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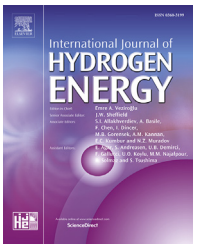

Decoration of Pt on the metal free RGO-TiO_2 composite photocatalyst for the enhanced photocatalytic hydrogen evolution and photocatalytic degradation of pharmaceutical pollutant β blocker

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ABSTRACT

Easy synthesis of graphene based composite photocatalyst with the incorporation of minimal quantity of noble metals for the enhanced photocatalytic hydrogen evolution as well as photocatalytic degradation and mineralization of recalcitrant pollutants under solar irradiation is an urgent requirement from the clean energy and environment point of view all over the globe. Herein, we demonstrate the decoration of Pt by photodeposition method on the hydrothermally synthesized RGO-TiO_2 nanocomposite. The various photocatalysts synthesized were successfully characterized by XRD, FTIR, Raman, UV–visible absorption spectra, XPS, SEM and TEM techniques. The well characterized photocatalysts were further investigated for the photocatalytic hydrogen evolution studies of methanol water mixtures under UV as well as simulated solar light irradiation. The optimized Pt-RGO-TiO_2 (1 wt % Pt and 10 wt % RGO) composite was found to show 14 fold increase in the photocatalytic hydrogen evolution efficiency under UV light irradiation and 20 fold increase under simulated solar light irradiation as compared to bare TiO_2 under UV light irradiation. The ternary photocatalyst showed very good recycle and reuse capability up to 4 cycles. The optimized Pt-RGO-TiO_2 was further tested for the enhanced photocatalytic degradation and mineralization of pharmaceutical pollutant namely β blocker Propranolol under UV as well as simulated solar light irradiation. The obtained results showed 79% and 94% reduction in COD of Propranolol under UV and simulated solar light irradiation respectively. The appreciable enhancement in the photocatalytic activity of the Pt decorated RGO-TiO_2 photocatalyst as compared to bare TiO_2 under UV and simulated solar light can be attributed to the use of maximum range of solar spectrum along with their excellent properties of charge separation by RGO and Pt.

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Introduction

Developing high efficiency and stable photocatalytic materials harvesting energy directly from solar light is a promising and environmentally friendly low cost approach for the photocatalytic hydrogen evolution as well as water remediation all over the globe. TiO_2 is the benchmark photocatalyst possessing favorable band–edges that straddle the redox potential of water photoelectrolysis for water splitting. Further its strong oxidizing power, non-toxic nature, and low cost makes it a suitable choice for photocatalytic applications [1,2]. However, despite its great potential, the energy conversion efficiency by TiO_2 photocatalytic water splitting is still low, basically due to the fast recombination of the photogenerated electron–hole pairs, fast backward reaction and inability to use visible light. Scientific community is focusing day and night to enhance the photocatalytic efficiency of TiO_2 to make the photocatalytic H_2 evolution system economically and practically viable using renewable solar energy. For improved photocatalytic efficiency TiO_2 has been modified by means of metal loading [3–5], metal ion doping, dye sensitization, composite semiconductor, anion doping and metal ion implantation [6]. However noble metals doping is expensive. Metal ion doping can expand its photo response to visible region through formation of impurity energy levels. However the effect of red shift is negligible and doped ions tend to become recombination centers. Metal free composites of semiconductors with carbon materials are currently being considered as potential photocatalysts to solve the energy and environment related problems. It has been shown previously that the composites of semiconductors [1] and carbon, including activated carbon [7], carbon nanotubes (CNTs), and fullerenes, exhibit enhanced photocatalytic performance than semiconductors alone with an added advantage of incorporating high surface area to the composite.

