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Fabrication of RuO_2-Ag_3PO_4 heterostructure nanocomposites: Investigations of band alignment on the enhanced visible light photocatalytic activity

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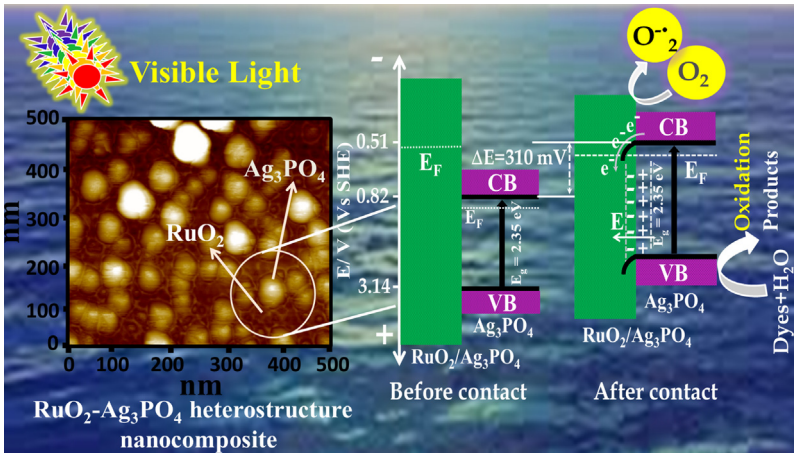
HIGHLIGHTS

- Ag_3PO_4, RuO_2 and RuO_2-Ag_3PO_4 heterostructure nanocomposites were prepared using simple wet chemical technique.
- The electric field at interface of pure Ag_3PO_4 and RuO_2-Ag_3PO_4 is found to be 310 mV.
- RuO_2-Ag_3PO_4 inhibits self oxidation of Ag_3PO_4 under this formed electric field.
- The enhanced electrons-holes separation leads the higher efficiency as well as stability for RuO_2-Ag_3PO_4.

GRAPHICAL ABSTRACT



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ABSTRACT

The RuO_2-Ag_3PO_4 heterostructured nanocomposite was successfully synthesized by facile in situ deposition of porous ruthenium oxide (RuO_2) nanoparticles on the surface of the silver phosphate (Ag_3PO_4). Under visible light irradiation, the 0.5 wt.% RuO_2-Ag_3PO_4 heterostructure photocatalyst exhibits enhanced photocatalytic efficiency compared to other composites of RuO_2-Ag_3PO_4 and Ag_3PO_4. The optimized 0.5 wt.% RuO_2-Ag_3PO_4 nanocomposites exhibited 1.5 times enhanced photocatalytic activity towards the degradation of methylene blue (MB) than Ag_3PO_4. Moreover, the degradation rate of 0.5 wt.% RuO_2-Ag_3PO_4 nanocomposite towards the cationic dyes MB and rhodamine B (RhB) was nearly 6.6 times and 4.7 times higher than that towards the anionic dye methyl orange (MO). The formed heterojunction electric field of 310 mV at the interface between RuO_2 and Ag_3PO_4 heterostructure induces downward band bending of Ag_3PO_4. Also, this electric field increases the separation efficiency of electrons-holes resulting higher degradation efficiency. The quenching effect of scavengers test confirms that holes are reactive species and the RuO_2-Ag_3PO_4 nanocomposite is highly stable, exhibited 88% of MB degradation after 4 recycles. The RuO_2-Ag_3PO_4 nanocomposites inhibit self oxidation of Ag_3PO_4 resulting improved efficiency and stability.

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1. Introduction

The photocatalysis has been regarded as one of the promising technology to harness solar energy to removal and degradation of hazardous dyes, water purification and water disinfection etc. In general, the UV spectrum region which accounts only 4% of the solar energy restricts its practical day-to-day applications. As a result, the photocatalysts based on visible light sensitive semiconductors [1–7] are developed for photocatalytic degradation of dyes. Significant efforts have been paid to tailor the properties of semiconductors by doping, forming nanocomposites or designing two semiconductors to form a heterostructure [8–14]. In heterostructures, the created electric field at the interface of semiconductors ultimately determines the photocatalytic activity and stability by increasing the lifetime of charge carriers [15]. Since, the creation of electric field, the direction of charge transportation and distance of charge separation at the interface junction of so-formed heterostructures are believed to be the feasible approach for the study of visible light irradiated photocatalytic activity.

In 2001, Thomas et al. [16] have characterized the structural and the dielectric properties of nanostructured silver phosphate (Ag_3PO_4). Later, in 2010, Yi et al. [17] have reported that the Ag_3PO_4 is an *n*-type semiconductor used for photocatalytic O_2 evolution and degradation of MB under visible light irradiation. The investigations on the size [18], crystal face and morphology [19,20] clearly demonstrated that Ag_3PO_4 exhibits higher quantum yield than other visible light active metal oxides [21,22]. Subsequently, much effort has been focused on GR, RGO, GO, MWCNT [23–26], carbon quantum dots (CQDs) [27] to composite into Ag_3PO_4 due to its higher electrical conductivity which ultimately enhances the separation efficiency of photogenerated electron-hole pairs. Several metal oxide based composites of Ag_3PO_4 with CeO_2 [28], $SrTiO_3$ [29], TiO_2 [30], AgI [31], and SnO_2 [32] were developed. Bu et al. reported the formation of electric field between PANI/Ag_3PO_4 interfaces that improves the photocatalytic activity [33]. If the photoexcited electrons or photogenerated holes of Ag_3PO_4 are not consumed by dye molecules, it gives negative impact on its stability [34]. Thus, the photooxidation of Ag_3PO_4 needs to be improved for better photocatalytic efficiency.

