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Photocatalytic degradation of crystal violet dye on the surface of Au doped TiO_2 nanoparticles

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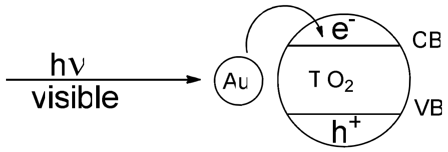
The photocatalytic degradation of crystal violet (CV), which is a cationic triphenyl methane dye in aqueous solution has been investigated with colloidal suspension of Au doped TiO_2 under both UV and visible light irradiation and compared with undoped TiO_2. The degradation has been studied by UV-visible absorption spectroscopy and it is found that Au doped TiO_2 is highly efficient for the dye degradation. Doped and undoped titanium dioxide (TiO_2) nanoparticles have been prepared as a colloidal suspension using sol-gel hydrolysis method and are characterized by XRD, TEM, and UV-visible absorption spectroscopy. The UV-visible absorption spectra reveal that the intensity of the characteristic peaks of CV diminish with time and within an hour the intensity drop below 3/4th of the maximum intensity and there is concomitant oxidative degradation of the dye. This process is accelerated under UV exposure.

Keywords: Cationic dye, Crystal violet, TiO_2 nanoparticles, UV-visible absorption

The textile industry is one of the major polluting industries producing large amount of wastewater containing various dye pollutants[1] characterized by low biodegradability, high toxicity[2] and high chemical oxygen demand, offensive smell and color, turbidity and in some cases carcinogenic[3] for living organisms. In aquatic system, dissolve oxygen oxidizes the dye and modifies its chemical and biological behaviour, which affects both eco- and bio-systems. Therefore, it is essential to treat the waste-water before discharging so that environment hazards can be minimized. In the preceding two decades various physical[4] chemical and biological[5,6] processes were developed for the treatment of dye degradation with special interest on 'Advanced Oxidation Processes' (AOPs)[7,8] which are based on the production of highly reactive oxidizing agent which completely destroys the dye-pollutants in waste-water. Among AOPs, the use of heterogeneous semiconductor photo-catalyst is an efficient, cost-effective and harmless method for removal of organic impurities. In photo-catalytic degradation processes, various semiconductor metal oxides dispersed in aqueous media are used, such as, TiO_2, ZnO, ZnS and CdS and as on[9-12] with the use of natural sunlight and ariel dioxygen as energy source and oxidant respectively. But among them, TiO_2 mediated photocatalysis under UV irradiation[13] is receiving more attention because of its high chemical stability, photo sensitivity[14], good natural abundance and non- toxicity. TiO_2 (anatase) upon interaction with high energy photon (higher than the band gap of 3.4 eV) there is charge separation with the generation of +ve hole (h^+) in the valence band and electron in the conduction band. This charge separation can collapse due to recombination. While the electron can fast diffuse in the surface of the semiconductor photocatalyst and interact with adsorbed dioxygen of air forming $O_2^{\bullet}$ with subsequent formation of hydro peroxide radical ($HOO^{\bullet}$) initiating of redox reaction on the surrounding substrate. The positive hole (h^+) can react with surface titanol group[15] to give highly reactive hydroxyl ($OH^{\bullet}$) and titanoxyl ($TiO^{\bullet}$) radicals. The reactive $OH^{\bullet}$ group attack organic molecules by either hydrogen abstraction or oxidation till it finally degraded completely. It would have been an optimum process if TiO_2 could photodegrade the organic molecules in ordinary visible light, but contrary to this, it exhibit photocatalytic activity in presence of UV light only. In solar radiation around 4% is UV light and rest are visible light and hence the limitation of TiO_2 as solar photocatalyst. In recent years, there is a vigorous attempt to extend the photocatalytic effect of TiO_2 to visible region by doping with metals or organic dyes[15] which injects electrons in the conduction band of TiO_2. However, doping TiO_2 with first row transition metals does not work as photocatalyst in the visible region because the doping site becomes centres for charge recombination[16]. It has been reported that surface or bulk modification of TiO_2 can produce photocatalyst active in visible light[16]. Li and Li have reported the photodegradation of methylene blue in aqueous solution by Au or Au^{3+} modified TiO_2 powder in visible light[17]. The photocatalytic activity of Au nanoparticle are dependent upon size, it shows surface plasmon (SP) band around 560nm, which arise due to collective oscillation of valence electrons confined in a quantum cage of nanoscale dimension. Due to this SP band it is possible to achieve visible photo response in TiO_2. As the CB energy (LUMO energy) of TiO_2 is comparatively low, the ejected electron coming from gold due to SP resonance band will populate this state causing charge separation in presence of visible light.



