

Synthesis and Characterization of TiO₂ and Au/TiO₂ Nanoparticles and Their Performance on Photodegradation of Methylene Blue

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ABSTRACT

Au-doped titanium dioxide nanoparticles with 2 wt % were prepared from aqueous tetraisopropyl orthotitanate (Ti(OC₃H₇)₄) solution by sol-gel method. The synthesized photocatalysts were used for the photodegradation of Methylene Blue in presence of UV and visible irradiation. The prepared nanoparticles were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). From X-ray powder diffraction data, the crystal phase presents 100% anatase phase. As seen in TEM images, the crystallites of photocatalysts are spherical particles with a crystallite size about 7–15 nm. Photocatalytic activities of nanoparticles showed that Au doping on TiO₂ enhanced the photocatalytic efficiency of TiO₂ nanoparticles especially in visible irradiation.

KEYWORDS: photodegradation, Au/TiO₂, nanoparticles, Methylene Blue, doping

INTRODUCTION

Heterogeneous photocatalysis initiated by colloidal semiconductors has drawn considerable attention over the last one decade in view of their large specific surface, high redox potential of the photogenerated charge carriers and selective reduction and oxidation of different class of organics at their interface [1–6]. Recently, photocatalysis has appeared as a promising approach for the handling of several different types of environmental problems. Among the several semiconductor materials tested for photocatalysis, TiO₂ has proved to be the best one due to its strong oxidizing power under UV illumination and its chemical stability [7–9]. Recently, there has been a great deal of interest in the synthesis of nanostructured titania [10–12], in an effort to increase the efficiency of these photochemical processes. The basic mechanism of TiO₂ photocatalysis involves the formation of electron-hole pairs by UV absorption and the reaction of these charge carriers with chemical species at the surface. The photogenerated holes in the valence band diffuse to the surface and, due to their strong oxidizing power, quickly react with adsorbed water molecules to produce hydroxyl radicals ([•]OH), which in turn oxidize organic molecules in the vicinity. Meanwhile, electrons in the conduction band react with molecular oxygen in the air to produce the superoxide radical anion (O₂^{•-}), which also participates in further oxidation processes. On the applications front, efforts have been made to make use of TiO₂ for both water and air purification [15–31].

The utilization of solar energy to effect these processes requires using the low bandgap material as a sensitizer. Besides, the high recombination rate of e⁻-h⁺ pair compared to the rate of electron transfer to the oxygen, being used generally as an electron acceptor, further limits the efficiency of this system [7].

It is well known that the photocatalytic activity of TiO₂ is greatly influenced by its crystal structure, specific surface area, doping, surface hydroxyl group content and so on [32–36]. A variety of attempts have been made to introduce various metal species into the TiO₂ matrix in an effort to enhance the photocatalytic activity and/or broaden the absorption of the solar spectrum by the doped TiO₂. Methods that have been used include ion exchange, impregnation and co-precipitation have used for preparing doped TiO₂ [13, 14]. Metals affect the surface properties by generating a Schottky barrier of the metal in contact with semiconductor's surface, which acts as an electron trap.

In the present work we have investigated the effect of addition of noble metal on the photoactivity of the TiO₂ photocatalyst.

MATERIALS AND METHODS

Synthesis

In order to get nanostructured TiO₂, a certain amount of Ti(OC₃H₇)₄ solution was taken and added to an appropriate amount of methanol then the sol was heated through heater-stirrer and refluxed about 3 h under magnetic stirrer, when the temperature of the solution raised up to 70°C, an exact molar ratio of

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double distilled water was added drop wisely into the hot solution during this period of time [37]. No care was taken to control the atmosphere. To synthesis Au-TiO₂, tetrachloroauric acid trihydrate (HAuCl₄.3H₂O) was dissolve in double distilled water and then reduced by NaBH₄ solution (5 mM). The previous solution was added to the sol-gel TiO₂ (which is presented previously). Afterwards, the prepared solution was dried at 70 °C for 12 h and calcined in different temperatures (300, 350, 400, 450, 500, 550, and 600°C) in about 4 hours.

