocatalysis. Photocatalysis has shown great results in the fields of energy storage and depollution of natural sources. Photocatalysis also enables the direct transformation of solar energy into chemical and splitting of water molecules. The importance of photocatalyst is regarded for the solution it gives from the environmental problems such as climate change and greenhouse gas emissions which elevate the need for more developed technologies for the benefit of the environment.

Photocatalytic activity mechanism of TiO<sub>2</sub> photocatalyst is shown in Fig. 6.3. Generally, an electron-hole pair is formed when an electron is moved to the conduction band from the valence band. Then the charge carriers and motivated conduction band electrons are transferred to the TiO<sub>2</sub> surface to make oxidation and reduction procedures. In order to form superoxide ions, the conduction band electrons of TiO<sub>2</sub> are captured by the oxygen molecules. Hydroxyl radicals are formed with an electron-hole pair when the superoxide ions respond with protons or water molecules. Lastly, these formed radicals ultimately lead to the dye degradation into harmless compounds.

#### 6.3.3.2 Different Forms of TiO<sub>2</sub> and Its Physicochemical Properties

TiO<sub>2</sub> shows photocatalytic activity in a non-exhaustive way. It is one of the oldest metal oxides to show the photocatalytic activity. TiO<sub>2</sub> shows exhibit abundant properties for being a good photocatalyst. Some of the properties executed by TiO<sub>2</sub> are as follows:

- (i) Non-exhaustive
- (ii) Low toxicity
- (iii) Great photocatalytic activity
- (iv) Chemical stability
- (v) Photostability
- (vi) Antipollution
- (vii) Antibacterial

Great efforts were made to enhance the existing photocatalytic technologies to get the best out of all the existing technologies. A lot of work has been done in order to find out materials that have higher efficiencies for being photocatalysts.  $\text{TiO}_2$  has great applications in the fields of photochemistry and nanotechnology.

$\text{TiO}_2$  occurs in three crystallographic phases:

- *Anatase*
  - (i) Bipyramidal tetragonal symmetry
  - (ii) Photocatalytically active
  - (iii) The structure comprises of octahedral
- *Rutile*
  - (i) Used as a pigment
  - (ii) In coating industry
  - (iii) Chemically inert
- *Brookite*
  - (i) Limited range of temperature
  - (ii) Orthorhombic symmetry

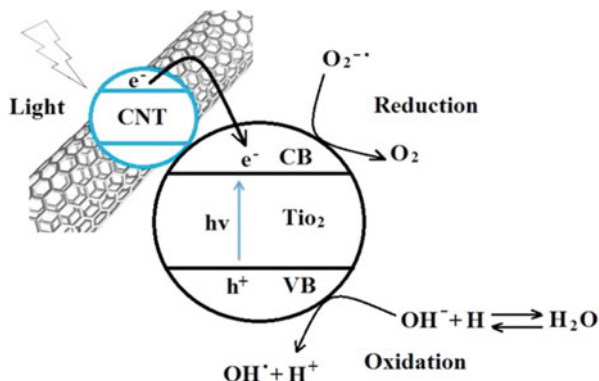
$\text{TiO}_2$  falls under the category of an n-type semiconductor.  $\text{TiO}_2$  semiconductors get activated by UV light (Kim et al. 2003b). The real efficiency of  $\text{TiO}_2$  depends on the phase composition along with the size, porosity and its composition.  $\text{TiO}_2$  shows a tendency to generate the holes and electron in the presence of UV light, due to which it is considered as an authentic material for the green technology.

The  $\text{TiO}_2$  which gets activated by visible light could be synthesized by the following methods:

- (i) Metal ion implantation
- (ii)  $\text{TiO}_2$  reduction
- (iii) Sensitizing  $\text{TiO}_2$  with dyes

Doping of  $\text{TiO}_2$  with other materials began in the 1980s. N-doped  $\text{TiO}_2$  was reported as light-sensitive photocatalyst. Studies have carried out on the large number of anions such as sulphur, carbon, etc. In the case of N-doped titanate semiconducting catalyst, the origin of visible-light sensitivity is the localized  $\text{N}_{2p}$  level. The hole movement should be low. The photo-produced hole in the high mobility region in  $\text{TiO}_2$ 's valence band should be used to attain high action under the visible light.

**Fig. 6.4** The photocatalytic mechanism of photocatalytic degradation over TiO<sub>2</sub>/carbon nanotubes hybrid photocatalyst. (Reprinted with permission from Mohamed et al. 2016, copyright (2016) Elsevier)



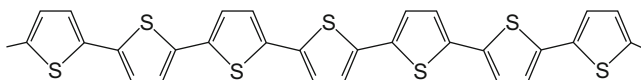
### 6.3.3.3 Structure of TiO<sub>2</sub>

Titanium dioxide exists as a polymorphic structure, and as discussed above, it has three polymorphic structures. Anatase and rutile are tetragonal, and brookite is orthorhombic. In anatase, TiO<sub>6</sub> octahedron is a bit distorted with two TiO<sub>2</sub> bonds greater than rest of the O-Ti-O bonds, which show a deviation from 90°. Anatase shows more deviation from rutile. Brookite formation occurs by joining of edges of distorted octahedral. They can find applications such as treatment of wastewater, air pollution control and water splitting.

### 6.3.3.4 Photocatalytic Mechanism of TiO<sub>2</sub>

The mechanism begins with adsorption of photons by an extremely reactive electronically excited molecule. The capability of photochemistry is controlled by the features of light adsorption. The process begins with the formation of charge carriers in the semiconductor materials. Titanium oxide's valence band comprises of oxygen's 2p orbital, whereas the conduction band of titanium comprises of 3d orbitals.

Absorption of photon initiates the photocatalytic mechanism. It should be noted that the energy of photon should be greater than the band gap titanium dioxide, which further causes generation of an electron-hole pair on titanium dioxide surface. The holes are generated in the valence band due to the excited electrons to the conduction band. To dissipate the energy as heat, the excited electrons and holes combine together, by getting trapped in the surface states or by reacting with the electron donors and acceptors which are adsorbed on the surface of the semiconductor (Fig. 6.4.)



**Fig. 6.5** Chemical structure of polythiophene

### 6.3.3.5 Hybrid Photocatalysts Based on $\text{TiO}_2$ and Organic Conjugated Polymers

#### 6.3.3.5.1 Properties of Polythiophene

The electronic and photonic properties of this polymer are the main cause of drawing and holding on attention. The  $\pi$  conjugation in the electronic structure allows the delocalization of the charge transporters when doping on the mobility of high charge carriers. The delocalized charged structures are responsible for the strong absorptions. Polythiophene comprises of a long chain of alternate double and single bonds (Vukmirovic and Wang 2009). The first and fourth carbons are combined by the sulphur atom which forms a thionyl ring molecule. This leads to increase in the single bond character. Weaker mesomeric effect pushes the band gap of polythiophene to blue. The sulphur groups present in the chain direct the electronic and optical properties, whereas the carbon conjugation directs the spectroscopic properties as shown in Fig. 6.5.