In the present paper the main objective is to investigate the photocatalytic degradation of the crystal violet (CV) dye by using aqueous colloidal suspension of Au doped and undoped TiO_2 nanoparticles under both UV and visible light irradiation.

Experimental Section

Titanium isopropoxide (assay: >98%) was purchased from Acros Organics and used as such, $HAuCl_4$ (Arora Matthey Ltd.) was used as a gold source for the Au doped TiO_2. The solvents were distilled and dried prior to use.

Crystallographic phases of the prepared products were investigated by X-ray power diffraction method (XRD) using X-ray diffractometer (ULTIMA IV, Rigaku, Japan), the morphologies of the as-prepared samples were characterized by transmission electron microscopy (JEM-100 CX II), selected area electron diffraction (SAED). UV-visible optical absorption spectra were recorded by UV-1700 Pharma Spec UV-visible spectrophotometer, irradiated by a 400 W high-pressure mercury lamp.

Preparation of photocatalyst

TiO_2 colloidal suspension was prepared by using a sol- gel method where titanium isopropoxide (TIPO), glacial acetic acid and water were maintained in the molar ratio 1:10:350. TIPO was hydrolyzed using glacial acetic acid at room temperature and then water was added dropwise with continuous stirring for 1 h, followed by ultrasonication for 15 min. The prepared solution was kept in dark for 24 h to allow the nucleation process, after that it was placed in oven for 10 h at 70°C for gelation and aging process. The gel was then dried at 100°C for 12 h and finally heated to 500°C in a furnace for 2 h. The Au doped TiO_2 colloidal suspension was prepared by the same method mentioned above with the addition of $HAuCl_4$. The doping concentration of the noble metals is expressed in wt%. In our case we have used 0.116 wt% of Au on TiO_2 suspension. These dried powders were subsequently subjected to TEM and X-ray diffraction (XRD) analysis. The Au source was reduced by photogenerated electrons, and Au metal was deposited on TiO_2 particles, resulting in the formation of Au/TiO_2.

Experimental procedure

Photocatalytic performance of both the synthesized sample was determined by evaluating the rate of the degradation reaction of CV under similar conditions. For measuring the photocatalytic reaction rate, 10 mL 0.25×10^{-5} M solution of CV was prepared in double distilled water and the *p*H of the colloidal suspension was raised to 6.8. CV solution (5 mL) was added to 50μL of colloidal TiO_2 or Au doped TiO_2. It was first kept in the dark place for complete absorption of CV on the surface of colloidal TiO_2. The zero time reading was taken and thereafter, the absorption spectra were taken after every 10 min intervals.

To study the recombination of electrons-holes in the photo-catalysts, the PL emission spectra of the samples were measured with a (Hitachi) F-2700 Fluorescence spectrometer. Absorption spectra were recorded using UV-1700 Pharma Spec UV-visible spectrophotometer. Visible light photocatalytic activities were calculated for crystal violet (CV) degradation in aqueous solution under the irradiation with 150 W tungsten lamp.

Results and Discussion

Characterization of Catalyst

The TiO_2 supported gold nanoparticles were synthesized by sol-gel method and the characteristic color of the metallic Au is purple in colour[18] represented as Au/TiO_2. The existence of metallic Au^0 particle was confirmed by UV-visible spectra, which showed a band at around 528 nm due to surface plasmon resonance (Fig. 1a). Both the photocatalysts TiO_2 and Au doped TiO_2 were also characterized by the XRD pattern and transmission electron microscope to determine the average particle size.