Sample Characterization

The microstructure of the pure and Au doped TiO₂ powders were analyzed directly by X-ray diffraction (XRD) and transmission electron microscopy (TEM). X-ray diffraction (XRD) patterns were measured at 298 K (RT) using a model D-5000 Siemens diffractometer (Cu K α , $\lambda = 0.154056$ nm, 30 mA and 40 kV) and were used to determine the identity of any phase present, phases ratio (anatase/rutile) and their crystallite size. The diffractograms were recorded in 2θ range of 15-75°. The crystalline phase can be determined from integration intensities of anatase (101), rutile (110) and brookite (121) peaks.

If a sample contains only anatase and rutile, the mass fraction of rutile (X_R) can be calculated from the following equation [38].

$$X_R = \frac{I_R}{0.8I_A + I_R} \quad (1)$$

where I_R and I_A represent the integrated intensity of the rutile (110) and anatase (101) peaks respectively.

The average crystallizes size of all the samples are estimated using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where β is the half-height width of the diffraction peak of anatase/rutile, $K = 0.89$ is a coefficient, θ is the diffraction angle, and λ is the X-ray wavelength (0.154056 nm) corresponding to the Cu K α radiation.

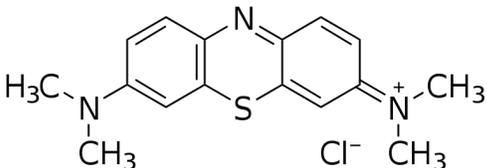
Transmission electron microscopy (TEM) images, which were obtained using a Philips CM10 equipped with a 35 mm camera by applying an acceleration voltage of 100 kV, were used to observe or determine the morphology, size and identity of nanocrystal particles in the pure and Au doped TiO₂.

Photocatalytic activity

The photocatalytic activity of TiO₂ and Au-TiO₂ nanoparticles was evaluated by using photocatalytic degradation decolorization of Methylene Blue aqueous solution. For reference, the structure of Methylene Blue and it's other properties shown in Table 1.

The prepared photocatalysts nanoparticles with 500 mg L⁻¹ concentration were added directly to the pollutant solution with 20 mg L⁻¹ concentration. The suspension was stirred continuously by means of oxygen gas flow in a batch photochemical tubular reactor system at room temperature for 30 min propose of obtaining equilibrium sample. Then the suspension was irradiated with Philips UV-C (15 W) light lamp or 500 W HALOGEN visible light lamp. At given irradiation time intervals (every 10 min), the samples (5 ml) were taken out and after centrifuging analyzed by UV-Vis spectrophotometer HACH DR-5000 at color's maximum lambda (665 nm).

Table.1. Structure and characteristics of Methylene Blue.

Structure	IUPAC name	C.I. number	λ_{\max} (nm)	M_w (g mol ⁻¹)
	3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride	52015	665	319.85

RESULTS AND DISCUSSION

Structure and morphology

Analysis of the X-ray diffraction (XRD) spectra (see Fig.1) showed only one considerable picks at $2\theta=25.2^\circ$ which associated with anatase phase. The crystallite size was found to get smaller by Au doping. The XRD spectra's showed that the crystallite sizes in both bare and Au doped TiO_2 grow by temperature. The average crystallite sizes of the pure and Au doped TiO_2 nanoparticles calculated using Scherrer's equations (1,2) from the main diffraction peaks were shown in Table 2.

Transmission electron microscopy (TEM) of a representative samples of pure and Au-doped mesoporous TiO_2 are shown in Fig. 2. Au- TiO_2 nanoparticles TEM micrograph show a variation in Au particle size in the range of 15–20 nm (Fig. 2 b). A possible reason for the substantial increase in the Au particle size might be due to the coalescence of gold nanoparticles on the surface of semiconductor particles. Both nanoparticles in Figs. 2a and 2b, size distributions are found to be very similar.