#### 6.3.3.5.2 Properties of Polyaniline

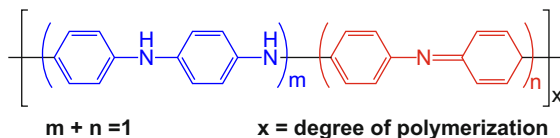
Some of the physicochemical properties of polyaniline are:

- (i) High conductivity
- (ii) Redox reversibility
- (iii) Swift change
- (iv) High stability in the air

Polyaniline is one of the most central organic conducting polymers due to the following properties (Vachon et al. 1987):

- (i) Outstanding electrical conductivity
- (ii) A rich number of intrinsic redox sites
- (iii) Easy processability
- (iv) Excellent environmental and thermal stability
- (v) Excellent physical and chemical characteristics

**Fig. 6.6** Chemical structure of polyaniline



Polyaniline is the leading conducting polymer to succeed worldwide commercial market for various industrial applications. The chemical structure of polyaniline is shown in Fig. 6.6. Polyaniline exists in a variety of different forms and structures. The green protonated emeraldine (green colour) is the most common, and it has an electrical conductivity on a semiconducting level of the order of 100 S/cm, several orders of magnitude higher than that of common polymeric materials such as polystyrene, polyethylene, etc. ( $<10^{-9}$  S/cm), but it is lower than that of typical metallic materials ( $>10^4$  S/cm). The protonated form of polymer (polyaniline hydrochloride) converts to a semi- or non-conducting emeraldine base (blue colour) when treated with a base such as sodium hydroxide and ammonium hydroxide.

#### 6.3.3.5.3 Properties of Polypyrrole

This chemical compound is formed by connecting a large number of pyrrole rings. Polypyrrole is the conducting materials. They belong to the rigid-rod polymer family; basically, all are derivative of polyacetylene. This was the first polymer to exhibit high conductivity. These are commonly known by the name “pyrrole black”. Polypyrrole has also shown natural existence with melanin and polyacetylene. Polypyrrole shows characteristics for radar absorbing material. Polypyrrole can be prepared using the following methods (Xu et al. 2006; Wang et al. 2004; Kilmartin and Wright 2001; Tan and Ge 1996):

- Chemical polymerization
- Electrochemical
- Plasma
- Vapour phase polymerization

Vapour phase polymerization is the most suitable method because it provides suitable thickness and great conductivity along with uniformity to the film.

The drawbacks of other techniques are:

- Poor electrical conductivity
- Demand for the conductive substrates
- Porosity
- Uneven thickness of the film
- Size of substrate



#### 6.3.3.5.4 Synthesis of TiO<sub>2</sub>-Based Hybrid Photocatalysts with Different Organic Conjugated Polymers

**Synthesis of TiO<sub>2</sub>/Polyaniline Hybrid Photocatalysts** Titania/polyaniline hybrid catalysts are synthesized by the following method. Two grammes of TiO<sub>2</sub> and 3.3 mL of distilled aniline was taken in a beaker containing 100 mL of 1 M HCl and continued to stir in the ice bath. The oxidant (peroxide) was then added to above solution and sonicate the mixture for an hour, and autoclave it for overnight. Then, the product was filtered and washed with deionized water and acetone in order to get rid of unreacted aniline, by-products and impurities.

**Synthesis of TiO<sub>2</sub>/Polythiophene Hybrid Photocatalysts** Two grammes of TiO<sub>2</sub> and 3.1 mL of distilled thiophene monomer was taken in a beaker containing 5 mL of acetonitrile. The mixer kept in an ice bath (−10 °C) under the magnetic stirring, and then add ferric chloride solution was added dropwise to above solution. The reaction mixture was sonicated and transferred to an autoclave and then heat in the oven for overnight. The product was filtered using the membrane filter and washed several times with an excess of deionized water and acetone to remove unreacted thiophene and by-products.

**Synthesis of TiO<sub>2</sub>/Polypyrrole Hybrid Photocatalysts** Two grammes of TiO<sub>2</sub> and 3.6 ml distilled pyrrole was taken in the beaker containing 10 ml of distilled water. The mixture was kept on an ice bath under constant stirring, and then add ferric chloride solution by dropwise. After sonicating the reaction mixture for an hour, autoclave it, and then keep in the oven for an hour. The obtained product was filtered and washed with an excess of deionized water and acetone to remove unreacted pyrrole and by-products.

#### 6.3.3.5.5 Characterization of TiO<sub>2</sub>/Conjugated Polymer-Based Hybrid Catalysts

**XRD** X-ray diffraction technique is chiefly used for the identification of crystalline material's phase, and it provides the information about the dimension of the unit cell. It could be specifically said that the power of XRD is used for the characterization of polycrystalline phases. The composition of the material is determined by grounding it, and then it's homogenized. Majority of the solid mass is described as crystalline. The diffraction pattern can be obtained when the X-rays comes in contact with the substance.

X-rays are based on the approach of constructive interference of monochromatic light. Generation of x-rays is through cathode ray tube. The use of diffraction technique is chemical analysis. It can further include phase analysis; the widest use of XRD technique is for the determination of the crystalline structure of

unknown crystals. It finds great application in the branch of geology, earth sciences, material sciences, etc. for the characterization of the crystalline material and the identification of the materials.

*Cyclic voltammetry:*

- Helps in the quantitative determination of organic and inorganic compounds.
- Measures kinetic rate.
- Determines the adsorption process.
- Determines the complexion values.
- It has great use in the pharmacy industry for the quantitative determination of compounds.
- It also helps in defining the thermodynamic properties.
- Helps in the calculation of the number of electrons in a redox reaction.

**Raman Spectroscopy** The Raman spectroscopy is utilized to determine some low-frequency modes such as rotation and vibration in a system. Raman spectroscopy occurs from inelastic collisions. The frequency difference of incident and scattered light corresponds to the vibrational and rotational spectra. It holds great use in the branch of chemistry because a vibrational spectrum provides authentic information about the bonds of the molecule. The orientation of any crystal could also be found out from the Raman spectroscopy.

#### 6.3.3.5.6 Antibacterial Activity of Photocatalysts

The photocatalytic effect of  $\text{TiO}_2$  is theoretically possible since this catalytic material is easy to fabricate with low cost in large scale (Tan and Ge 1996; Cheng et al. 2009). One of the potential applications of  $\text{TiO}_2$  photocatalysts is the antibacterial activity. The antibacterial reagents act as an inactivate cell viability, but the pyrogenic and toxic ingredients like endotoxins remain even after the killing of bacteria. The endotoxin is the cell wall constituent of bacteria that consisting of a carbohydrate chain, which is expressed as the complex lipid and O-antigen. Endotoxin is highly toxic and causes serious and risky problems in the manufacturing industries of pharmaceuticals and medical devices (Ishibashi et al. 2000).

