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Ag deposition effects on the photocatalytic activity of nanoparticulate TiO_2 — Comparison of gamma irradiation and UV irradiation methods

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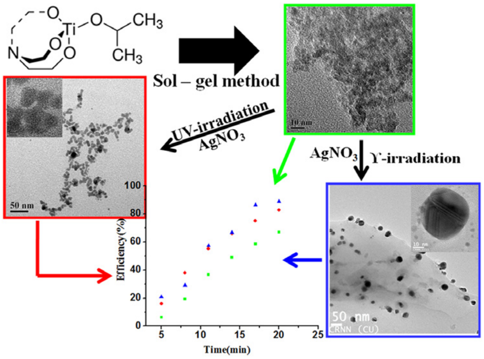
HIGHLIGHTS

- Rutile TiO_2 was synthesized using modified polyol method.
- UV and γ-irradiation techniques were applied for the synthesis of Ag–TiO_2 nanocomposites.
- Ag–TiO_2 nanocomposites perform better as photocatalysts.
- Nanocomposites prepared by γ-irradiation show better crystallinity and size distribution.
- Most important the composites contain the MP-Ti suboxide Ti_2O_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Rutile phase TiO_2 nanoparticles were synthesized first by a modified polyol based sol–gel technique. One important aspect of this work is that the less common rutile phase of TiO_2 could be synthesized under mild conditions of temperature and pH. Then these TiO_2 nanoparticles were impregnated with Ag using radiation methods i.e. UV-radiation and γ-radiation. This resulted in the formation of Ag–TiO_2 nanocomposites. The differences in structure, crystallinity and size of the Ag–TiO_2 nanocomposites depends strongly on the reductive power of the reducing species involved as has been ascertained by TEM, XRD and XANES study. The weakly reducing free radicals generated from glycerol via the UV-irradiation method leads to formation of tetrapod precursor like composite nanoparticles of lower crystallinity. On the other hand, the strongly reducing hydrated electron (in the γ-irradiation method) leads to single crystalline, discrete and spherical Ag–TiO_2 nanocomposites with traces of Ti_2O_3. We have been successful in preparing Ti_2O_3 which is a Magneli phase (MP) Ti sub-oxide, without calcination at very high temperatures. The photocatalytic efficiency of the composites is better than TiO_2 itself. The photocatalytic efficiency of the nanocomposites depends on their structure and crystalline nature which can be ultimately correlated to the efficiency of production of active oxygen species like •OH. The presence of the narrow band gap Ti_2O_3 phase enhances photocatalytic activity of rutile TiO_2.

1. Introduction:

Semiconductors and metal nanoparticles are scientifically very attractive materials because of their shape and size dependent

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optical, electronic and catalytic properties [1–8]. Heterostructures comprising noble metal–semiconductor oxides such as Ag/TiO_2 and Au/TiO_2 are important because of their special properties and photocatalytic activity [9–14]. There is one recent study on Cu/TiO_2 heterostructures [15]. TiO_2 is a promising material due to its nonphotocorrosive and nontoxic in nature [16,17] and Ag is also particularly suitable for various applications because of its lower toxicity compared with other metals. The deposition of Ag on the surface of TiO_2 has been shown to exhibit enhanced efficiency for energy storage, catalysis and environmental remediation. In these heterostructured systems, Ag particles can act as electron scavenging centres and thus lead to increased electron and hole separation [18]. Xu et al. have done extensive work on M@TiO_2 (M=Au, Pd, Pt) core shell nanocomposite and have demonstrated their superior visible light photocatalytic activity over TiO_2 [19,20]. Kamat et al. have worked extensively on Au/TiO_2 core shell nanostructures [21,22]. Apart from metal doping, self-doping of carbonate species onto semiconductor catalysts lead to surface oxygen vacancies, causing improved charge transfer and reduced recombination rates [23,24]. Moreover, as reported by Huang et al., the reactive oxygen species generated in the photocatalytic process are largely significant in environmental chemistry applications [25].

The use of semiconductor materials in photocatalysis is common because their band gaps are suitable for effectively utilizing light energy [26–28]. Over the past few decades, numerous studies have been devoted to the development of more and more efficient TiO_2nanomaterials for this purpose [29,30]. In the past TiO_2 nanomaterials have been synthesized by a wide variety of methods viz. the popular sol–gel method [31,32], template-based methods [33,34], electrochemical [35], microwave-based [36], solvothermal [37–40] and hydrothermal methods [31,39,41–43]. One of the lesser known methods is the polyol method [44]. However in terms of low cost and simplicity of execution, it is one of the most effective methods. The conventional polyol method involves the use of alcohols [45]. Glycerol has also been occasionally used in the past in a modified polyol method [44,46,47]. Glycerol here behaves as both solvent and reducing agent. In the past glycerol has been used in colloidal synthesis to increase the monodispersity of various nanostructures [47–50]. The monodispersity of the nanostructures in glycerol is attributed to the hydroxyl groups present which increases the stability of the nanoparticles against oxidation or ripening. Also the high viscous nature of glycerol slows down the migration velocity of the NPs leading to the formation of uniform spherical nanostructures with increased crystalline nature [47–50]. However, the use of polyol method for the synthesis of TiO_2 nanomaterials is not too common [36–38]. The novelty of this work lies mainly in the synthesis of the less common polymorph of TiO_2 i.e rutile . Most synthetic methods give rise to the anatase form of TiO_2. In the past, rutile could be synthesized only at high temperature or low pH [39]. This work employs relatively mild conditions for synthesis of rutile i.e room temperature and near neutral pH. Also rutile form was found to function as an efficient photocatalyst contrary to popular belief that only anatase is a good photocatalyst [39].