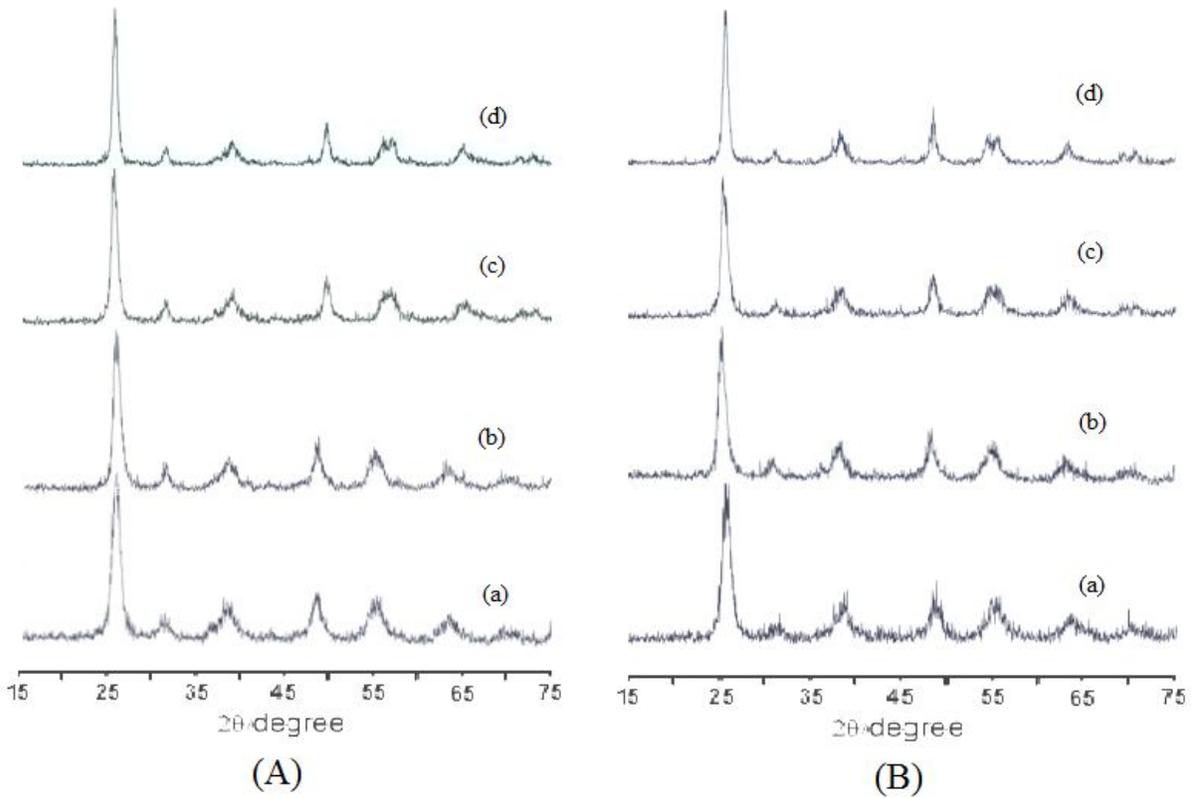


Fig.1. X-ray diffraction patterns in different calcination temperatures. A: bare- TiO_2 and B: Au/ TiO_2 (2 wt. % Au), (a) 400°C, (b) 450°C and (c) 500°C (d) 550°C.

Table.2. XRD data of bare- TiO_2 (1) and Au/ TiO_2 (2 wt. % Au) (2).

Sample	Crystallite Size of anatase phase			
	400 °C	450 °C	500 °C	550 °C
1	7.334	8.8	11.223	14.52
2	7.05	8.05	9.39	12.52