The photocatalytic reaction of  $\text{TiO}_2$  has been used to inactivate a wide range of microorganisms as explained below (Kim et al. 2003b; Duffy et al. 2004; Chamorn and Yasuyoshi 2006). The certain amount of the photocatalyst was dispersed into saline solution (0.9%) and then sterilized the mixed solution by autoclaving at the high temperature of 1200 °C and pressure of 15 lbs for 30 min. After cooling it to room temperature, the product was mixed with 1 mL of the bacterial cell suspension under the magnetic stirring to avoid the settling of photocatalyst and then irradiated the solution under visible light (150 W ozone-free Xe lamp) that has a wavelength of 420–630 nm. The bacterial suspension was also irradiated in the absence of photocatalyst to determine the antibacterial activity. After irradiation process, 1 mL of catalyst suspension was distributed over the Petri dish that consists of the nutrient agar and incubated it for 2 days at 370 °C, and then it was taken out for the

counting. It was found that the antibacterial efficiency of TiO<sub>2</sub> photocatalyst was increased as the decrease of a number of colonies.

### 6.3.3.6 Environmental Application of Different Photocatalysts

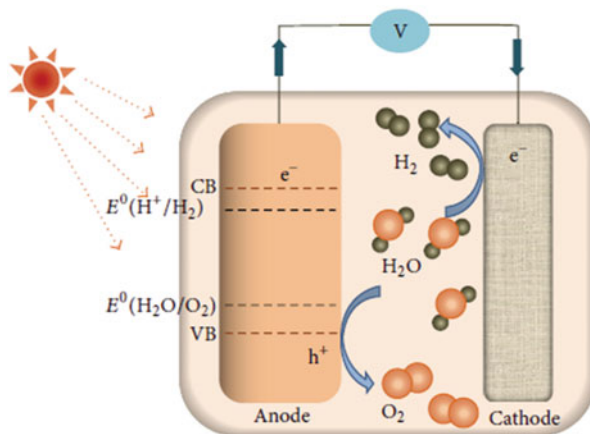
#### 6.3.3.6.1 Water Purification

The photochemical degradation of hazardous pollutants such as dyes, pharmaceutical effluents and metallic discharge was performed under visible-light irradiation (oriel lamp). The photodegradation % of dyes and 4-nitrophenol was analysed using the equation,  $((C_0 - C)/C_0) * 100$ , where  $C_0$  and  $C$  represent the initial and final concentration of the photocatalysts. Phenol, bisphenol-A and antibiotic sulfamethoxazole were studied using high-performance liquid chromatography (HPLC) with the reverse phase column. The antibacterial studies were also carried out under visible-light irradiation to study *Salmonella typhi* which is the typhoid-causing bacteria. The antibacterial activity was determined using the colony counting technique.

With the growing demand for water and lack of clean sources due of the quick advancement of industrialization, population growth and long dry period have turned into the critical issue around the world. The amount of safe and drinking water for day by day is decreasing slowly, and this issue can be resolved urgently. It is estimated that ~4 billion individuals experience to have no or little access to spotless and purified drinking water supply and a great many individuals passed on of serious waterborne sicknesses yearly. These measurable figures are required to develop in near future, as drastically increasing the water pollution due to the release of organic contaminants and micro hazardous pollutants into water. It is necessary to develop effective clean water technologies to treat the wastewater, resulting in human well-being.

Among the advanced oxidation processes (AOP), the heterostructured photocatalysis utilizing semiconducting catalysts (e.g. TiO<sub>2</sub>, CdS, ZnO, GaP, ZnS, ZrO<sub>2</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc.) has shown its effectiveness in photodegrading an extensive variety of equivocal headstrong organic pollutants into promptly biodegradable compounds that mineralized in the long-run to the harmless small molecules such as carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). Among various semiconductor photocatalysts, TiO<sub>2</sub> has gotten the best enthusiasm for the research and development of photocatalysis innovation. It has two main crystal phases such as anatase and rutile with the band gap values of 3.2 eV and 2.0 eV. The multifaceted TiO<sub>2</sub> photocatalyst has unique properties such as chemical stability, environmental stability and protection from the synthetic breakdown, and their solid mechanical properties have advanced its wide range of photocatalytic applications in an area of wastewater treatment. Various imperative highlights for the heterostructured photocatalysts which have expanded their potential uses in wastewater treatment are the following (Fujishima et al. 2007): (i) an ambient working environment,

**Fig. 6.7** The schematic representation for PEC water splitting of  $\text{TiO}_2$ . (Reproduced from Kochuveedu 2016, copyright (2016) Hindawi publisher)



(ii) the total mineralization of guardians and it halfway mixes without optional contamination and (iii) the process operates at low cost.

The post-partition of the semiconductor  $\text{TiO}_2$  impetus after wastewater treatment stays as the significant hindrance towards the reasonableness as an industrial process.  $\text{TiO}_2$  molecule size and its surface vitality make the solid inclination for the impetus aggregates in the middle of an operation process. Such aggregated particles are exceedingly impeding in perspectives of particle measure protection, surface region lessening and its expectancy of recyclability. Other specialized difficulties incorporate into the impetuses improvement with more extensive photoactivity and it's joining with the feasible catalytic reactor framework.

The proposed mechanism for photoelectrochemical water splitting of  $\text{TiO}_2$  is shown in Fig. 6.7. Reduction and oxidation are the elementary chemical reactions that ensue through water splitting. As stated, for the evolution of  $\text{H}_2$  and  $\text{O}_2$ , the conduction band and valence band positions of materials have to fit into the water reduction and oxidation potential respectively. Upon light irradiated, the photo-generated electrons are excited to the CB from the VB and leaving the same amount of holes. Finally, the photoexcited electrons and holes are involved in the generation of hydrogen and oxygen.

### 6.3.4 Graphene Oxide (GO)-Based Photocatalyst for Dye Degradation and $\text{H}_2$ Evolution

Recently, graphene-based composite materials have been considered as a promising candidate in both technical and scientific communities because of its tremendous properties (Zhang et al. 2015; Novoselov et al. 2012). The preparation of graphene-based composite photocatalyst materials has progressed into numerous fields, such as energy storage and transformation, optoelectronics, nanoelectronics, biosensors,

supercapacitors, etc. (Yang and Xu 2016). In detail, the abundance preparations of the graphene-based catalysts for enhancing the solar energy transformation ability have been observed in recent years (Zhang et al. 2014; Yuan et al. 2014; Han et al. 2015; Pan et al. 2014).

