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Transfiguring UV light active "metal oxides" to visible light active photocatayst by reduced graphene oxide hypostatization

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ABSTRACT

This work explains about the visible light photocatalytic activities of wide band gap metal oxides (TiO_2, ZnO, CeO_2, Eg > 3.0 eV) after the overture of reduced graphene oxide. The reduced graphene oxide and metal oxide heterostructures (RGO-MO) *Ca.* RGO-TiO_2, RGO-ZnO, RGO-CeO_2 were synthesized through microwave, template assisted, and hydrothermal methods respectively. This explains about the activity of the photocatalysts towards hydrogen production via water splitting, water treatment towards inorganic contaminants with or without dye sensitization activity as well. RGO-MO having particle size 5–10 nm which shows great activity towards various photocatalytic activities. Pure TiO_2, CeO_2 and ZnO are UV active semiconductors having wide band gap 3.2 eV. However, when these semiconductors are modified with RGO they are showing better visible light activity towards photoreduction of Chromium (VI) and hydrogen production by half reaction of water.

1. Introduction

From last two to three decades, the top worldwide issues at the moment are those bothered with ensuring supply of clean water and energy at reasonable cost. For these reasons studies are going on advanced materials and processes for water purification, along with the production of clean and renewable hydrogen fuel by photocatalytic, photoelectrocatalytic water splitting, the photocatalytic reduction of carbon dioxide to fuels efficiently, at low cost and with less energy.

One of the serious pollution problems now is the discharge of toxic heavy metals into aquatic environment. Among these toxic heavy metals pollutants, the most severe environmental concern is chromium due to its high toxicity, potential carcinogenicity, and high mobility in water.

Fossil fuels cannot be termed as ideal fuel as it destined to be run out and the combustion of fossil fuels, such as coal and petroleum, will produce carbon dioxide (CO_2), which is one of the major greenhouse gases that causes climate change [1]. For this several alternative energies developed for the replacement of fossil fuels which should have lower carbon emission compared to the fossil fuels. But, these processes of developing the renewable energies require double the energy to produce and are more expensive.

However, solar energy is free and inexhaustible which can be converted to electrical energy *via.* water splitting which yields the hydrogen energy having high energy density, environmentally friendly as the end product is free of pollutants, greenhouse gases. Again the hydrogen can be stored in gaseous, liquid or metal hydride form and can be distributed over large distances through pipelines or *via* tankers [2]. For any photocatalytic reaction, the catalyst should be active under visible range of solar spectrum, as the solar spectrum contains only 5% of UV light and 43% of visible light. Consequently, visible light active photocatalysis gains much attention due to its enormous availability through solar light.

TiO_2, ZnO, CeO_2 are non toxic, cost effective and have appropriate band positions for any redox reactions for the last so many years. TiO_2-based photocatalysis has grown into a fascinating research field since Fujishima and Honda's first reports of UV-light-induced redox chemistry on TiO_2 [3]. ZnO is considered as alternative to TiO_2, used in various photocatalytic applications *via* modification of its wide band gap. Apart from the most commonly used TiO_2 and ZnO catalysts, cubic fluorite cerium dioxide (CeO_2), a semiconductor with a band gap energy similar to that of TiO_2 [4], also shows promising photocatalytic activity for the degradation of various organic dye pollutants such as Methylene Blue, Methyl Orange and C.I. Reactive Black 5 [5,6]. CeO_2 has also successfully been employed in water splitting for H_2 production, phenol and chlorinated phenol photodegradation under UV illumination [7,8]. But due their wide band gap, these catalysts are quite unutilised in the whole solar spectrum. Accordingly, to utilise these UV active catalysts in visible region, many attempt are taken *Ca.* Impurity doping [9,10], sensitisation [11], surface modification [12],

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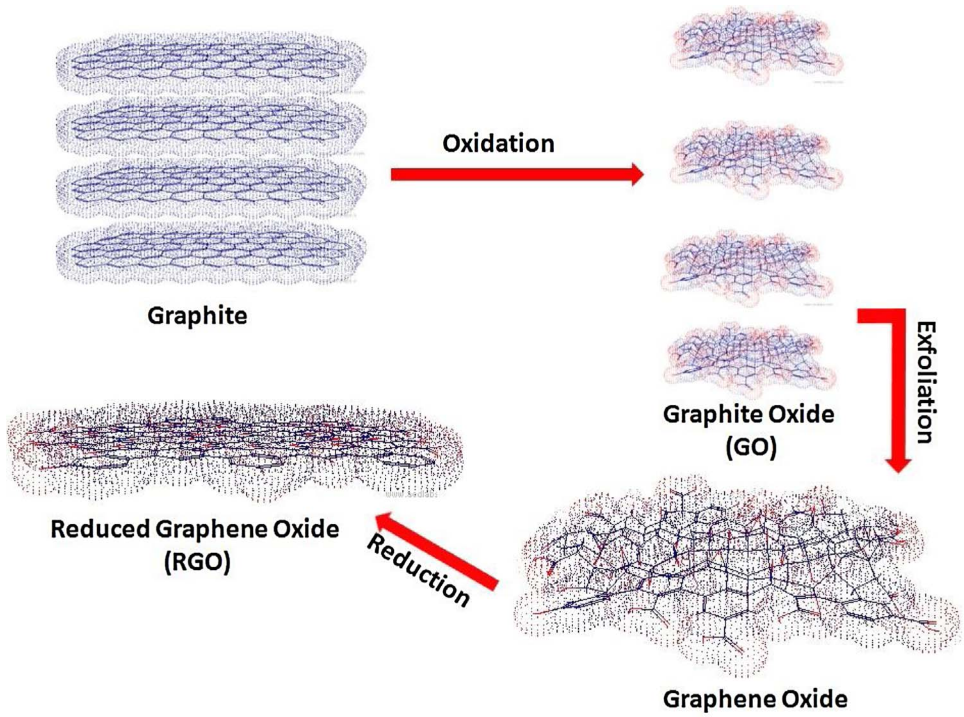

