

Sol–gel synthesis of Au/TiO₂ thin films for photocatalytic degradation of phenol in sunlight

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Abstract

Thin films of Au/TiO₂ on glass substrates have been prepared by simple sol–gel dip coating method using a sol of colloidal gold doped titanium peroxide (Au/TiO₂ sol). The sol of colloidal gold and titanium peroxide forms a viscous gel after 1–3 h depending on the concentration of both colloidal gold and titania. The sol of particular viscosity range (140–2800 cps) was used to deposit the Au/TiO₂ thin films of uniform thickness on various substrates such as glass slides, glass helix and silica rashig rings. Films deposited on glass plates after drying were transparent, uniform in color as well as thickness. Optical characterization by UV–vis spectrophotometer showed a shift in optical absorption wavelength to visible region may be due to the incorporation of gold nanoparticles into titania structure. The optimum concentration of gold loading was found to be 1–2% (by weight) beyond this the gold particles disturb the gel network resulting the formation of gelatinous precipitate. Thin film photo-catalyst prepared was characterized by various techniques such as UV–vis, TG-DTA, XRD, ICP-OES and TEM. The photo-activity of the thin films was tested in sunlight using phenol as model pollutant. The kinetic study showed that the rate of decomposition of phenol using Au/TiO₂ photo-catalyst was improved by 2–2.3 times than undoped TiO₂.

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1. Introduction

Environmental pollution is the area of concern and there is need to pay more attention on it. Due to industrial growth, the environmental pollution has been increased and it has attained a level high in developing countries. Photo-oxidation by using TiO₂ photo-catalyst is being widely studied as a relatively new technique of pollution abatement [1–3]. TiO₂ is a commonly used photo-catalyst because of its stability in UV light and water. However, the need of an ultraviolet (UV) excitation source restricts its technological utility for limited applications. For widespread applications, TiO₂ photo catalyst effective in visible radiation or solar light needs to be developed as future generation photo-catalytic material. TiO₂

absorbs only 3–5% energy of the solar spectrum hence numerous studies have been performed to extend the photo-response and to enhance the photo-catalytic activity by modifying its surface structure, surface properties and composition [4–9]. The surface modification by doping with metal ions and organic polymers has been proven to be an efficient route to improve the photo-catalytic activity of TiO₂ [10–22]. In an attempt to modify the optical properties of TiO₂ we were successful by doping Fe into titania structure which shifted the absorption into visible region [23].

Gold nanoparticles supported on titania in highly dispersed state exhibit a surprisingly high activity for several reactions including CO oxidation [10–17]. Recent investigation on gold titania nanocomposite particles show that metal ion doping extended the response of the photocatalyst into visible region. It is now well established that the catalytic properties of Au depends on the support, the preparation method and particularly the shape and size of the Au clusters

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[17]. In most of the earlier studies gold-titania colloids were used as photocatalysts and the separation of this colloidal catalysts pose problems. To overcome this problem gold titania thin film catalysts will be an attractive alternative and very few studies have dealt with gold titania thin films [11,24,25]. In continuation of our efforts to improve the photo-catalytic activity, the titania thin films have been prepared by doping with colloidal gold nanoparticles. In sol–gel methods reported earlier for preparation of TiO_2 thin films, the sol used contains organic solvent as a major constituent. This sol when used for thin film deposition releases the vapors of solvent during aging of gel and drying the films. This causes environmental pollution. In order, to overcome this problem, few researchers have tried aqueous base titanium peroxide sol (prepared either by reaction of titanium alkoxide or titanium and hydrogen peroxide) and deposited films using this sol by various techniques such as spray pyrolysis and spin coating. Since these techniques need sophisticated equipments and the sol prepared was also unstable for deposition of thin films, we have studied the sol–gel behavior of this process first time and reported in our previous publications [23,26]. Through this study, we could successfully develop aqueous base sol–gel dip coating method for deposition of thin films of TiO_2 where no organic groups or solvent is involved in sol–gel. By following this method films have been deposited on various substrates and used for degradation of various organic compounds. In the present study, we are reporting the method for preparation Au/ TiO_2 thin films. To the best of our knowledge no one has reported previously the preparation of Au doped TiO_2 using titanium peroxide sol–gel method. The main advantages of this process are, it is aqueous base, easy for operation, cost effective and the problem of releasing organics in environment can be overcome. Au/ TiO_2 thin films were prepared on various substrates and effect of Au doping on optical, thermal and structural properties as well as catalytic activity of TiO_2 films has been studied. Thin films as well as the powder obtained after drying the gel was characterized by various instrumental techniques to elucidate the structure and other properties. The usefulness of the catalyst was studied by decomposition of phenol in sunlight and the results were discussed.

2. Experimental

All the chemicals and reagents used in this study were analytical grade. The organic pollutant used in this study, i.e. phenol and other reagents were procured from Qualigen India Ltd. The TiO_2 precursor (Ti-Isopropoxide) was obtained from Aldrich.