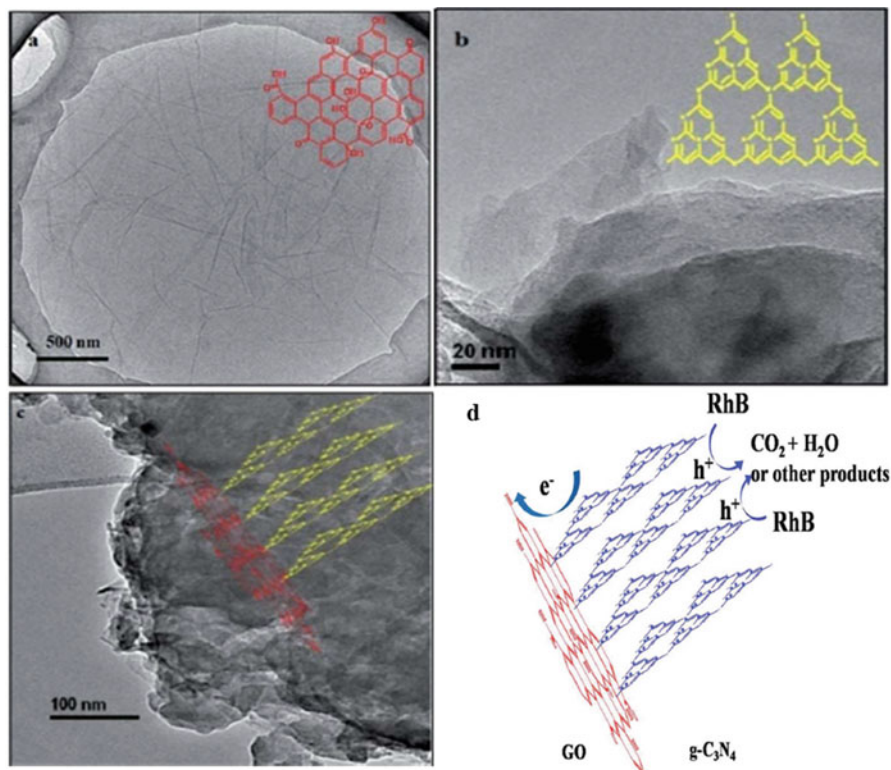
Graphene is a suitable material for photocatalyst support and an electron acceptor/trapper due to its huge surface area, greater work function, good optical transmittance and outstanding electronic conductivity (Yang and Xu 2013; Yang et al. 2014; Han et al. 2017). As per literature survey, it is significantly noticed that the addition of a suitable quantity of graphene-associated materials for the photoactive mechanisms is necessary for the conversion of solar energy. Generally, the actual form of graphene in the graphene-based catalysts is different from its original state, which is owing to the existence of defects, oxygenated functional groups and grouping of the graphene sheets. Hence, it is difficult to get maximum properties of graphene. Such a condition intensely advises that (i) the incorporation of graphene with a photocatalyst semiconductor to make new multicomponent composite photocatalyst materials gives a favourable approach for fabricating the next-generation simulated photosynthetic systems and (ii), furthermore, there is still enormous room to increase the catalytic activity of graphene-based composite catalysts through improving the properties of the synthesized graphene composite catalysts.

However, due to its poor photocatalytic performance, different approaches have been suggested to increase its photocatalytic activity. Therefore, graphene and its products have been effectively exposed as a photocatalyst for PEC water splitting reactions. Another method to enlarge its advantages is the hybridization with other compounds like g-C<sub>3</sub>N<sub>4</sub> (graphitic carbon nitride). Polymeric g-C<sub>3</sub>N<sub>4</sub> shows a graphite-like structure, and it has been developed as a visible-light and metal-free reactive catalyst in the photosynthesis and environmental remediation.

#### 6.3.4.1 Photodegradation of Chemical Pollutants

Photodegradation of pollutants is one of the most potential eco-friendly sanitization technologies owing to its inexpensive, no secondary pollution and simple handling. In this concern, a graphene/g-C<sub>3</sub>N<sub>4</sub> hybrid composite is a green visible-light catalyst and has involved significant research attention since its favourable advantages in the dye decomposition of hazardous contaminants, such as dye degradation of organic substance via oxidation, diminished metal ion and NO<sub>x</sub> reduction. Generally, a photocatalytic decomposition reaction via photocatalytic oxidation of pollutants with O<sub>2</sub> under photo illumination makes CO<sub>2</sub>, H<sub>2</sub>O or other compounds. To estimate the photocatalytic performance, different organic pollutant dyes have been used as contaminants such as rhodamine B (RhB), methylene orange (MO), congo red (CR) and methyl blue (MB).

Li et al. successfully synthesized cross-linked g-C<sub>3</sub>N<sub>4</sub>/reduced graphene oxide (rGO) composites using the combination of cyanamide and GO with various weight proportions under thermal treatment (Li et al. 2013). It is observed that a suitable rGO ratio in the g-C<sub>3</sub>N<sub>4</sub>/rGO nanocomposite caused a positively shifted VB



**Fig. 6.8** TEM image and schematic representation (inset) of (a) GO, (b) g-C<sub>3</sub>N<sub>4</sub>, (c) GO/g-C<sub>3</sub>N<sub>4</sub> and (d) proposed mechanism for charge transfer and photodegradation of RhB for the hybrid nanocomposite. (Reproduced with permission from Liao et al. 2012, copyright (2012) Royal Society of Chemistry)

potential and reveals an improved oxidation ability. Moreover, the hybrid sample exhibited enhanced light absorption capacity, improved conductivity and better electron transport properties due to the existence of rGO. Accordingly, an optimized rGO ratio of 2.5% in the nanohybrid exhibited three times greater photocatalytic degradation of RhB than pristine g-C<sub>3</sub>N<sub>4</sub>. Furthermore, the optimum photocatalyst was also displayed 2.7 times greater efficient of 4-nitrophenol degradation than bare g-C<sub>3</sub>N<sub>4</sub>. This enhanced photocatalytic performances could be due to the better utilization of visible light, oxidation power, properties of electron movement, decreased band gap, movement of band edge potential and better electronic conductivity.

A modified GO/g-C<sub>3</sub>N<sub>4</sub> nanocomposite has been fabricated by Liao et al. (2012) using a sonochemical synthesis method for superior catalytic activity. The transmission electron microscopic (TEM) images of pristine GO, g-C<sub>3</sub>N<sub>4</sub> and GO/g-C<sub>3</sub>N<sub>4</sub> hybrid composite are shown in Fig. 6.8a–c. From the result and analysis, it is signifying the GO performances as a separation centre and acceptor of an electron

in the hybrid composite. Under visible-light irradiation, the separation of active photoexcited carriers improved the photocatalytic activity. In case of GO/g-C<sub>3</sub>N<sub>4</sub>, the evaluated dye degradation rate constants for RhB and 2,4-dichlorophenol were found to be 3.80 and 2.08, which compared with bare GO and g-C<sub>3</sub>N<sub>4</sub>. Based on the structural, morphological studies and their properties, the effective catalytic activity would be mostly associated with the detachment of charge carriers. Figure 6.8d shows the suggested catalytic activity of hybrid GO/g-C<sub>3</sub>N<sub>4</sub> nanocomposite.