In comparison with CNTs, graphene has perfect sp^2-hybridised two dimensional carbon structure with better conductivity and larger surface area as unrolled CNTs [8,9]. Furthermore graphene is easy to produce from natural graphite through chemical oxidation-dispersion-reduction procedure at a low cost [10]. It has also been established as best cocatalyst for photocatalytic H_2 production due to its excellent thermal conductivity, charge carrier mobility and chemical stability [11]. In addition of acting as an excellent electron sink, incorporation of graphene into TiO_2 provides with the advantage of increased absorptivity as well as extended visible light absorption [12]. Li et al. has studied the photocatalytic hydrogen evolution with TiO_2-graphene composite using methanol as a sacrificial agent and observed the hydrogen evolution to be 80 $\mu molh^{-1}$ which was 2.3 times higher than bare TiO_2 under UV light irradiation [13]. With the composite of commercial P25 with graphene, H_2 evolution was observed to be 26 $\mu molh^{-1}$ which was found to be 3.8 times higher than commercial P25 under UV irradiation using methanol as a sacrificial agent. When $Na_2S + Na_2SO_3$ were used as sacrificial agent the hydrogen evolution was found to be 4.7 $\mu molh^{-1}$ for 5 wt% mass fraction of graphene [14–16]. Haitham et al. [17] has observed 36 $\mu molh^{-1}$ hydrogen evolution rate with P25 TiO_2-RGO (5 wt%) as compared to 2.8 $\mu molh^{-1}$ for bare P25-TiO_2 with 20% (v/v) methanol aqueous solution using 300 W Xenon lamp. Gupta et al. has reported the eco-friendly and cost effective γ radiolysis assisted synthesis of TiO_2-RGO (1 wt % of RGO) photocatalyst for efficient hydrogen evolution [18]. Zhang et al. has reported green one step hydrothermal method for the synthesis of TiO_2-graphene sheets showing 1.6 times higher photocatalytic hydrogen evolution capacity over commercial P25 [19]. This enhancement in the photocatalytic hydrogen evolution capacity was attributed to the excellent electron conductivity of graphene sheets and the chemical bonding between TiO_2 and graphene sheets. Cheng et al. has observed enhanced (668 $\mu molh^{-1}$) H_2 evolution for 0.5% RGO-TiO_2 (P25) composite in aqueous methanol solution under 300 W Xe lamp, which was 68% more than that of bare P25 [20].

In recent past although the focus had been shifted to noble metal free photocatalyst for cost effectiveness but the amount of hydrogen evolved for such graphene based photocatalysts was far low as compared to noble metal doped semiconductor (TiO_2). Recently Lasa et al. has reported the synthesis of Pt-mesoporous TiO_2 photocatalyst with promising quantum yield of 22.6% for the 2.5 Pt wt% using black light blue lamps as the light source and ethanol as a sacrificial agent [21]. Zhou et al. has reported the H_2 evolution rate of 1023.71 $\mu molh^{-1}\,g^{-1}$ of 1% Pt doped TiO_2 hallow spheres under visible light irradiation in methanol water mixture [22]. Antony et al. has reported that 1.25 wt% of Pt on TiO_2 shows 30 $\mu molh^{-1}\,g^{-1}$ of hydrogen evolution under incident light of 254 nm wave length [23]. The photocatalytic H_2 evolution tests reported by Zhang et al., indicate that the Pt/TiO_2 hybrid nanofibers possesses high efficiency of H_2 evolution from photocatalytic water reduction under visible light irradiation due to the extended visible-light absorption by Pt doping and efficient interfacial charge-transfer caused by the electron-sink and activation roles of Pt NPs [24]. Few literatures report that the co-presence of RGO and Pt on TiO_2 surface synergistically enhances the visible light driven photocatalytic reduction of CO_2 [25]. Haitham et al. reports the fabrication of RGO with commercially available TiO_2 (P25) by hydrothermal method and the effect of incorporation of Au or Pt for hydrogen evolution reaction [26]. Zhou et al. has reported the synthesis of TiO_2-NS/Pt/GO (TPGA) aerogel for the degradation of chlortetracycline under visible light irradiation. They observed that with the presence of both Pt nanoparticles and GO in TPGA, the recombination rate of electrons and holes has been highly reduced. They have reported the excitation of Pt nanoparticles by the light irradiation to produce photogenerated electron-hole pairs through Surface Plasmon Resonance (SPR) effect, which helps to enhance the photocatalytic activity of TPGA [22]. One more important quality towards increased photocatalytic activity is the formation of Schottky junctions when noble metal (Ag or Pt) nanoparticles directly contact with metal oxide semiconductors [27,28].

The incorporation of graphene has been envisaged as one of the ways to minimize the % of costly Pt doping in the ternary composite with TiO_2. In view of all these, fabrication of multicomponent hybrid photocatalyst viz. Pt-RGO-TiO_2 for the improved solar photocatalytic H_2 evolution and photocatalytic degradation of recalcitrant pollutants is highly indispensable. Here we report the synthesis of RGO-TiO_2

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