RuO_2 is a transition metal oxide which can be used in various applications such as supercapacitor [35], photocatalytic water splitting [36] and photocatalytic dye degradation [37,38] due to its high chemical stability, electrical (metallic) conductivity and excellent diffusion barrier properties [39]. As the presence of small amount of RuO_2 would act as an efficient hole and electron transfer catalyst on TiO_2, an excessive amount may act as recombination centre [40,41]. RuO_2 on the ZnO nanocomposites leads the flow of holes into the RuO_2 and the band bending between RuO_2 and ZnO enhances efficient charge separation which also increases the lifetime of interfacial charge carriers thus accounting higher photocatalytic activity [42]. Therefore, compositing RuO_2 into Ag_3PO_4 to form a RuO_2-Ag_3PO_4 heterostructure nanocomposite might be a positive strategy to enhance charge transfer as well higher efficiency visible light driven photocatalyst.

In this work, we report the preparation of RuO_2-Ag_3PO_4 heterostructure nanocomposites based on the different weight percentage of RuO_2 (0.5, 1, 3, 5 wt.%) with Ag_3PO_4 by in-situ wet chemical method. The prepared samples show enhanced degradation of MB, RhB (cationic) and MO (anionic) dyes, under visible light irradiation. The MB degradation using of g-C_3N_4 and WO_3 also tested and compared with as-prepared samples. The downward band bending of Ag_3PO_4 is proposed due to an electric field formed at interface between RuO_2 and Ag_3PO_4. The effective charge separation and transportation can be achieved due to the presence of electric field between RuO_2 and Ag_3PO_4, played a major role in the higher efficiency and stability of RuO_2-Ag_3PO_4 heterostructure.

2. Experimental section

2.1. Chemicals

Ruthenium (III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$) was purchased from SRL chemicals, India. Sodium tungstate ($Na_2WO_4 \cdot 2H_2O$), sodium hydroxide (NaOH), ammonia solution (25%), nitric acid (69%), methylene blue (MB), rhodamine B (RhB) and methyl orange (MO) were purchased from Merck, India. Silver nitrate ($AgNO_3$), disodium hydrogenphosphate (Na_2HPO_4) and melamine ($C_3H_6N_6$) were purchased from Alfa Aesar, United Kingdom. All the chemicals were of analytical grade and used without any further purification. The double distilled water was used in all the experiments.

2.2. Synthesis of RuO_2 nanoparticles

The RuO_2 nanoparticles were synthesized using wet chemical technique [43]. In a typical synthesis procedure, 0.02 M of $RuCl_3 \cdot 6H_2O$ was dissolved into 100 mL of double distilled water and heated at 100 °C for 10 min. NaOH solution (1 M in 20 mL) was added drop wise into the above solution. Then, the heating was extended to 45 min with the same temperature and the resulting precipitate was subsequently centrifuged and washed several times with double distilled water. The obtained powder was dried at 80 °C for 6 h in hot air oven. Finally, the as-prepared powder was annealed at 300 °C for 3 h.

2.3. Synthesis of RuO_2-Ag_3PO_4 heterostructure nanocomposites

The RuO_2-Ag_3PO_4 heterostructure nanocomposites were prepared as follows: An appropriate amount of RuO_2 nanoparticle was dispersed into 20 mL of double distilled water. The silver ammonia complex was added (0.3 M, 1.25 mL of ammonia) into the above dispersion and stirred for 30 min (solution A). On the other hand, 0.1 M of Na_2HPO_4 was dissolved into 20 mL of double distilled water and named as solution B. Then, the solution B was added dropwise into the solution A. The solution pH was adjusted to 7.5 by simultaneous addition of 1 mL of HNO_3 resulting in the formation of RuO_2-Ag_3PO_4 composites and the solution was further stirred for 4 h under dark condition. Finally, the precipitates were centrifuged and washed several times with double distilled water. The obtained solid product of RuO_2-Ag_3PO_4 heterostructure nanocomposites was dried at 100 °C for 6 h in hot air oven. The addition of RuO_2 to Ag_3PO_4 was varied as 0.5, 1, 3, and 5 wt.% and their results were analyzed and compared with the pure Ag_3PO_4 nanopowders. The detailed synthesize procedure of g-C_3N_4, WO_3 and characterization techniques were given in the supplementary information.

3. Results and discussion

3.1. Formation mechanism of RuO_2-Ag_3PO_4 heterostructure nanocomposites

The RuO_2-Ag_3PO_4 heterostructure nanocomposites were synthesized using in-situ wet chemical method and the schematic representation is illustrated in Fig. 1(i). RuO_2 is sonicated for 30 min in water. Then, freshly prepared $[Ag(NH_3)_2]^+$ solution was added into RuO_2 solution to form RuO_2 $[Ag(NH_3)_2]^+$ complex as demonstrated in equation (1). When Na_2HPO_4 solution was dropped into the mixture, the adsorbed Ag^+ would react with PO_4^{2-} to form Ag_3PO_4 resulting RuO_2-Ag_3PO_4 heterostructure nanocomposites.