Upon light illumination, the photoexcited electrons of g-C<sub>3</sub>N<sub>4</sub> moved from the valence band to the conduction band. Due to the heterojunction construction between GO and g-C<sub>3</sub>N<sub>4</sub>, the photoexcited  $e^-$  then moved to the GO sheet, which decreases the possibility of charge carrier's recombination rate and improved the separation competence. Furthermore, this led to ample holes left on the VB of g-C<sub>3</sub>N<sub>4</sub>. Hence, due to the VB edge potential of g-C<sub>3</sub>N<sub>4</sub> (1.57 V vs Ag/AgCl), RhB and 2, 4-DCP was oxidized to CO<sub>2</sub>, H<sub>2</sub>O or other intermediates. Yu et al. (2014) reported a porous g-C<sub>3</sub>N<sub>4</sub>/graphene nanocomposite was prepared by mixing graphene with porous g-C<sub>3</sub>N<sub>4</sub> for methyl blue dye degradation.

The hybrid sample showed a noticeable improvement of photocatalytic decomposition of MB, and the enhancement was six times higher than that of pristine g-C<sub>3</sub>N<sub>4</sub>. In another similar work, GO/g-C<sub>3</sub>N<sub>4</sub> composite was effectively synthesized using an anchoring exfoliated g-C<sub>3</sub>N<sub>4</sub> onto a GO surface by Dai et al. (2014) for methyl blue (MB) organic pollutant dye degradation. The optimal weight fraction of GO hybrid sample was exhibited largely reinforced photocurrent. Thus, the resultant catalytic performance of the hybrid composite was significantly enhanced with the optimized photocurrent. The optimized hybrid composite sample exhibited greater MB dye degradation activity than the pure g-C<sub>3</sub>N<sub>4</sub>, commercial P25 and the physical mixture of g-C<sub>3</sub>N<sub>4</sub> and GO as a photocatalyst.

When compared to binary hybrid composite materials, the development of heterojunction photocatalysts can efficiently detach the photo-induced holes ( $h^+$ ) and electrons ( $e^-$ ) and produce more active radical species, which are useful for practical applications. In recent times, heterojunction nanocomposites like g-C<sub>3</sub>N<sub>4</sub>-Ag<sub>x</sub> ( $X = VO_4^{3-}$ ,  $CO_3^{2-}$ ,  $PO_4^{3-}$ ,  $S^{2-}$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$ ) have been concerned great consideration and broadly studied due to their promising separation of charge carriers and photocatalytic performance (Wang et al. 2014). Apart from the graphene/g-C<sub>3</sub>N<sub>4</sub> binary nanohybrid composites, graphene/g-C<sub>3</sub>N<sub>4</sub> synthesized ternary heterojunctions have also been studied. In this respect, Li et al. (2015) reported a novel AgBr assisted on g-C<sub>3</sub>N<sub>4</sub>-deposited N-doped graphene ternary super hybrid (AgBr/g-C<sub>3</sub>N<sub>4</sub>/NG<sub>x</sub>) composite that was successfully developed using a polymerization followed by ion exchange method.

The optimized AgBr/g-C<sub>3</sub>N<sub>4</sub>/NG-50 photocatalyst sample (the content of g-C<sub>3</sub>N<sub>4</sub>/NG in AgBr/g-C<sub>3</sub>N<sub>4</sub>/NG-x was 50 wt%) exhibited the greater photocatalytic degradation activity compared to other samples. Furthermore, when further increased g-C<sub>3</sub>N<sub>4</sub>/NG content, decreased photocatalytic activity. This result specified that the additional g-C<sub>3</sub>N<sub>4</sub>/NG generate active sites on the photocatalyst surface and decrease the light diffusion distance in the catalytic reaction process. This enhancement in degradation is due to the effective detachment of charge carriers at

the boundary of AgBr/g-C<sub>3</sub>N<sub>4</sub>/NG hybrid and enhanced the separation rate of photo-induced holes ( $h^+$ ) and electrons ( $e^-$ ), which led to the outstanding catalytic performance of MO dye degradation.

In another report, Liu et al. described Fe(III) incorporated into a graphene/g-C<sub>3</sub>N<sub>4</sub> binary nanocomposite was successfully developed in order to introduce the interfacial charge transfer effect by a simple impregnation technique (Liu et al. 2016). Moreover, an innovative ternary nanocomposite (Fe(III)/graphene/g-C<sub>3</sub>N<sub>4</sub>) has been fabricated by a direct mixing of graphene and the binary Fe(III)/g-C<sub>3</sub>N<sub>4</sub> nanocomposite. From the result and analysis, it was observed that the synthesized photocatalyst displayed improved absorption ability of light and decreased the charge separation rate and better photocatalytic performance than the other prepared samples.

It is noticed that the incorporation of graphene and Fe exhibited well organization, small in size, and comparatively high content than the binary composite, and this shows the effect of graphene and Fe species in the composite. Therefore, the ternary Fe(III)/graphene/g-C<sub>3</sub>N<sub>4</sub> catalyst exhibited the greater photocatalytic performance than binary composite, due to its better photo immersion ability and detachment of charge carriers. In another study, g-C<sub>3</sub>N<sub>4</sub> combined CdS nanoparticles and rGO sheets (g-C<sub>3</sub>N<sub>4</sub>/CdS/rGO) ternary nanocomposite have been successfully fabricated by Rajendra et al. (2014). Consequently, the prepared g-C<sub>3</sub>N<sub>4</sub>/CdS/rGO ternary composite exhibited greater dye degradation of RhB and congo red organic pollutants. Significantly, no considerable alteration in the degradation competence was noticed after three sequential cycles, concluding that the g-C<sub>3</sub>N<sub>4</sub>/CdS/rGO nanocomposite has decent reusability and stability for practical applications. Moreover, noble metal nanoparticles are supported by graphene and g-C<sub>3</sub>N<sub>4</sub> and the SPR effect due to the loaded noble metal ions, which can improve the immersion of light capacity. Hence, the total photocatalytic activity has been enhanced.

#### 6.3.4.2 Hydrogen (H<sub>2</sub>) Evolution Reaction by g-C<sub>3</sub>N<sub>4</sub>-Based Functional Photocatalysts

Using a suitable photocatalyst, the hydrogen evolution reaction (HER) is an effective method for hydrogen generation via water electrolysis (Zheng et al. 2015). However, several nonnoble metal photocatalysts suffer intrinsic erosion for the HER, thus resultant in reduced constancy. Nevertheless, carbon-related photocatalysts, particularly nitrogen-/carbon-related materials, are capable substitutes owing to the strong tolerance to acid/alkali surroundings and the improved  $\pi$  bonding to increase their electron donor/acceptor properties (Shalom et al. 2014).

In past years, graphene/g-C<sub>3</sub>N<sub>4</sub> hybrid composites have been used as potential catalysts for electrocatalytic HER activity. Qiao et al. (Zheng et al. 2014) established the application of g-C<sub>3</sub>N<sub>4</sub>/NG hybrid (g-C<sub>3</sub>N<sub>4</sub> attached nitrogen-doped graphene) photocatalyst for HER performance through hypothetical investigation and experimental studies. From the experimental observations, it is revealed that the



electrocatalytic properties are initiated from its intrinsic chemicals and electronic coupling, which encourages the adsorption of proton and reduced kinematics.