In order to determine the size and to study the structural properties of the synthesized nanoparticles of Au/TiO_2, the powder XRD analysis was performed. Figure 1(b) shows the X-ray diffractogram of the as prepared Au/TiO_2 nanoparticles that present mainly in highly in crystalline anatase phase. XRD patterns exhibited strong diffraction peaks at 2θ values of 25.1°, 47.7° and 53.8° indicating TiO_2 in the anatase phase[19]. The X-ray diffraction peak for gold was detected at 2θ values of 37.7°, 47.7°, 63°, 74° and 82° corresponding to the (111), (200), (220), (311) and (222) planes[20]. Some of peaks of anatase TiO_2 are overlapped with the peaks of gold (2θ= 47.4°) (JCPDS card no. 84-1286). In addition to these five peaks there are some anonymous peaks appeared in the XRD pattern.

The transmission electron microscopic analysis was carried out to confirm the actual size of the Au doped TiO_2 (Fig. 2a) and undoped TiO_2 (Fig. 2b) nanoparticles, their growth pattern and the distribution of the crystallites and it can be seen that Au nanoparticles seen as darker spots are deposited on TiO_2 nanoparticles. The synthesized AuNPs are spherical in shape and vary from 15 to 20 nm in size. Selective area electron diffraction (SAED, in the inset) shows well resolved diffraction cycles indicative of a highly crystalline TiO_2 and Au/ TiO_2 framework.

Photocatalytic degradation of crystal violet dye

Photocatalytic performance of Au doped TiO_2 and undoped TiO_2 under UV light: The absorption spectrum of CV has main peaks at around 583 nm. Figure 3 shows absorption spectral changes when the crystal violet aqueous solution was degraded with the colloidal suspension of TiO_2 photocatalytic for 180 min. The intensity of the maximum absorption peak decreased due to the degradation of CV. An absorption spectral change of CV in aqueous solution degraded by an Au-TiO_2 photocatalyst is shown in Fig. 3(a). The intensity of the maximum absorption peak decreases due to the adsorption of CV on the surface of the TiO_2 photocatalyst. The degree of photodegradation of CV by the Au-TiO_2 photocatalyst is found to be large compared with only TiO_2. It is reported that metal particles, such as Ag, Pt, or Au enhance[21-23] the photocatalytic performance of TiO_2, because the photogenerated electrons are trapped by these particles, causing high efficiency of charge separation[24]. In this case, UV excites an electron from the valence band (VB) to the conduction band (CB) of TiO_2 which combines with the molecular oxygen to form a superoxide radical anion $[O_2^{\bullet}]^-$, which subsequently gets protonated to yield $HOO^{\bullet}$. These species photo-oxidize the organic dye to produce some peroxy or hydroxylated intermediates and finally the degraded products. It is well known that doped metals are

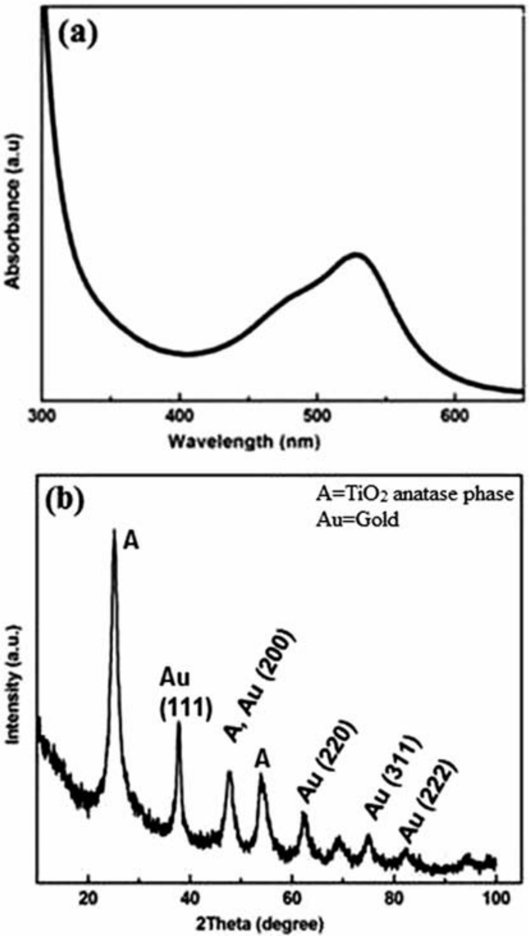
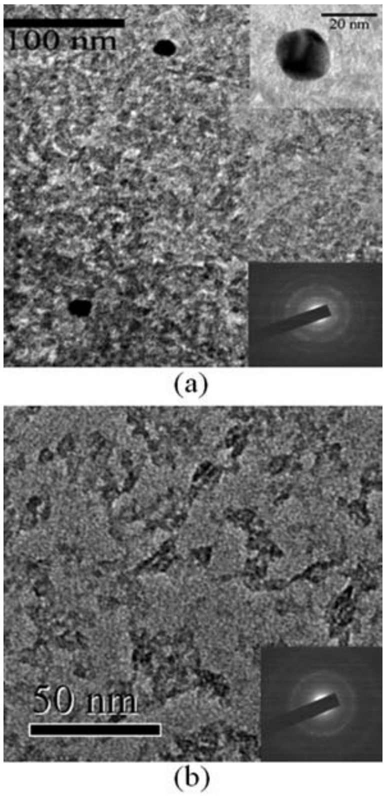