2.1. Preparation of colloidal Au/ TiO_2 sol

Ti-peroxide sol was prepared by the method described in our previous publication [26]. The known amount of Ti-isopropoxide (1.72 g) was taken and hydrolyzed with H_2O .

After hydrolysis a white Ti-hydroxide precipitate formed was then dissolved in 10 ml H_2O_2 (15%). After complete dissolution the orange TiO_2 sol was formed. This sol was diluted with water as per requirement and allowed to stand for few hours. The gold colloidal solution used for doping was prepared by reduction of HAuCl_4 with NaBH_4 as a reducing agent. The formation of Au° was monitored using UV–vis spectrophotometer. HAuCl_4 solution (10 mM) shows an intense absorption band in UV region at 290 nm (characteristic band of Au^{3+} ions). Addition of NaBH_4 (5 mM) to HAuCl_4 solution changes the color from yellow to pinkish red. The samples collected at various intervals during addition of reducing agent shows decrease in intensity of band at 290 nm and a new band emerged at 530 nm. (characteristic band of Au° or metallic Au). Upon further addition of NaBH_4 solution, the band at 530 nm intensifies. At one stage the band at 290 nm disappears and the band at 530 nm stabilizes, this indicates the complete reduction of AuCl_4^- ions to Au° . This solution was kept in air tight vessel and it was quite stable for long period, i.e. for months.

Ti-peroxide sol prepared by above method was stirred with the help of magnetic stirrer and to this required quantity of gold colloidal solution was added drop wise. Addition of gold solution into yellow Ti-peroxide sol changes the color of the sol to light red. This Au/ TiO_2 sol was diluted as per requirement and allowed to stand 1–3 h before using for film deposition. The very dilute sol of Au/ TiO_2 (0.001 M Ti solution) is quite stable for 36–48 h with no change in viscosity but films deposited using this sol are very thin, non uniform and this sol can not be used for deposition of number of layers to increase the film thickness. This is because, at second and repeated cycles of deposition, the sol does not get adhered uniformly to the substrate. To avoid this problem, the concentrated sol (0.01–0.025 M) can be used. This sol after 1–3 h starts to form the polymer network of titanium peroxide ions, as a result the viscosity of sol increases. The increase in viscosity is beneficial for the deposition of uniform, transparent and more thickness films (100–2000 nm thick) and as the viscosity of the sol used for deposition increases, the film thickness also increase. So the required thickness of Au/ TiO_2 films can be adjusted by depositing at particular viscosity only. Viscosity of the sol can be adjusted as per our requirement by simple dilution accompanying vigorous stirring at any stage.

2.2. Preparation of Au/ TiO_2 thin films

The Au/ TiO_2 sol prepared by this method starts to form viscous liquid after 1–3 h. The liquid after attaining the particular viscosity range of 140–2800 cps was used for deposition of thin films on soda-lime glass. As the viscosity of sol used for deposition of thin film increases the film thickness also increases. Before deposition of the films, the substrates were cleaned with mixture of H_2SO_4 and H_2O_2 (3:1) followed by 2–3 times wash with double distilled water. These substrates were dried and stored in desiccators and used whenever

required. For deposition on soda-lime glass plates the substrate was dipped in Au/TiO₂ sol of required viscosity and kept immersed for 2–3 min. After this, the substrate was pulled out at approximate pulling rate of 1 mm/s. The sol adhered to the substrate upon drying at room temperature in open atmosphere forms a uniform thin film. These substrates were further dried at 100 °C in an electric oven for 2 h and used for characterization.

For deposition of Au/TiO₂ thin films on silica rashing rings and glass helix, known amount of helix were added into the Au/TiO₂ sol and allowed to dry in open atmosphere. After drying and heating at 100 °C these substrates were used for photo-catalytic decomposition of phenol.

For transmission electron microscope (TEM) measurements, the films were deposited on Cu grids using a Au/TiO₂ sol of very low viscosity to get very thin films on the grids followed by drying in open atmosphere, whereas for powder samples, the sample (Au/TiO₂) was dispersed in ethanol and sonicated in an ultrasonic bath for 30 min to get better dispersion.

The gold and titanium content of the films as well as dried powder was estimated by using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). For this, the known weight of Au/TiO₂ sample was dissolved in mixture of H₂SO₄ (98%) and H₂O₂ (30%) (3:1 proportion). The solution obtained after complete dissolution was diluted to required volume. By using this method samples containing various concentration of gold were prepared. The samples were analyzed for gold content using most sensitive wavelength of 242.795 nm. For estimation of titanium content the solutions were further diluted 100–1000 times and then used. The most sensitive wavelength of 334.94 nm was used for estimation of titanium. The results obtained are presented in Table 1.