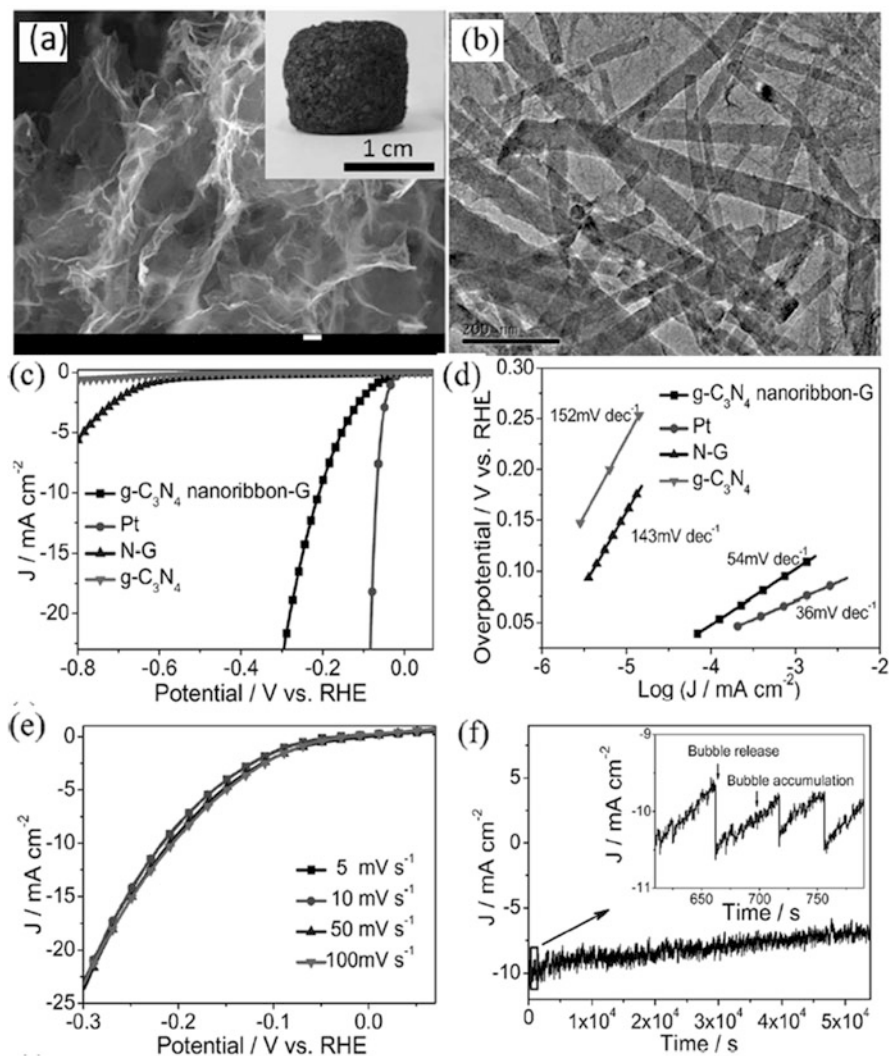
The preparation of a flexible 3D film by mixing the porous  $C_3N_4$  nanolayers with N-doped graphene sheets was composed through a simplistic process via low-price precursors for HER electrodes without any substrates has been reported (Duan et al. 2015). This nonmetal electrocatalyst has showed unbeatable HER activity with an identical positive onset potential near to commercial Pt (8 mV vs 0 mV of Pt/C vs RHE @  $0.5 \text{ mA cm}^{-2}$ ), extraordinary conversation current density of  $0.43 \text{ mA cm}^{-2}$  and remarkable strength (seldom activity loss >5000 cycles). The exhibited outstanding HER activity is due to (i) in-plane pores into  $C_3N_4$  and exfoliation of  $C_3N_4$  into nanosheets, (ii) highly ordered porous structure and (iii) 3D conductive graphene network. Moreover, the prepared material showed an outstanding stability owing to the active lodging of graphene and sheets  $C_3N_4$ .

Recently, by using a hydrothermal technique, a 3D nanoribbon construction of g- $C_3N_4$  nanoribbon-G was prepared (Zhao et al. 2014). SEM and TEM image of the prepared g- $C_3N_4$  nanoribbon-G is shown in Fig. 6.9a, b. Because of the mass transportation and multipath way of charge, the hybrid composite showed extraordinary HER activity with a Tafel slope of  $54 \text{ mV decade}^{-1}$  and a low onset overpotential of 80 mV as shown in Fig. 6.9c, d. The g- $C_3N_4$  nanoribbon-G catalyst with better strength under various scan rates showed a low overpotential of 207 mV to get a  $10 \text{ mA cm}^{-2}$  HER current density, which is lesser than those of g- $C_3N_4$ /NG hybrids as shown in Fig. 6.9e. Instantaneously, the resulting nanohybrid exhibited outstanding durable constancy that is essential for sensible hydrogen production as shown in Fig. 6.9f.

Bonding of layer materials into 2D single-atom sheets has encouraged excellent properties, because of its greater surface area, great intrinsic charge carrier movement and noticeable modifications in the band structure. Qu et al. synthesized a dual mesh of 2D g- $C_3N_4$  meshes in situ formed on 2D graphene meshes (g-CN@G MMs) by a direct template-free technique (Han et al. 2016). The unique mesh-on-mesh g- $C_3N_4$ @G MM catalyst composite displays an excellent HER activity, because of its extremely extended surface area, plentiful hydrogen adsorption locations, numerous electron carriage channels and great ability of electron movement. Under visible-light irradiation, the fabricated of single layers g- $C_3N_4$  shows a  $H_2$  generation rate ( $8510 \mu\text{mol h}^{-1} \text{ g}^{-1}$ ) and quantum efficiency (5.1%).

## 6.4 Conclusion

Through the studies, it was concluded that carbon-based hybrid materials (graphitic carbon nitride and graphene) were found to be efficient in removal of waste from water. They found to be responsible for increasing photocatalytic activity and very effective in decontamination of water. The factors responsible for the decontamination of wastewater are the surface area, temperature, pH and composition. The efficiency could also be improved by functionalization of these nanostructured



**Fig. 6.9** (a) SEM images of the synthesized  $g\text{-C}_3\text{N}_4$  nanoribbon-G. The inset of (a) is a photo of the as-prepared  $g\text{-C}_3\text{N}_4$  nanoribbon-G, (b) TEM images of the prepared  $g\text{-C}_3\text{N}_4$  nanoribbon-G, (c) the HER polarization curves, (d) the consistent Tafel plots of numerous catalysts ( $g\text{-C}_3\text{N}_4$  nanoribbon-G, Pt wire, NG and  $g\text{-C}_3\text{N}_4$ , respectively), (e) the polarization curves of  $g\text{-C}_3\text{N}_4$  nanoribbon-G with a scan rate from 5 to 100  $\text{mV s}^{-1}$  and (f) time dependence of the current density at 200 mV versus RHE. (Reprinted with permission from Zhao et al. 2014, copyright (2014) Wiley)

carbon materials by various kinds of functional groups and with various dopants and semiconducting metal oxides. They show promising results in the photocatalysis process.

