



Hydrogenated mixed phase Ag/TiO₂ nanoparticle – A super-active photocatalyst under visible radiation with multi-cyclic stability

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ABSTRACT

The synergistic effect of silver nanoparticle sensitization and surface disordering of mixed phased titania makes it highly active photocatalyst under visible light. The physico-chemical analysis of the samples indicates that surface plasmon induced local field enhancement, reduction in the band gap due to hydrogenation, intrinsic band offset at the phase interface and the resultant swift migration of photo-generated carrier to catalyst surface makes the catalyst highly visible active. The photoactivity of the hydrogenated mixed phase Ag/TiO₂ catalyst is found to be about ~28.2 times high compared to the reference catalyst DP25 in degradation of methylene blue under visible light irradiation while an opposite behavior is observed under UV light. One the most distinctive feature of the catalyst concluded on the basis of its reusability test is the multicyclic-stability of its performance under visible light which shows it to be robust.

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1. Introduction

Titanium dioxide has been extensively studied since its discovery by Fujishima and Honda in 1972 [1]. It has emerged as a promising photoactive material because of its unique opto-electronic properties, physico-chemical stability, and environmentally benign characteristics; and has promising applications in organic contaminant degradation [2], hydrogen energy production [3], solar cells [4], gas sensing [5], self-cleaning [6] and air purification [7]. However, a viable photocatalyst should be efficient and for that it should have characteristics such as superior light harvesting, effective generation of charge-carriers, swift separation/transport of charge-carriers and availability of numerous active reaction centers on its surface to perform photo-induced catalytic transformations. Since the band gap of unmodified monophasic (anatase) titania (3.2 eV) is high, the photoactivity of the catalyst is limited only to ultraviolet (UV) radiation. It is identified to be the major drawback of titania. In addition to that reasonably high carrier recombination rate in monophasic (rutile, band gap ~3.0 eV) titania also affects its photocatalytic performance adversely. The strategies to overcome these limitations are mostly band gap engineering and morphological modifications such as doping with

anionic/cationic elements [8], sensitization with organic dyes/noble metals [9,10], compositization with other semiconductors [11] along with nanostructuring and/or surface modification. The surface plasmon resonance based broadening of the radiation absorption spectrum of the noble metal sensitized photocatalyst, overlapping the visible region, provides an opportunity to improve the performance of the photocatalysts [12]. The plasmonic metal acts as an antenna for the incident visible light and stores the incident energy in a localized surface plasmon mode, which increases the visible light absorption surrounding the semiconductor material. Also, due to the high density of states in the conduction band, titania is referred as a good electron-accepting metal oxide and it allows fast electron injection through metal-semiconductor Schottky junction [13–15]. The accumulated energy in the localized surface plasmon resonance excitations may decay via transferring to the electrons in the conduction band of the semiconductor material [13]. Thus, an optimal deposition of noble metal silver (Ag) and the resultant surface plasmon resonance (SPR) enhances the generation and, subsequent, separation of photo-generated charge carriers and ensures reduced recombination [16,17]. Apparently in spite of the existence of SPR absorption band in the visible region the photo-generation and/or separation of photo-generated charge carriers of unmodified pristine titania does not appear to be energetically favorable under visible irradiation. Notably, the SPR phenomena are only possible while visible radiation flux is being used. Recently, surface plasmon induced local

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electric field enhancement of Ag loaded titania with improved photoreactions under visible illumination were reported by Li et al. [18]. In their study, the photocurrent responses due to local electric field enhancement under visible light were shown to be more prominent compared to UV light. A similar study on strong plasmonic enhancement in the photoactivity under visible light has been reported by Liu et al. [19]. They observed a substantial reduction in the performance under UV radiation, which is mainly due to the lack of SPR effect. Concurrently, black titania with high visible and infrared optical absorption has been developed by introducing surface disorder in titania through hydrogenation [20]. It could possibly yield mid-gap states and thus reduce the band gap of the titania. They reported large enhancement in the photocatalytic activity in hydrogen production and methylene blue (MB) decomposition under solar radiation range compared to the white (unhydrogenated) titania. Subsequently, several studies on hydrogenated black titania have been reported which provide further insight to the phenomenon of enhancement in the activity of the catalyst [21–24]. The unexpected enhancement in the photocatalytic activity of black titania are attributed to the reduction of band gap due to creation of defect states in the crystal [20–23]. In addition, the creation of oxygen vacancies or Ti^{3+} as trapping sites results in reduction of recombination of photogenerated carriers in the hydrogenated titania [20,24,25]. Furthermore, the presence of mixed phase (anatase and rutile) in the titania matrix enhances the charge carrier separation through interfacial transport mechanism [17,26,27]. Now there is an opportunity to investigate the synergy of the three different approaches - metal sensitization, hydrogenation and phase complexation (in the form of mixed phase titania matrix) for the achievement of higher activity under visible radiation. As discussed above, all the studies carried out earlier have focused on the approaches either in isolation or in a combination of two.