Fig. 1 — (a) UV-Vis spectra and (b) XRD pattern of as-prepared Au/TiO_2 nanoparticle



(a)

(b)

Fig. 2 — TEM image of (a) Au/TiO_2 and (b) TiO_2 nanoparticles

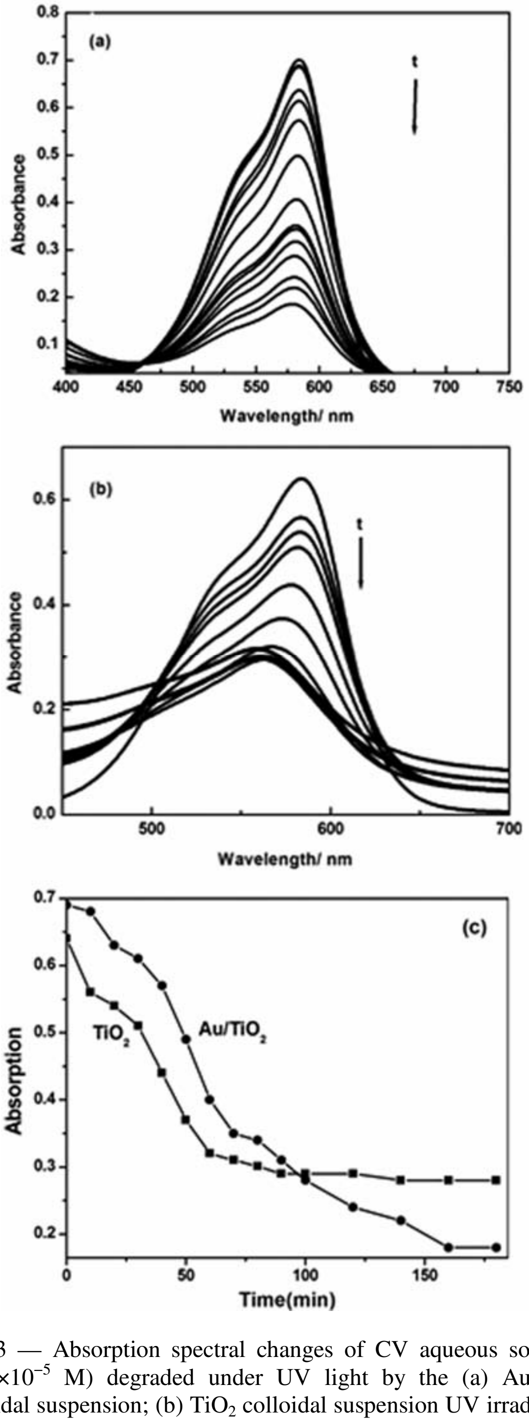


Fig. 3 — Absorption spectral changes of CV aqueous solution (0.25×10^{-5} M) degraded under UV light by the (a) Au-TiO_2 colloidal suspension; (b) TiO_2 colloidal suspension UV irradiation time t is: 0-180 min; (c) Photo-degradation of CV versus irradiation time.