Fig. 1. Preparation of graphene oxide by the Hummers' method.

and fabrication of heterostructures with other materials [13]. Though these attempts to induce visible-light absorption in semiconductors are successful partly, they don't be up to snuff to constitute an efficient visible-light photocatalyst, because the reactivity of photogenerated charge carriers in doped levels or narrowed bands are much less than those in valence band (VB) and conduction band (CB). A different strategy used to improve the visible light photocatalytic activity of wide band gap photocatalysts is to combine it with conductive materials, which include doping of noble metal particles, carbon nanotubes, dye sensitization and reduced graphene oxide (RGO).

Recently, dye sensitization to enable the efficient utilization of visible-light for photo-induced hydrogen production is a promising route [13]. The organic dyes acquires efficient light-harvesting ability over noble metal complexes with many beneficial characteristics. Tiwari et al. and Wang et al. synthesized dye sensitized TiO_2 and evaluated its catalytic activity under UV/Visible light towards dye degradation and H_2 production with or without using Pt noble metal [13]. Also visible-light induced hydrogen generation through dye-sensitized water splitting was reported by previous researchers [13].

But apart from dye sensitization, graphene markedly is a new two-dimensional system with excellent charge carrier mobility, extremely large theoretical specific surface area, high thermal conductivity and outstanding mechanical properties, [14] has been widely applied as an extraordinary two dimensional support and electron transport material. In recent times, Reduced graphene oxide (a derivative of graphene oxide) has been combined with variety of metal oxides such as TiO_2 [15], ZnO [16], Cu_2O [17], $ZnFe_2O_4$ [18], $CuFe_2O_4$ [19] and Bi_2WO_6 [20] are found to be excellent photocatalysts for the degradation of synthetic dyes. Graphene oxide derivatives prevent the corrosion and leaching of the metal oxide nanoparticles into the water thereby enhancing the longevity of the photocatalyst along with limiting the electron-hole recombination in a photocatalytic system. Apart from this, the construction of π–π stacking between aromatic rings of graphene and organic pollutants also facilitates the adsorption of pollutants on the photocatalyst thereby enhancing the quenching of pollutants [21].

Wang et al. [16] synthesized reduced graphene oxide (RGO) coated with ZnO nanoparticles (NPs) by a self-assembly and in-situ photo-reduction method, and reported the application for removing RhB dye from water *via* UV–vis irradiation. Liu et al. [16] designed ZnO–reduced graphene oxide (RGO) composites *via* UV-assisted photocatalytic reduction of graphite oxide by ZnO nanoparticles in ethanol, reported its performance in reduction of Cr(VI) with a maximum removal rate of 96% under UV light irradiation as compared with pure ZnO (67%).

Though, toxic reducing agents such as hydrazine is used for the reduction of GO, in our work reduction of GO to RGO was achieved in-situ without using any external reducing agent. Herein, we firstly synthesized GO by hummers method, and then coupled with TiO_2, ZnO, CeO_2 to form a new binary heterostructure photocatalyst for the reduction of Chromium-VI and also for the hydrogen production by partial splitting of water under visible light irradiation. For the first time we are introducing type II-like heterostructure with RGO, derived and compared its activity under visible and UV light. Also we have sensitized the RGO-TiO_2, RGO-ZnO and RGO-CeO_2 with Coumarine dye (C_{334}) and studied the improvement of photocatalytic activity of sensitized photocatalytsts for the reduction of Cr-VI under visible light irradiation. In our work, rather than using RGO as sensitizer or co-catalyst we have taken it as another hybrid catalyst and predicted a new possible photocatalytic mechanism, as RGO, a semiconductor having band gap of 2.5 eV whose CB and VB levels are *Ca.* −0.75 and 1.75 V (*vs.* NHE) [22–24].

2. Experimental

2.1. Materials

All the chemicals used in this experiment are of analytical grade (AR) and is used without further purification.

Chemicals: Graphite powder (Sigma-Aldrich), Ti $(OCH_2CH_2CH_2CH_3)_4$ (Sigma-Aldrich), Urea (Merck), Zn $(NH_3)_4CO_3$ (Merck), $(NH_4)_2CO_3$ (Merck), NH_4OH (Merck), Ce $(NO_3)_3{\cdot}6H_2O$ (Sigma-Aldrich), NaOH (Merck), Coumarine dye (C_{334}) (Sigma-Aldrich).