2.3. Photocatalytic study

Photo-degradation of organic compounds using Au/TiO₂ catalyst occurs when catalyst is illuminated with light of energy more than or equal to the band gap energy. In this study, sunlight was used as energy source for excitation of electrons from filled valence band to empty conduction band. The photo-catalyst in presence of sunlight and water containing dissolved oxygen, decomposes the organic species to CO₂ and H₂O.

The photo-catalytic activity of the catalyst was tested using an in house fabricated quartz reactor. The reactor as described in our previous study [23] consists a quartz tube of dimensions 20 mm diameter × 250 mm length having arrangement for bubbling the air during reaction and cooling jacket for circulation of water. The TiO₂ and Au/TiO₂ deposited on silica rings as well as on glass helix were taken as photo-catalyst. The catalyst coated silica rings (20 g) were loaded into the reactor column. Then 30–50 ppm solution of phenol (50 ml) was fed into the reactor column and kept in dark place for 30 min. After 30 min the reactor was kept in

sunlight and air bubbled at the rate of 10 ml/min throughout the experiment. The temperature of phenol solution was maintained by circulating water through the cooling jacket. During irradiation of phenol in sunlight samples were collected at different time intervals. The change in concentration of phenol of irradiated samples and formation of any intermediates during the photo-reaction was monitored using UV–vis as well as HPLC. The instruments were calibrated first using standard phenol solution (5–100 ppm) and then samples were analyzed keeping the instrumental parameters constant. Phenol shows an intense absorption peak at 269.4 nm in UV and the intensity of this peak changes with concentration. The change in concentration of phenol of sample irradiated for different time intervals was compared with sample kept in darkness as well as blank (i.e. silica rings without coated with catalyst were used in place of catalyst coated rings) kept in sunlight at the same experimental condition.

The HPLC technique was mainly used to monitor the formation of any intermediates during the photo-reaction of phenol mineralisation. In the quantitative analysis, among the three mobile phases (100% MeOH, 70% MeOH and 50% MeOH) better separation of peaks obtained when 50% methanol was used as mobile phase. So all samples analyzed using 50% methanol as a mobile phase by keeping the other instrumental parameters such as sample volume and run time (60 µl and 20 min, respectively) constant. The prominent peak of phenol was obtained at around 2.90–2.97 min retention time (RT). There is 35% (approximately) decrease in intensity of peak at 2.94 RT for the sample irradiated for 1 h, whereas the sample irradiated for 2 and 4 h shows 67 and 96% (approximately) decrease in intensity when 1% Au/TiO₂ was used as a catalyst. The intensity of prominent peak decreases with irradiation time but apart from the phenol peaks no new peaks were identified. This suggests that complete mineralisation of phenol takes place in sunlight via certain intermediates. The reason for not detection of any peaks for intermediate may be the formation of intermediates at very low level. The HPLC results and UV–vis results are in good agreement with each other.

2.4. Characterization of thin films

The optical characterization of the photo-catalyst was carried out using UV–vis spectrophotometer (Hitachi, U-3210) in the wavelength range from 300 to 800 nm with scanning speed of 300 nm/min. The structural characterization was carried out using X-ray diffraction technique (Rigaku, Miniflex) with Cu K α radiation. The Au content of the films as well as powder was analyzed using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, P-1000, Perkin-Elmer). The surface properties were observed under Transmission Electron Microscope (TEM, JEOL). Thermal characterization was performed on TG/DTA (Mettler-Toledo) instrument with heating rate of 5 °C/min in nitrogen (N₂) atmosphere. The concentration of phenol before and after photo-reaction was analyzed using High Performance Liquid

Chromatography (HPLC, Waters, Millennium 32). The instrument was first standardized using 50% methanol as a mobile phase with the help of Zorbax C8 L28089 column and PDA (UV) detector.

3. Results and discussion

3.1. Effect of Au addition on sol–gel behavior and optical properties

The Ti-peroxide sol prepared by this method was initially red colored having viscosity nearly equal to water and As time passes, the color intensity of the sol decreases, the viscosity of the sol increases and finally it turns to dense gel after 10–24 h. The gel formed was transparent, light yellow colored and it is stable for 5–10 days. Addition or doping of colloidal gold into this sol changes the sol–gel behavior of the titanium peroxide sol. The Au addition at 1–2% does not show much change in gel behavior except the time required for gel formation and color but increase in Au content more than this results in violet or red gelly precipitate rather than a perfect transparent gel.