In this present study, we investigate the synergy of all the three approaches by synthesizing hydrogenated Ag-sensitized mixed phase titania and carrying out comparative study on the photoactivity under both UV and visible radiation. For this, initially Ag-sensitized titania was prepared through sol-gel method and later on it was hydrogenated. MB was used as organic contaminant probe for studying photocatalytic decomposition kinetics. Remarkably, the photocatalytic performance of hydrogenated Ag nanoparticle sensitized mixed phase titania under visible light was found to be 28.27 times of that of the commercial catalyst DP25. Another distinctive feature of catalyst concluded through reusability test was its multicyclic-stability under visible light which reveals the robustness of its performance. It was observed that even pristine anatase titania after hydrogenation and sensitization showed substantially improved photoactivity and multicyclic stability under visible light. This is contrary to the well-established fact that pristine anatase titania is mainly UV active. In fact the photoactivity of the all Ag-sensitized samples decreased under UV irradiation.

2. Experimental

2.1. Material synthesis

The monophasic anatase and Ag-deposited titania nanoparticle were synthesized by sol-gel method using titanium iso-propoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) purchased from Sigma-Aldrich; and isopropyl alcohol ($(\text{CH}_3)_2\text{CHOH}$) and silver nitrate (AgNO_3) purchased from Merck (India). Double distilled water was used during the experiment.

In the sol-gel method, used to synthesize the sample, the monophasic titania sol was prepared by mixing of titanium iso-propoxide and isopropyl alcohol in 1:10 ratio. After that 2 ml of 1 M HNO_3 and 0.5 ml double distilled water were added under constant stirring condition which continued for 24 h at room

temperature. Then the solution kept for aging for 12 h to form the gel which was heated at 80 °C for 12 h. The resultant powder was then calcined at 500 °C for one hour, to obtain the monophasic anatase titania ($\text{TiO}_2(\text{A})$). The Ag deposited monophasic (anatase) and mixed phase titania were synthesized with 1 wt% AgNO_3 solution as reported in the earlier study [17]. The prepared AgNO_3 solution was added drop wise into the mixture of titanium iso-propoxide and isopropyl alcohol (1:10 v/v ratio) under constant stirring condition. Afterwards the same process was followed to obtain the sample in powder form. Subsequently, the sample was calcined at 500 °C and 700 °C to obtain monophasic (anatase) and mixed phase titania, respectively. Hereafter the monophasic Ag-deposited titania sample is referred to as $\text{Ag}/\text{TiO}_2(\text{A})$ and mixed phase (biphasic) Ag-deposited titania as $\text{Ag}/\text{TiO}_2(\text{M})$.

2.2. Hydrogenation

The hydrogenation of Ag deposited monophasic and mixed phase titania samples was carried out with a low energy intensive approach as reported in the earlier work [28]. The sample was kept in a quartz boat inside a tube furnace with two-inlet quartz connectors for nitrogen and hydrogen, respectively, and also bubblers both at the inlet and the outlet of the furnace to maintain the inert/desired environment. Initially tube furnace was purged with nitrogen gas and then it was slowly replaced by hydrogen with a flow rate of 15 sccm. The temperature of the tube furnace was maintained at 300 °C for 3 h before allowing it to cool down slowly to room temperature. Henceforth the hydrogenated monophasic and mixed phase titania sample are referred to as $\text{H-Ag}/\text{TiO}_2(\text{A})$ and $\text{H-Ag}/\text{TiO}_2(\text{M})$, respectively.

2.3. Characterization

The phase composition and crystallinity of the samples were investigated by X-ray diffraction (XRD) diffractometer (Rigaku Mini-flex, Japan) using $\text{Cu K}\alpha$ radiation at 30 kV and 450 W at 0.05 $2\theta/\text{s}$ scanning rate. The morphology of the samples was investigated using Scanning electron microscope (SEM) model Jeol 6390LV, Japan at 15 kV. Energy Dispersive X-ray analysis (EDAX) was done using the EDAX (Oxford Instruments, UK) attached to scanning electron microscope (Jeol 6390LV, Japan). The crystal lattice structure was analyzed using transmission electron microscope (TEM) model Tecnai G2 F20S-Twin, FEI, USA and JEM-1000CX II, JEOL Japan both at 200 kV. The UV-Vis diffuse reflectance spectrophotometer (Shimadzu UV-2200, Japan) was used to study the spectral response of the material. The trap states were identified from photoluminescence (PL) spectra using the photoluminescence spectrometer (Perkin Elmer LS55, USA). Fourier-transform infrared (FTIR) spectroscopy was done using FTIR spectrometer (Nicolet Impact I – 410, USA) to analyze the functional groups. Raman spectra were obtained using a Raman spectrophotometer (Basis series, Renishaw, UK with 514 lasers). EPR signals of the catalysts were recorded using Electron Paramagnetic Resonance (EPR) Spectrometer (JEOL, JES-FA200, Japan) to study the presence of oxygen vacancies. The XPS spectra of the catalysts were measured on a XPS spectrometer (ESCA, Instrument, VSW, UK) with $\text{AlK}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) at 75 W.

2.4. Photocatalytic test

Photocatalytic activity of $\text{TiO}_2(\text{A})$, $\text{Ag}/\text{TiO}_2(\text{A})$, $\text{H-Ag}/\text{TiO}_2(\text{A})$ and $\text{H-Ag}/\text{TiO}_2(\text{M})$ were evaluated by degradation of MB under visible (Philips 18W/54 1M7 India, intensity 14.5 W/m^2) and UV light source (Philips 15W/G15 T8 Holland, intensity 0.16 W/m^2). The experiments were performed with 0.5 g/l loading of the catalyst. The pH of the MB solution before loading is found to be 8.0 and no

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