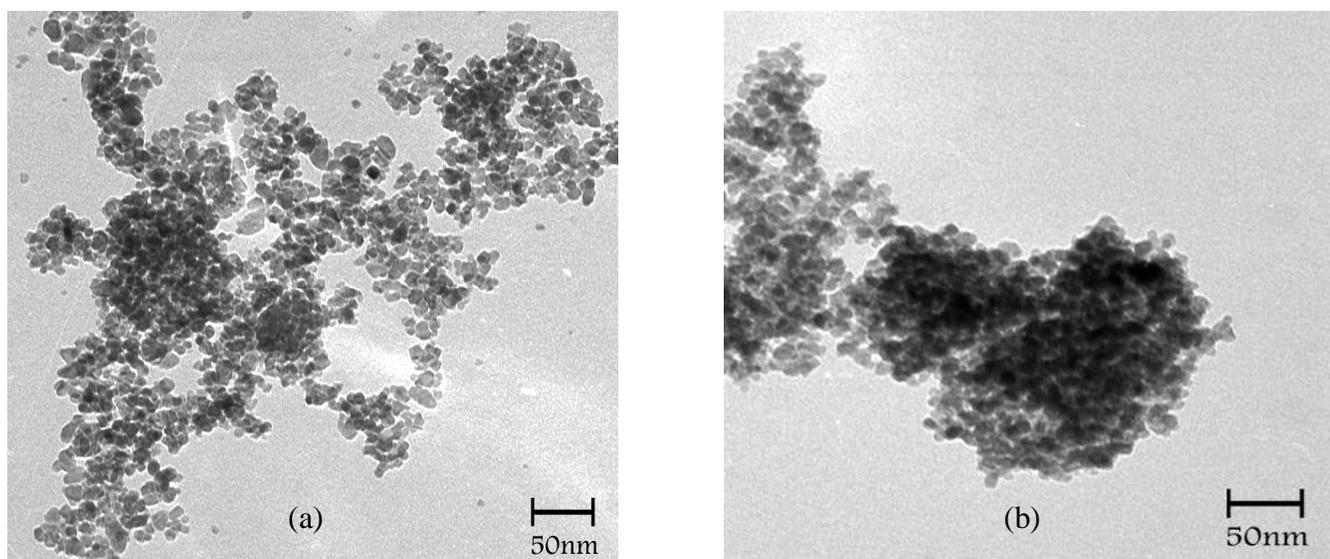


Fig.2. TEM micrographs of the samples: a) bare-TiO₂ and b) Au/TiO₂ (2 wt. % Au)

Photocatalytic activity

The photo-catalytic activity of pure and Au doped (2% wt) TiO₂ were tested in visible light by using the quartz reactor fabricated in-house as described in section 2.3. In this investigation, the attempt was made to increase the photo-response and photo-catalytic activity of TiO₂ by Au doping. To confirm the effect of Au on photo-activity of TiO₂ we have used the Au/TiO₂ nanoparticles for photocatalytic degradation of methylene blue using UV and visible light lamps as a source of energy. The MB photodegradation results in different calcination temperatures of synthesizing process are presented in Fig. 3, 4. The results of our study show that there is appreciable increase in photo-catalytic activity (2–2.3 times more than undoped). This is because, in our process there is a charge transfer between Au and TiO₂ and this will lead to increasing the photo-catalytic activity in the presence of visible irradiation. Results shows that, within 1 hour of irradiation in presence of pure TiO₂ photocatalyst 10 % methylene blue was removed, whereas by using 2 wt% Au/TiO₂ within 1 h 16.5% methylene blue was removed.

This increase may be attributed to combine effect of shift in absorption wavelength to visible, the shift in fermi level to more negative potentials and improved efficiency of interfacial charge transfer process [39]. The shift in fermi level accumulates more electrons in Au/TiO₂ system and improves the energetic of the system which ultimately results in enhanced photo-catalytic activity.

The effect of calcination temperature on the catalytic behavior of the doped catalyst was studied by using the photocatalyst powder calcined at various temperatures. From the catalytic study (Fig. 3) it was observed that, among the all Au/TiO₂ photocatalyst samples, the catalyst calcined at 500 °C shows highest catalytic activity as compare to samples calcined at higher or lower temperatures. This may be attributed to the formation of photo-catalytically most active pure anatase phase at this temperature and the particle size.

Under visible light, undoped TiO₂ exhibits almost no activity, when Au doped TiO₂ sample shows good photocatalytic activity.

The increase in photoactivity may be attributed to the effect of Au in following ways; increased absorption in visible region by intercalation of Au in titania structure, the electron scavenging by Au (III) ions and the decrease in fermi level to more negative side subsequently improvement in interfacial charge transfer process at the TiO₂ interface by Au⁰ particles. So it is the combine effect of all these processes at the surface of semiconductor nanoparticles which results in overall increase in photo-activity of TiO₂.