In this work, aim of doping Au into TiO₂ was to shift the absorption edge towards the visible side of the UV–vis spectrum and increasing the photo-activity of TiO₂. Fig. 1 (curves a–c) shows the UV–vis spectra of the titanium peroxide gel, 1% Au/TiO₂ and 2% Au/TiO₂ viscous sol and films deposited using this sol, respectively. From the figure, it is observed that, pure TiO₂ sol shows absorption in the UV region, i.e. at around 360 nm. However, the sol and films prepared by addition of 1% Au shows the absorption edge at around 400 nm and an additional peak shoulder at around 540 nm was observed. In curve 'c' the absorption edge of TiO₂ is further shifted to visible (430–440 nm) and the height of the peak at 540 nm was also increased. The shift in absorption edge to

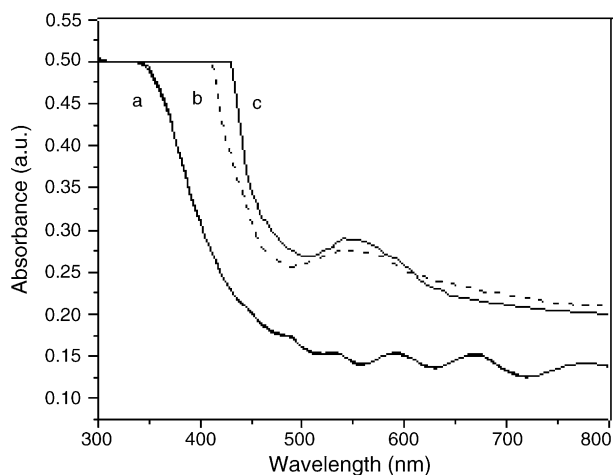


Fig. 1. UV–vis absorption spectra of the (a) Ti-peroxide film; (b) 1% Au/TiO₂ film; and (c) 2% Au/TiO₂ film deposited by using the respective sol aged for 4 h.

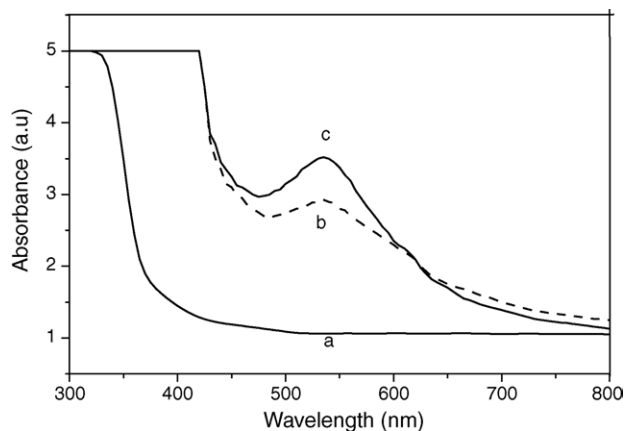


Fig. 2. UV–vis absorption spectra of the (a) Ti-peroxide sol; (b) 1% Au/TiO₂ sol; and (c) 2% Au/TiO₂ sol aged for 4 h.

visible side is ascribed to the insertion of part of added gold into TiO₂ lattice because in metal doped TiO₂, if the extent of shift is dependent on concentration of dopant it is attributed to the insertion of metal ions into the TiO₂ at substitutional sites [27]. The remaining gold in the TiO₂ matrix shows the peak shoulder at around 540 nm which is the well SPR band of spherical Au nanoparticles [28–30]. In fact, Au colloidal sol used for doping purpose shows the UV absorption band at around 530 nm (not shown in figure). This absorption is due to collective oscillation of free conduction band electrons of the gold particles in response to optical excitation. The position of this band totally depends on the size and shape of the gold particles [31] and this band is not observed in bulk material of same composition. When the same Au sol (SPR at 530 nm) was added into the Ti-peroxide sol, the SPR absorption peak at 530 nm shows red shift (540 nm) which is attributed to the surrounding TiO₂ medium (Fig. 2). The red or blue spectral shift of SPR band depends on the dielectric constant of the embedding medium [28,31]. A strong red shift in the SPR of Ag nanoclusters incorporated in SiO₂ or TiO₂ matrix was reported by Kriebig et al. The dependence of shift on the chemically differing embedding medium indicates the high sensitivity of SPR band to cluster–matrix interface properties.

3.2. Crystallization of the gel

The crystallization behavior of the powdered gel was studied by using TG/DTA and X-ray diffraction techniques.

Fig. 3 shows the TG/DTA curve of 2% Au doped TiO₂. The 5–10 mg portion of the sample was used for TG analysis and heated at the heating rate of 5 °C/min in N₂ atmosphere. In TG curve, in the temperature range between 100 and 400 °C a considerable weight loss (16%) is observed which is attributed to the loss of water and transformation of Ti-peroxide to TiO₂. DTA of 2% Au/TiO₂ shows an endothermic peak at 100 °C and exothermic peaks at around 200–275 °C and a hump (no clear peak) at around 340–500 °C. The endothermic peak at 100 °C is due to the loss of water and other solvents, peak at 200 °C is due to transformation of Ti-