## References

- Bivins AW, Sumner T, Kumpel E, Howard G, Cumming O, Ross I, Nelson K, Brown J (2017) Estimating infection risks and the global burden of diarrheal disease attributable to intermittent water supply using QMRA. *Environ Sci Technol* 51:7542–7551
- Castillo A, Vall P, Baserba MG, Comas J, Poch M (2017) Selection of industrial (food, drink and milk sector) wastewater treatment technologies: a multi-criteria assessment. *J Clean Prod* 143:180–190
- Chamorn M, Yasuyoshi H (2006) Antifungal activity of TiO<sub>2</sub> photocatalysis against *Penicillium expansum* in vitro and in fruit tests. *Int J Food Microbiol* 2:99–103
- Chandana L, Subrahmanyam C (2017) Non-thermal discharge plasma promoted redox transformation of arsenic (III) and chromium (VI) in an aqueous medium. *Chem Eng J* 329:211–219
- Chen S, Wang LW (2012) Thermo-dynamic oxidation and reduction potentials of photocatalytic semiconductors in aqueous solution. *Chem Mater* 24:3659–3666
- Chen JF, Wang YU, Guo F, Wang XM, Zheng C (2000) Synthesis of nanoparticles with novel technology: high-gravity reactive precipitation. *Ind Eng Chem Res* 39:948–954
- Cheng CL, Sun DS, Chu WC, Tseng YH, Ho HC, Wang JB, Chung PH, Chen JH, Tsai PJ, Lin NT, Yu MS, Chang HH (2009) The effects of the bacterial interaction with visible-light responsive titania photocatalyst on the bactericidal performance. *J Biomed Sci* 16:7. (10 pgs)
- Colmenares JC, Luque R (2014) Heterogeneous photocatalytic nanomaterials: prospects and challenges in selective transformations of biomass-derived compounds. *Chem Soc Rev* 43:765–778
- Dai K, Lu L, Liu Q, Zhu G, Wei X, Bai J, Xuan L, Wang H (2014) Sonication assisted preparation of graphene oxide/graphitic-C<sub>3</sub>N<sub>4</sub> nanosheet hybrid with reinforced photocurrent for photocatalyst applications. *Dalton Trans* 43:6295–6299
- Dasireddy VBCC, Likozar B (2017) Activation and decomposition of methane over cobalt-copper and iron-based heterogeneous catalysts for CO<sub>x</sub>-free hydrogen and multi walled carbon nanotube production. *Energy Technol* 5:1344–1355
- Duan J, Chen S, Jaroniec M, Qiao SZ (2015) Porous C<sub>3</sub>N<sub>4</sub> nanolayers@N-graphene films as catalyst electrodes for highly efficient hydrogen evolution. *ACS Nano* 9:931–940
- Duffy EF, Al Touati F, Kehoe SC, McLoughlin OA, Gill LW, Gernjak W, Mc Guigan KG (2004) A novel TiO<sub>2</sub>-assisted solar photocatalytic batch-process disinfection reactor for the treatment of biological and chemical contaminants in domestic drinking water in developing countries. *Sol Energy* 77:649–655
- Fujishima A, Zhang X, Tryk DA (2007) Heterogeneous photocatalysis: from water photolysis to applications in environmental cleanup. *Int J Hydrogen Energ* 32:2664–2672
- Gillan EG (2000) Synthesis of nitrogen-rich carbon nitride networks from an energetic molecular azide precursor. *Chem Mater* 12:3906–3912
- Han C, Chen Z, Zhang N, Colmenares JC, Xu Y-J (2015) Hierarchically CdS decorated 1D ZnO nanorods-2D graphene hybrids: low temperature synthesis and enhanced photocatalytic performance. *Adv Funct Mater* 25:221–229
- Han Q, Wang B, Gao J, Cheng ZH, Zhao Y, Zhang ZP, Qu LT (2016) Atomically thin mesoporous nano mesh of graphitic C<sub>3</sub>N<sub>4</sub> for high-efficiency photocatalytic hydrogen evolution. *ACS Nano* 10:2745–2751
- Han Q, Chen N, Zhang J, Qu L (2017) Graphene/graphitic carbon nitride hybrids for catalysis. *Mater Horiz* 4:832–850
- Hathway T, Rockafellow EM, Jenks WS, Chul Oh Y (2009) Photocatalytic degradation using tungsten-modified TiO<sub>2</sub> and visible light: kinetic and mechanistic effects using multiple catalyst doping strategies. *J Photochem Photobiol A* 207:197–203
- Ishibashi KI, Fujishima A, Watanabe T, Hashimoto K (2000) Detection of active oxidative species in TiO<sub>2</sub> photocatalysis using the fluorescence technique. *Electrochem Commun* 2:207–210
- Job WK, Kang HJ (2013) Polyacrylonitrile-TiO<sub>2</sub> fibers for control of gaseous aromatic compounds. *Ind Eng Chem Res* 52:4475–4483