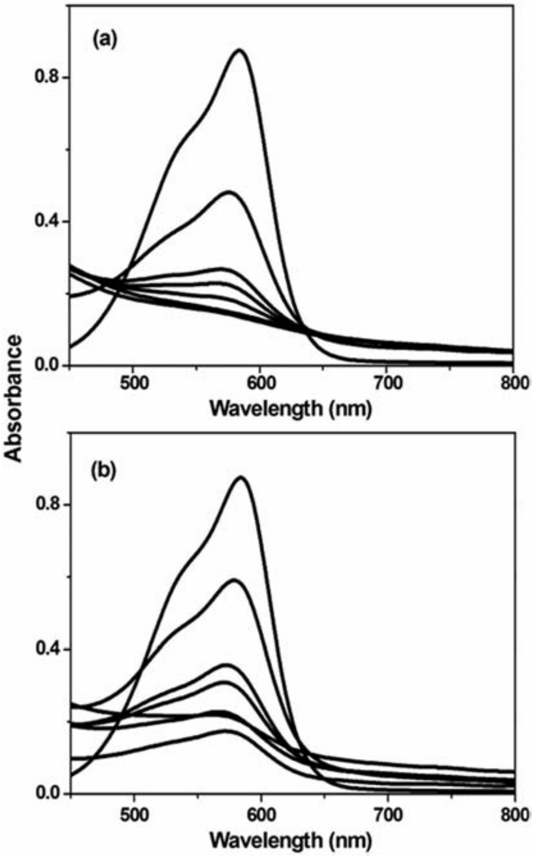


Fig. 4 — Degradation of crystal violet under visible light using (a) Au-TiO_2 and (b) TiO_2 colloidal suspension. t= 0-180 min

electron traps which facilitate charge separation and preclude recombination[25].

In the present case, the AuNPs could be trap for electron produced due to UV irradiation of TiO_2, resulting a hole in TiO_2 and charge separation or combination of effect due to surface plasmon resonance (SPR) by AuNPs[26,27] which is dependent on nanoparticle size distribution. Therefore, further study is required to know the significance of particle size on the photocatalytic reaction in the present Au-TiO_2 composite system.

Photocatalytic performance of Au doped TiO_2 and undoped TiO_2 under visible light

The sequential absorption spectrum of CV aqueous solution under visible light illumination in the presence of Au doped TiO_2 and undoped TiO_2 for different irradiation times starting from 0 to 180 min is shown in Fig. 4.

The CV dye shows strong characteristic absorption at 583 nm and the intensity of the absorption maxima gradually decrease as the exposure time of visible light increases to 180 min indicating the photodecomposition of the dye. The intense purple colour of the CV solution disappears gradually and becomes almost colourless as the irradiation time increased. In presence of Au doped TiO_2 complete degradation of CV was observed at 180 min whereas for undoped TiO_2 a complete degradation was not observed within 180 min. In this case, initially the adsorbed CV dye got excited under visible light, as a result of which an electron is injected from the excited dye into the TiO_2 particle. The driving force for this charge injection process is the energy difference between the oxidation potential of the excited dye and the band gap of TiO_2 semiconductor.

Mechanism

The probable photocatalytic action of Au-TiO_2 suspension on the degradation of dye can be shown as follows[28]

$$\text{Au-TiO}_2 + h\nu \longrightarrow e^- + h^+$$
$$(O_2)_{ads} + e^- + (O_2)_{ads}$$
$$\text{Ti (IV)-OH} + h^+ \longrightarrow \text{Ti (IV) - OH}^\bullet$$
$$\text{Ti (IV)-H}_2\text{O} + h^+ \longrightarrow \text{Ti (IV) - OH}^\bullet + H^+$$

The $OH^\bullet$ radical formed on the illuminated catalyst surface are extremely strong oxidant which can easily oxidize the adsorbed dye molecule to their final degradation product.

Conclusion

In conclusion, a facile approach was used for preparing nanocrystalline titanium dioxide colloidal suspensions and they are modified by AuNPs, characterized, and successfully tested for the photocatalytic degradation of the pollutant crystal violet dye. The Au-doped TiO_2 enhanced the photocatalytic activity owing to the inhibition of charge carrier recombination and the higher absorbance for long wavelength light resulting from the plasmon effect. Such a scheme may find industrial applications, where destruction of toxicity of certain waste chemicals such as dyes is essential before releasing to the environment. A systematic study is needed to evaluate the effect of particle size on the photocatalytic activity of TiO_2 nanoparticles.

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