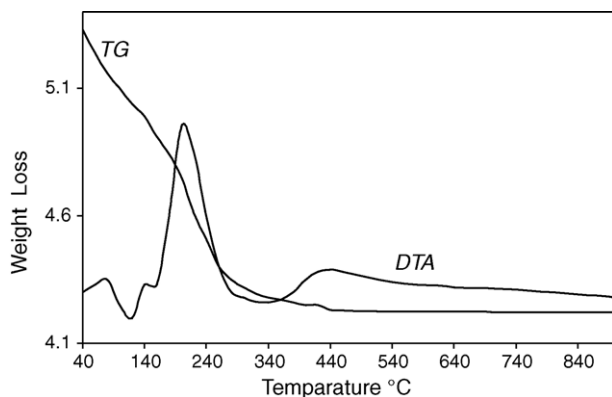


Fig. 3. TG/DTA curve of the 2% Au/TiO₂ powder obtained after drying gel.

peroxide to crystalline anatase Au/TiO₂. Initially we thought that, the hump at 340–500 °C is due to slow transformation of anatase to rutile phase. However, in the XRD analysis the samples heated at this temperature range were not pure rutile phase but mixture of anatase and rutile where rutile is in the range of 10–20%. So it is very difficult to conclude that anatase to rutile transformation takes place at this temperature range. In previous studies it was stated that in Au doped TiO₂ the anatase to rutile transformation has not been reported so far. Ti-peroxide shows transformation from Ti-peroxide to anatase TiO₂ in the range of 400–600 °C, whereas the same transformation occurs in Au/TiO₂ at 200–275 °C. As compare to pure titanium peroxide the crystallization temperature of anatase phase has been lower in 2% Au/TiO₂. This may be ascribed to lower crystallization temperature of Au in the TiO₂ matrix. Au starts to crystallize at 100 °C so the Au available in the titanium peroxide starts to crystallize at this temperature which may act as a nuclei or seeds for crystallization of TiO₂. This ultimately results in lowering the crystallization temperature of anatase. The formation of rutile in Au/TiO₂ starts at 350–500 °C, whereas the complete transformation of anatase to rutile does not takes place hence it can be concluded that, the initiation of crystallization (not complete transformation) of rutile phase has also been occurs at lower temperature in Au/TiO₂. The results were also confirmed by XRD techniques.

The X-ray diffraction pattern of 1% Au/TiO₂ and 2% Au/TiO₂ are presented in Figs. 4 and 5, respectively. Curve 'a' in both the diffraction patterns corresponds to as prepared samples (dried at 100 °C), it suggests that, TiO₂ is in amorphous state, this is as usual in most samples prepared by sol–gel. However, two peaks at 2θ value of around 38.2° and 44.1° were observed revealing the presence of metallic gold (Au) particles into TiO₂. A more intense sharp peak at 38.2° is attributed to the presence of Au⁰ and suggests that the metallic gold starts crystallization at 100 °C. Upon calcinations of the samples at various temperature (200–800 °C) the crystallization of Au/TiO₂ takes place. Both sample heated at 200 °C does not show much change in the XRD pattern (Curve 'b'). Curve 'c' of both XRD patterns (Figs. 4 and 5) corresponds to the samples obtained by calcination of Au/TiO₂ gel at 300 °C,

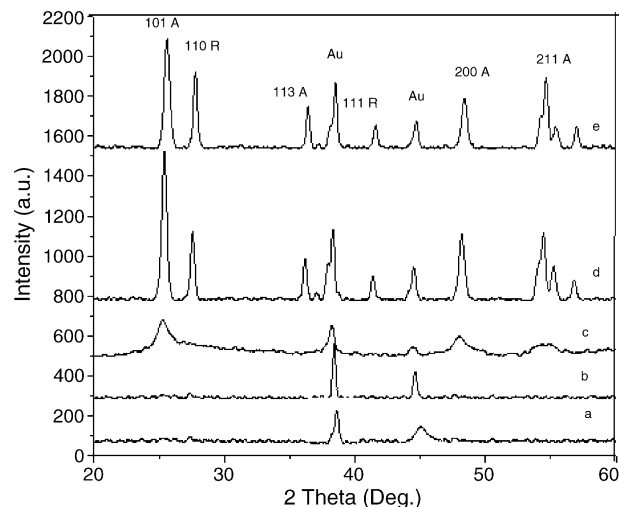


Fig. 4. X-Ray diffraction patterns of the 1% Au/TiO₂ powder (a) as prepared; (b) calcined at 250 °C; (c) calcined at 400 °C; and (d) calcined at 600 °C.