- Kilmartin PA, Wright GA (2001) Photoeffects to characterise polypyrrole electrodes and bilayers with polyaniline. *Electrochim Acta* 46:2787–2794
- Kim J, Sohn D, Sung Y, Kim ER (2003a) Fabrication and characterization of conductive polypyrrole thin film prepared by in situ vapor-phase polymerization. *Synth Met* 132:309–313
- Kim B, Kim D, Cho D, Cho S (2003b) Bactericidal effect of TiO<sub>2</sub> photocatalyst on selected food-borne pathogenic bacteria. *Chemosphere* 52:277–281
- Kochuveedu ST (2016) Photocatalytic and photoelectrochemical water splitting on TiO<sub>2</sub> via photosensitization. *J Nanomater*. <http://dx.doi.org/10.1155/2016/4073142>
- Komatsu T, Nakamura T (2001) Polycondensation/pyrolysis of tris-s-triazine derivatives leading to graphite-like carbon nitrides. *J Mater Chem* 11:474–478
- Li Y, Zhang H, Liu P, Wang D, Li Y, Zhao H (2013) Cross-linked g-C<sub>3</sub>N<sub>4</sub>/rGO nanocomposites with tunable band structure and enhanced visible light photocatalytic activity. *Small* 9:3336–3344
- Li HY, Gan SY, Wang HY, Han DX, Niu L (2015) Intercorrelated superhybrid of AgBr supported on graphitic-C<sub>3</sub>N<sub>4</sub>-decorated nitrogen-doped graphene: high engineering photocatalytic activities for water purification and CO<sub>2</sub> reduction. *Adv Mater* 27:6906–6913
- Liang Q, Jin J, Zhang M, Liu Q, Xu S, Yao C, Li Z (2017) Construction of mesoporous carbon nitride/binary metal sulfide heterojunction photocatalysts for enhanced degradation of pollution under visible light. *Appl Catal B* 218:545–554
- Liao G, Chen S, Quan X, Yu H, Zhao H (2012) Graphene oxide modified g-C<sub>3</sub>N<sub>4</sub> hybrid with enhanced photocatalytic capability under visible light irradiation. *J Mater Chem* 22:2721
- Liu Q, Guo YR, Chen ZH, Zhang ZG, Fang XM (2016) Constructing a novel ternary Fe(III)/graphene/g-C<sub>3</sub>N<sub>4</sub> composite photocatalyst with enhanced visible-light driven photocatalytic activity via interfacial charge transfer effect. *Appl Catal B* 183:231–241
- Man MKL, Margiolakis A, Jones SD, Harada T, Wong EL, Krishna MBM, Madeo J, Winchester A, Lei S, Vajtai R, Ajayan PM, Dani KM (2017) Imaging the motion of electrons across semiconductor heterojunctions. *Nat Nanotechnol* 12:36–40
- Miller DR, Wang J, Gillan EG (2002) Rapid, facile synthesis of nitrogen-rich carbon nitride powders. *J Mater Chem* 12:2463–2469
- Mohamed AA, El-Sayed R, Osman T, Toprak M, Muhammed M, Uheida A (2016) Composite nanofibers for highly efficient photocatalytic degradation of organic dyes from contaminated water. *Environ Res* 145:18–25
- Novoselov KS, Falco VI, Colombo L, Gellert PR, Schwab MG, Kim K (2012) A roadmap for graphene. *Nature* 490:192–200
- Pan X, Yang MQ, Tang ZR, Xu Y-J (2014) Noncovalently functionalized graphene-directed synthesis of ultralarge graphene-based TiO<sub>2</sub> nanosheet composites: tunable morphology and photocatalytic applications. *J Phys Chem C* 118:27325–27335
- Rajendra CP, Varsha K, Caroline SYL (2014) Hybrid photocatalysts using graphitic carbon nitride/cadmium sulfide/reduced graphene oxide (g-C<sub>3</sub>N<sub>4</sub>/CdS/RGO) for superior photodegradation of organic pollutants under UV and visible light. *Dalton Trans* 43:12514–12527
- Ramirez KB, Kim D, Cho D, Cho S (2015) 4-chlorophenol removal from water using graphite and graphene oxides as photocatalysts. *J Environ Health Sci Eng* 13:33. (10pgs)
- Samsudin EM, Goh SN, Wu TY, Ling TT, Bee S, Hamid A, Juan JC (2015) Evaluation on the photocatalytic degradation activity of reactive blue 4 using pure anatase nano-TiO<sub>2</sub>. *Sains Malays* 44:1011–1019
- Shalom M, Gimenez S, Schipper F, Herraiz-Cardona I, Bisquert J, Antonietti M (2014) Controlled carbon nitride growth on surfaces for hydrogen evolution electrodes. *Angew Chem Int Ed* 53:3654–3658
- Szabó T, Berkesi O, Forgó P, Josepovits K, Sanakis Y, Petridis D, Dékány I (2006) Evolution of surface functional groups in a series of progressively oxidized graphite oxides. *Chem Mater* 18:2740–2749
- Tan SN, Ge H (1996) Investigation into vapour-phase formation of polypyrrole. *Polymer* 37:965–968

- Vachon DD, Angus RO, Lu FL, Nowak M, Liu ZX, Schaffer H (1987) Polyaniline is poly-para-phenyleneamineimine: proof of structure by synthesis. *Synth Met* 18:297–302
- Vukmirovic N, Wang LW (2009) Electronic structure of disordered conjugated polymers: polythiophenes. *J Phys Chem B* 113:409–415
- Wang J, Neoh KG, Kang ET (2004) Comparative study of chemically synthesized and plasma polymerized pyrrole and thiophene thin films. *Thin Solid Films* 446:205–217
- Wang X, Blechert S, Antonietti M (2012) Polymeric graphitic carbon nitride for heterogeneous photocatalysis. *ACS Catal* 2:1596–1606
- Wang S, Li D, Sun C, Yang S, Guan Y, He H (2014) Synthesis and characterization of g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>3</sub>VO<sub>4</sub> composites with significantly enhanced visible-light photocatalytic activity for triphenylmethane dye degradation. *Appl Catal B* 144:885–892
- Xu J, Hou J, Zhang S, Zhang R, Nie G, Pu S (2006) Electrosyntheses of high quality poly(5-methylindole) films in mixed electrolytes of boron trifluoride diethyl etherate and diethyl ether. *Eur Polym J* 42:1384–1395
- Yan SC, Li ZS, Zou ZG (2009) Photodegradation performance of g-C<sub>3</sub>N<sub>4</sub> fabricated by directly heating melamine. *Langmuir* 25:10397–10401
- Yang MQ, Xu YJ (2013) Selective photo redox using graphene-based composite photocatalysts. *Phys Chem Chem Phys* 15:19102–19118
- Yang MQ, Xu YJ (2016) Photocatalytic conversion of CO<sub>2</sub> over graphene-based composites: current status and future perspective. *Nanoscale Horiz* 1:185–200
- Yang MQ, Zhang N, Pagliaro M, Xu YJ (2014) Artificial photosynthesis over graphene–semiconductor composites. Are we getting better? *Chem Soc Rev* 43:8240–8254
- Yu Q, Guo S, Li X, Zhang M (2014) Template free fabrication of porous g-C<sub>3</sub>N<sub>4</sub>/graphene hybrid with enhanced photocatalytic capability under visible light. *Mater Technol* 29:172–178
- Yuan L, Yang MQ, Xu YJ (2014) Tuning the surface charge of graphene for self-assembly synthesis of a SnNb<sub>2</sub>O<sub>6</sub> nanosheet–graphene (2D–2D) nanocomposite with enhanced visible light photoactivity. *Nanoscale* 6:6335–6345
- Zhang J, Xiao FX, Xiao G, Liu B (2014) Self-assembly of a Ag nanoparticle-modified and graphene-wrapped TiO<sub>2</sub> nanobelt ternary heterostructure: surface charge tuning toward efficient photocatalysis. *Nanoscale* 6:11293–11302
- Zhang N, Yang MQ, Liu S, Sun Y, Xu YJ (2015) Waltzing with the versatile platform of graphene to synthesize composite photocatalysts. *Chem Rev* 115:10307–10377
- Zhao Y, Zhao F, Wang X, Xu C, Zhang Z, Shi G, Qu L (2014) Graphitic carbon nitride nanoribbons: graphene-assisted formation and synergic function for highly efficient hydrogen evolution. *Angew Chem Int Ed* 53:13934–13939
- Zheng Y, Jiao Y, Zhu Y, Li LH, Han Y, Chen Y, Du A, Jaroniec M, Qiao SZ (2014) Hydrogen evolution by a metal-free electrocatalysts. *Nat Commun* 5:3783
- Zheng Y, Jiao Y, Jaroniec M, Qiao SZ (2015) Advancing the electrochemistry of the hydrogen-evolution reaction through combining experiment and theory. *Angew Chem Int Ed* 54:52–65