Here TiO_2 nanoparticles have been synthesized by a modified polyol method using glycerol. Then the Ag–TiO_2 nanoparticles have been produced by radiation techniques — both gamma irradiation and UV irradiation in presence of glycerol. The gamma-radiolysis route for reduction of silver ions has been used due to its important advantages: (i) controlled reduction of metal ions can be performed without using an excess of reducing agent, (ii) reducing agent is generated uniformly in the solution, (iii) the method provides metal nanoparticles in fully reduced, highly stable state, (iv) no interfering impurities like metal oxides are introduced, (v) the method is reproducible and (vi) synthesis can be carried out at ambient conditions [51]. The UV irradiation and γ-irradiation based methods have not commonly been used for synthesis of Ag–TiO_2 in the past.

One very important implication of this work is the synthesis of MP Ti sub-oxide Ti_2O_3. Very recently [52] Magneli phase (MP) Ti sub-oxides with general formulae Ti_nO_{2n-1} have received considerable attention due to their high electronic conductivity. Ti_2O_3 is an MP Ti sub-oxide. To accommodate oxygen deficiency, in MP Ti sub-oxides there occurs face sharing of TiO_6 octahedra. These show much higher electronic conductivity than TiO_2. MP Ti sub-oxides have previously been synthesized only after calcination at very high temperature, i.e 1000^0C. We have successfully synthesized Ti_2O_3 phase at ambient temperatures but upon UV/γ-irradiation of Ag doped TiO_2. Ti_2O_3 has narrower band gap than TiO_2 [53] and electrons may be excited to the conduction band even upon visible light irradiation which is a big advantage.

2. Materials and methods

2.1. Materials

Titanium (IV) triethanolaminatoisopropoxide (TTEAIP) was obtained from Sigma-Aldrich. Glycerol, Silver nitrate ($AgNO_3$) and hydrochloric acid were obtained from Merck, India. *p*-nitrophenol was obtained from Loba Chemie.

2.2. Methods

2.2.1. Preparation of TiO_2 nanoparticles

For the synthesis of TiO_2 nanoparticles, the sol gel method was used in presence of glycerol. In a round bottomed flask 2.5 mL of water and glycerol were taken and to the mixture 0.05 M HCl solution (0.12 mM) was added to initiate the hydrolysis of the titanium precursor. Then TTEAIP was added making the final concentration of the Titanium precursor in the reaction mixture equal to 5×10^{-3} M. The solution was stirred continuously for 4 h.

2.2.2. Preparation of Ag–TiO_2 colloids by UV radiation method

For the synthesis of Ag–TiO_2 nanocomposites, the sol–gel technique was used. To 5 mL of the TiO_2 nanoparticles (prepared in 2.2.1) $AgNO_3$ (0.1 M) was added and the mixture was stirred for 10 min. The final concentration of $AgNO_3$ was 1×10^{-4} M. The solution was then exposed to UV irradiation for one hour. A brown coloured solution, characteristic of Ag–TiO_2 nanocomposite was obtained.

2.2.3. Preparation of Ag–TiO_2 nanocomposites by Gamma irradiation method

To 50 ml of the TiO_2 nanoparticles (prepared in 2.2.1), $AgNO_3$ solution (0.1 M) was added in proper amounts and the mixture stirred for 10 min. Final concentration of $AgNO_3$ was 1×10^{-4} M. The resulting colourless mixture was divided into five test tubes containing equal amounts (10 ml) of solution and exposed to γ-irradiation of different doses. The formation of Ag–TiO_2 nano composites was indicated by the appearance of yellow to brown colouration.

2.3. Instrumentation

The resulting nanoparticles were characterized by their absorption spectra, recorded with a Shimadzu spectrophotometer, Model No. UV2401PC. The size distribution and hydrodynamic radii were determined by Dynamic light scattering (DLS) carried out with a Nano-ZS (Malvern) instrument which is equipped with a 4 mW He–Ne laser ($\lambda = 632$ nm). The resolution of the experimental setup is 0.6 nm. TEM studies of the nanoparticles were carried out at a resolution of 1.9 Å with a JEOL, JEM-2100 electron microscope