all peaks in these patterns are broad in nature and are mostly of anatase phase of TiO₂. This shows that crystallization of anatase begins at or before 300 °C (as discussed in TG/DTA). The samples calcined at 400 and 600 °C (curves 'd' and 'e' of both XRD pattern) shows a well crystallized peaks. In both these samples along with anatase phase, peaks corresponding to rutile phase were also observed, it shows that the anatase to rutile conversion starts at or before 400 °C. However, in the undoped Ti-peroxide this anatase to rutile transformation takes place at 600–900 °C temperature (reported in our earlier paper [25]). From curves 'd' and 'e' of both patterns it is seen that, rutile peaks are less intense in 2% Au/TiO₂ than in 1% Au/TiO₂ which means that the increase in Au content decreases anatase to rutile transformation. The sample heated at 800 °C (curve 'f' in Fig. 5) does not show much change in XRD pattern suggests that, transformation of anatase to rutile TiO₂ is inhibited or slowed down due to presence of more Au content. This may be because, in Au/TiO₂ prepared

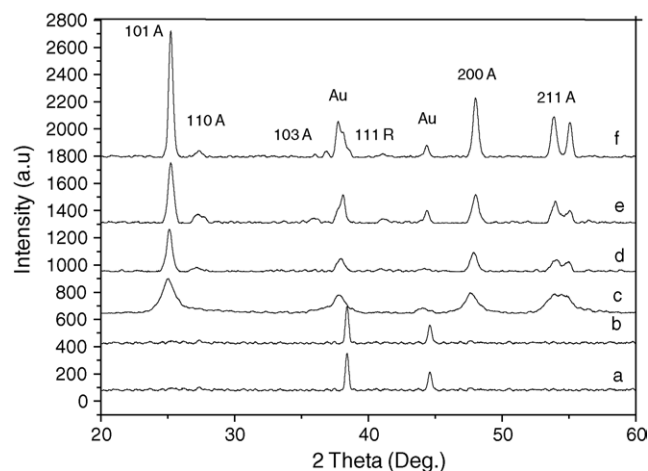


Fig. 5. X-Ray diffraction patterns of the 2% Au/TiO₂ powder (a) as prepared; (b) calcined at 250 °C; (c) calcined at 400 °C; and (d) calcined at 600 °C.

by sol–gel method, the Au particles are supported on TiO₂ particles and as concentration of Au in the gel increase, the particle density of Au or number of Au particles around the TiO₂ particle increases. This restricts the contact between one TiO₂ particle with other, as a result the particle growth is inhibited. Since Anatase TiO₂ is thermodynamically most stable at low particle dimension (less than ca 14 nm), the formation of rutile will not be favored at particle dimensions less than 14 nm [32]. This suggests that, Au particles are only responsible for inhibiting the particle growth and to stabilizing the anatase phase.

3.3. TEM analysis

The particle size, morphology and distribution of Au in TiO₂ films was studied by observing the samples under Transmission Electron Microscope. In the images of 1% Au/TiO₂ thin film and 1% Au/TiO₂ powder (not shown) some dark spheroidal particles were observed. These uniformly distributed dark spheroidal particles are nothing but Au colloids into the TiO₂ matrix. The Au particles were slightly elliptical in appearance this slightly elliptical appearance of the Au colloid is typical for particles in metal sols which generally exhibit some polydispersity in both metal colloid particle size and shape [33,34]. Measurement of several Au particles in the film by TEM indicates that, an average particle size of Au particles in these films is within 15–20 nm range. The increase in concentration of Au into the sol increases the particle density of Au as well as small increase in particle size.

3.4. Estimation of gold and titanium content

The results of compositional analysis of Au/TiO₂ catalyst samples by ICP-OES and EDX technique are presented in Table 1. The results suggest that, the estimated gold and titanium content are in good agreement with the expected theoretical values. There is a small (2–5%) deviation in results for Au and titanium content as compare to theoretical values. This may be attributed to the instrumental errors as well as personal (human) errors during the sample preparation and sample analysis. The results obtained by both these techniques are comparable to theoretical values.

3.5. Photo-catalytic activity

The photo-catalytic activity of samples of TiO₂, 1% Au/TiO₂ and 2% Au/TiO₂ was tested in solar light (sunlight)

Table 1
Estimation of Au and Ti content by ICP-OES

Theoretical composition of catalyst	ICP-OES analysis results		EDX results	
	% Ti	% Au	% Ti	% Au
1% Au/TiO ₂	59.4	1.05	58.95	1.03
2% Au/TiO ₂	58.5	1.98	58.3	2.02

by using the quartz reactor fabricated in-house as described in our previous publication [23]. The 0.2 g Au/TiO₂ coated on silica rings was used as catalyst. All the experiments were performed on very sunny day with solar irradiation of about 4.5–5 Wm²/day between 9.00 a.m. and 17.00 p.m. in the month of April and May 2004.