However, some researchers thought the dye, not TiO₂ was excited by visible light in the presence of TiO₂ and injected an electron into the conduction band of TiO₂, from where it was scavenged by preadsorbed oxygen to form active radicals [40].

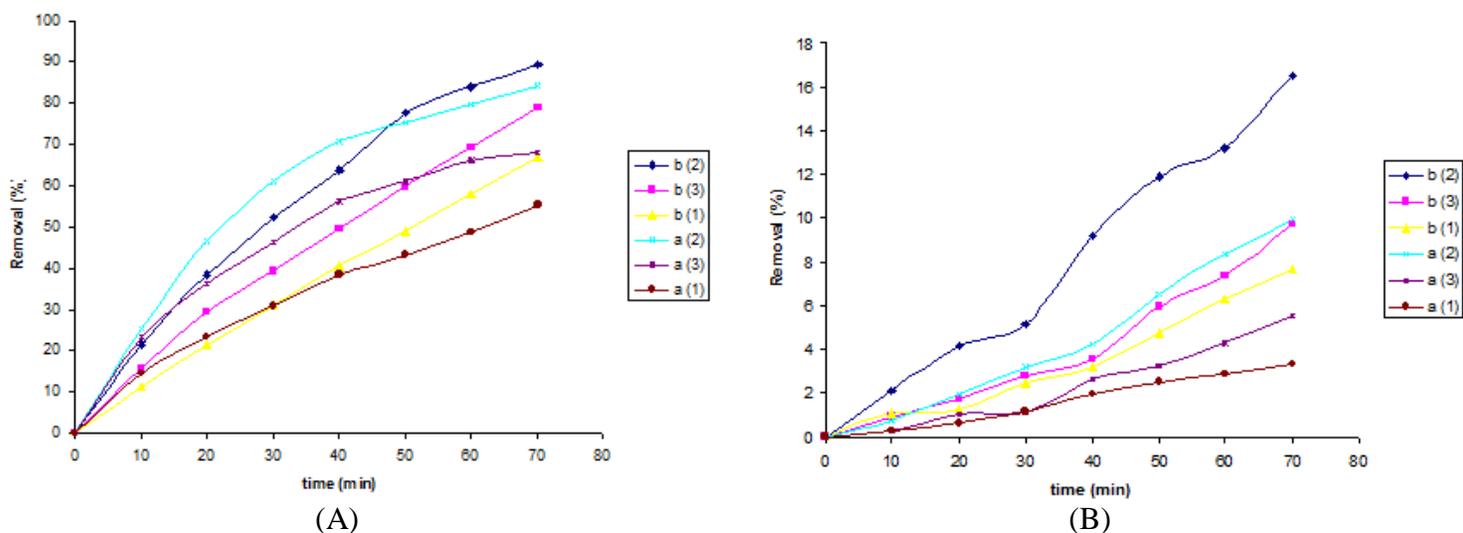


Fig.3. Removal percent of MB in (A): UV and (B): Visible light. a: bare-TiO₂ and b: Au/TiO₂ (2 wt. % Au), (1) 400°C, (2) 500°C and (3) 600°C.

Conclusions

A simple sol-gel method was developed for the preparation of pure TiO₂ multiphase nanoparticles. The nanoparticles were doped by addition colloidal Au solution (2 wt%) in titanium dioxide sol to increase the photoresponse of TiO₂ in visible light. The increase in photoresponse was tested by photocatalytic decomposition of aqueous solution of methylene blue in the presence of visible light (500 W) irradiation. Doping 2 wt% Au into TiO₂ improved the photocatalytic activity by 1.8–2 times than undoped in the presence of visible light irradiation. The nanoparticles were very stable and after centrifuge it can be used for number of times with no much change in efficiency for long term use. The improved photocatalysis in degradation of MB might be ascribed to the decrease of e^-/h^+ pair recombination rate by Au dopants which could act as electron (or hole) traps.

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