In recent investigations, the attempt was made to increase the photo-response and photo-catalytic activity of TiO₂ by doping metal ions such as Pt, Ru, Au, Fe, Cu etc in TiO₂ matrix. However, the increase in photo-catalytic activity reported by few workers was very less. Kamat and co-workers [11] reported that TiO₂ electrode modified by deposition of Au on it using electrophoretic deposition method shows only 10–15% increase in photo-catalytic efficiency. This may attributed to the improper distribution Au into TiO₂ matrix and the interaction of Au with TiO₂. Because, in this and most of the other studies reported, Au was deposited on the surface of TiO₂ film, i.e. first the films of TiO₂ were prepared and then Au deposited on these films. So the distribution of Au in TiO₂ as well as the contact between Au particles and TiO₂ may be restricted on the surface of the film. Because of this, the interfacial charge transfer process may not be so efficient which ultimately affects the photo-catalytic activity, as a result no appreciable increase in photo-catalytic activity was observed. To confirm the effect of Au on photo-activity of TiO₂ prepared by titanium peroxide method, we have used the films of Au/TiO₂ deposited on silica substrates for photo-catalytic decomposition of phenol using sunlight as a source of energy. Although the degradation involves many organic intermediates but the extended irradiation results in complete degradation of phenol (Fig. 6). The results of our study shows that there is appreciable increase in photo-catalytic activity (2–2.3 times than undoped). This is because, in our process Au is doped in TiO₂ sol and then films were deposited by using this sol, so the distribution of Au into TiO₂ in sol, films and powder obtained after drying the gel must be uniform and the interfacial interaction as well as charge transfer between Au and TiO₂ will be better as compare to films pre-

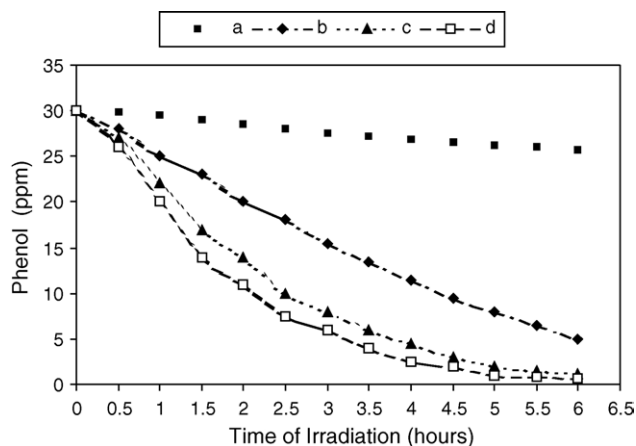


Fig. 6. Rate of decomposition of phenol in sunlight by using (a) blank; (b) TiO₂; (c) 1% Au/TiO₂; and (d) 2% Au/TiO₂ thin film photo-catalyst.

Table 2
Kinetic parameters and photocatalytic efficiency of films towards the degradation of phenol (30 mg/l) in sunlight

	Blank	TiO ₂	1% Au/TiO ₂	2% Au/TiO ₂
Percentage of phenol remain after 1 h	98.33	83.33	66.66	56.66
Time required for complete mineralization (h)		9	4	3.5
Rate constant (min ⁻¹)		0.0049	0.0104	0.0112
Enhancement in rate		1	2.1	2.3

pared by method reported earlier. This results positively on increasing the photo-catalytic activity. From the kinetic study, the parameters such as percentage mineralization after 1 h irradiation, rate constant and time required for complete mineralization were obtained (Table 2).

Results shows that, within 1 hour of irradiation in presence of TiO₂ thin film catalyst 16.6% phenol was mineralised, whereas by using 1% Au/TiO₂ and 2% Au/TiO₂ within 1 h 33.3 and 43.3%, respectively, phenol was mineralized. However, for complete decomposition of phenol (95%) TiO₂ thin film catalyst require 9 h, 1% Au/TiO₂ requires 4 h and 2% Au/TiO₂ requires 3.5 h, respectively. This suggests that reaction rate has been enhanced by doping Au into the TiO₂ matrix. The rate constant obtained by linear regression method gives an idea regarding the increase in rate of reaction. The rate constant of pure TiO₂ catalyzed reaction was 0.004945 min⁻¹, whereas the rate constants of 1% Au/TiO₂ and 2% Au/TiO₂ were 0.01041 min⁻¹ and 0.01128 min⁻¹, respectively. The increase in photo-catalytic activity of Au doped TiO₂ films was observed. 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 [11]. 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 catalyst powder calcined at various temperatures. From the catalytic study (Table 3) it was observed that, among the all Au/TiO₂ catalyst samples, the catalyst calcined at 275 °C shows highest catalytic activity as compare to samples calcined at higher temperature. This may be attributed to the formation of photo-catalytically most active pure anatase phase at this temperature and the particle size. At lower temperature the particle growth will be limited so ultimately the

Table 3
Effect of calcinations temperature on the catalytic activity of 2% Au/TiO₂ photo-catalyst

	As prepared Au/TiO ₂	Au/TiO ₂ calcined at		
		275 °C	400 °C	500 °C
Percentage of phenol degradation after 1 h (approximately)	5–6	35–40	28.5–32	26–29.5
Time required for complete mineralization (h)	15–16	3–3.5	4.5	5.5

surface area as well as number of active sites will be more hence the photo-catalytic activity obtained is more than as prepared Au/TiO₂ and catalyst calcined at higher temperature.

In most studies, the aim of doping the transition metal or noble metal ions was to improve the photo-activity as well as efficiency of photo-catalyst. However, it is suspected that the deactivation of catalyst surface in metal ion doped TiO₂ may be faster than undoped. Because the generation of electron-hole pair at the TiO₂ surface and subsequently formation of hydroxyl radicals and •O₂⁻ radicals during the photo-catalytic reaction may oxidize the metal (Au) nanoparticles [11,35] since both are very strong oxidants. As a result the surface of Au/TiO₂ may get deactivated faster as compare to undoped TiO₂. This will adversely affect on the life of the catalyst so the increase in activity of the TiO₂ will be for short span and the catalyst can not used for long term use. This restricts the applicability of doped catalyst, such type of the decrease in photo-catalytic activity was reported earlier [36]. We have studied the same phenomenon in our case by conducting several experiments on decomposition of phenol in sunlight using the same catalyst. After each decomposition reaction the catalyst coated substrates were separated and used again. After repeated use of the catalyst for five consecutive experiments, no such appreciable decrease in catalytic activity was observed. Results of this study are as shown in Table 4.

Based on the photo-catalytic reactions the following mechanism has been proposed:

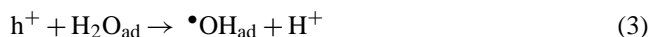
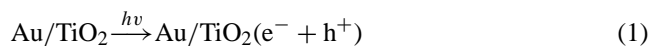
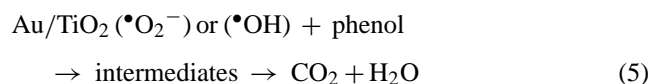


Table 4
Repeated cycle use of 2% Au/TiO₂ photo-catalyst for degradation of phenol (50 mg/l) in sunlight

Catalyst use cycle	Percentage of phenol degradation after 1 h	Time required for complete degradation
1	31.5	4.5
2	31.2	4.5
3	31	4.55
4	31	4.6
5	30.9	4.6

The photo-generated holes at the valence band migrates to the surface and combines with OH^- adsorbed on TiO_2 surface (as per Eq. (1)) results in formation of OH radicals. The electrons in conduction band, combines with O_2 (as per Eq. (4)) and forms O_2^- radical. Both these radicals are strong oxidants which oxidizes the organic molecules land on the surface of TiO_2 resulting the formation intermediate organic species and subsequently complete oxidation of these species to water and carbon dioxide as given below:



The presence of Au on the surface of TiO_2 improves the photo-catalytic activity of TiO_2 . The increase in photo-activity 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 TiO_2 interface by Au^0 particles. It is also proposed that, electron in conduction band migrate to the Au on the surface of photo-catalyst and improves the charge separation process. Further regarding electron transfer process at the interface of TiO_2 and the interfacial contact between Au on TiO_2 , it is assumed that, the contact is not a ohmic type but a schottky barrier type so the electron after excitation migrates to metal through conduction band driven by an electric field as a result the charge separation becomes easier [34] which ultimately minimizes the electron hole recombination and helps in improving the photo-catalytic efficiency of the catalyst. So it is the combine effect of all these processes at the surface of semiconductor films which results in overall increase in photo-activity of TiO_2 . However, it is also reported that, the doping at certain concentration level is beneficial for improving photo-activity as well as efficiency of catalyst and if the Au concentration is increased further it shows decrease in photo-activity [24,37]. To study the same phenomenon in our case, we have prepared Au/ TiO_2 samples containing (1 and 2% Au/ TiO_2) used it for photo-catalytic study but in our samples no such effect has been observed for these samples. In Ti-peroxide doping of Au more than 2% (by weight) changes the sol-gel behavior and perfect transparent gel could not be obtained hence it was not possible for us to study the effect of Au loading at higher level.

4. Conclusion

A simple method for deposition of films of Au/ TiO_2 on various substrates such as soda lime glass plates, glass helix and silica rashing rings by sol-gel dip coating has been developed. The films were modified by addition colloidal Au solution in titanium peroxide sol to increase the photoresponse of TiO_2 in visible light. By addition of 1–2% Au the absorption wavelength of TiO_2 was shifted from 340 nm in UV to

450 nm in visible region. The increase in photoresponse was tested by photocatalytic decomposition of aqueous solution of phenol in sunlight. Doping 1–2% Au into TiO_2 improved the photocatalytic activity by 2–2.3 times than undoped. The catalyst was very stable and it can be used for number of times with no much change in efficiency for long term use.

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