Research Article

Au/TiO$_2$ Reusable Photocatalysts for Dye Degradation

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Nanogold doped TiO$_2$ catalysts are synthesized, and their application in the photodegradation of dye pollutants is studied. The materials are characterized using different analytical techniques such as X-ray diffraction, transmission electron microscopy, UV-visible diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy. The results revealed the strong interaction between the metallic gold nanoparticles and the anatase TiO$_2$ support. Au doped systems showed very good photoactivity in the degradation of dye pollutants under UV irradiation as well as in sunlight. A simple mechanism is proposed for explaining the excellent photoactivity of the systems. The reusability studies of the photocatalysts exhibited more than 98% degradation of the dye even after 10 repeated cycles.

1. Introduction

Even though dyes are classified as pollutants, they are widely applied in the textile manufacturing industries. The discharge of dyes causes soil as well as water pollution depending on its mode of disposal. In addition, since the dye stuffs are intentionally designed to resist aerobic oxidation by microorganisms, only partial degradation of dye molecules are possible with aerobes, and it results in the formation of volatile carcinogenic compounds. So the treatment of these dye effluents is highly desired for the preservation of clean air, soil, and water.

TiO$_2$, in the anatase form, is one of the best photocatalysts for pollutant degradation [1]. However, because of the relatively high intrinsic band gap of anatase TiO$_2$ (3.2 eV), ultraviolet (UV) irradiation is required for its photoactivity [2, 3], and thus only 4% of the sunlight (UV fraction of solar spectrum) can be utilized effectively [4]. Thus, pure TiO$_2$ based systems have been found to be inactive under sunlight. Application of UV lamps has serious disadvantages including high energy consumption and handling problems.

Keeping this in mind, researchers focused to develop TiO$_2$ based systems having decreased band gap so as to show photocatalytic activity in the visible region. This will enable the use of sunlight for photocatalysis [5]. Several modification methods are available to shift the wavelength of absorption of TiO$_2$ from UV to visible region, among which anion doping succeed in this matter [6–11]. Nitrogen is the widely studied anion dopant where the photoactivity of the N doped TiO$_2$ even arises by the presence of molecularly adsorbed N$_2$ [12]. Thus, the activity may decrease by storing the catalyst for long time.

The second main drawback associated with the photocatalytic activity of TiO$_2$ is that most of the activated charge carriers will undergo recombination before reaching the surface, preventing interaction with adsorbed molecules. In fact, 90% of the charge carriers may be lost within a nanosecond of their generation leading to low photoactivity of TiO$_2$ [13]. The high recombination rate of photogenerated electron-hole pairs, which controls the photocatalytic efficiency of semiconductors, can be reduced by trapping the electrons with noble metals [14]. The noble metals such as Pt, Ag, and

Au, when deposited over TiO$_2$, can act as electron traps, since they have the high Schottky barriers among the metals [15–19].

Our aim is to develop highly competent catalysts, which can prevent the recombination of charge carriers effectively, so that the photocatalysts can act well even by utilizing the UV light from the sun. In the present work, the surface doping of sol gel TiO$_2$ has been done with gold nanoparticles (AuNPs), with an aim to trap the electrons to prevent recombination. The selection of AuNPs as dopant was also based on its property of UV light absorption, causing the transition of 5d electrons to the 6sp band (interband transition) [20, 21]. It is also reported that due to the high photon energy, UV light is able to drive chemical reactions on AuNPs [22]. AuNP supported over zeolite, ZrO$_2$, and SiO$_2$, were found to be effective for the degradation of dye pollutant sulforhodamine-B [22]. The incorporation of nanogold over supports other than TiO$_2$ required high percentage loading of gold for its effective photocatalytic activity [22]. Thus, a combination of AuNP and TiO$_2$ can lead to the formation of a cost effective photocatalyst.

In the present study, nanogold particles were doped over TiO$_2$ catalysts, using chloroauric acid as the gold precursor, by deposition-precipitation method. TiO$_2$ was prepared by sol-gel method. Highly dispersed gold nanoparticles with diameter less than 5 nm were found to be deposited over TiO$_2$. All the TiO$_2$ based catalysts of the present study were found to exist in the anatase phase. The reaction parameters were varied in the degradation of methylorange (MO) for attaining best conditions for photocatalysis.

2. Experimental

2.1. Preparation of Titania Support. Titania photocatalysts using titanium (IV) isopropoxide (Sigma Aldrich) as titanium precursor were prepared by sol-gel method with slight modifications from the reported procedure [23]. 0.0628 mol titanium (IV) isopropoxide and 0.8563 mol ethyl alcohol (Hamberg Chemicals), were mixed first. Then a mixture of 0.8563 mol ethyl alcohol, 0.2186 mol glacial acetic acid (R &M Chemicals) and 6.25 mL distilled water was added to the above solution. The resultant solution was stirred to get transparent titania sol. It was then aged for 2 days and dried in an air oven at 80°C. Ground into fine powder and calcination was done at 400°C for 5 h to obtain TiO$_2$ powder.

2.2. Preparation of Nanogold Doped Titania. For the preparation of nanogold, 2.1×10^{-3} M chloroauric acid (Sigma Aldrich) solution was used as the gold precursor, and NaOH (R&M Chemicals) was added to it under stirring so as to adjust the pH of the solution to 8. For nanogold doping over TiO$_2$, required amount of TiO$_2$ powder was added to the freshly prepared nanogold solution where the pH of 8 was kept constant at 70°C, and the solution was stirred well for 2 hours. The mixture was filtered, and the residue was washed with distilled water to remove chloride ions. The nanogold incorporated TiO$_2$ was dried at 80°C and calcined at 200°C for 5 h. The doped systems were designated as n%Au/TiO$_2$,

where n indicates the weight percentage of gold taken for doping over TiO$_2$.

2.3. Catalyst Characterization. XRD patterns of the samples were recorded for 2θ between 3 and 80° on a Bruker AXS D8 Advance diffractometer employing a scanning rate of 0.02°/S with Cu Kα radiation ($\lambda = 1.5418$ Å). Transmission electron microscopic (TEM) analyses were conducted using ZEISS LIBRA 200 electron microscope. XPS of 1.5%Au/TiO$_2$ sample was recorded with a SPECS spectrometer using nonmonochromatic AlKα source (1486.6 eV) run at 150 W (12 kV and 12.5 mA). Survey scan was obtained with 70 eV pass energy and high resolution scan of Ti 2p, O 1s and Au 4f with 40 eV pass energy. The binding energies reported here were calculated with reference to C 1s peak at 284.6 eV. Au 4f core level was curve fitted into several components with Gaussian-Lorentzian peaks after subtracting Shirley background. Diffuse reflectance Ultraviolet-visible spectroscopy (UV-vis DRS) of powder catalyst samples was carried out at room temperature using a Varian, Cary 5000 spectrophotometer in the range of 200 to 800 nm. Elemental composition of the prepared samples was determined by using Thermo Electron IRIS INTREPID II XSP DUO Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

2.4. Photoactivity Measurements. The efficiency of the nanogold doped TiO$_2$ photocatalysts was examined by the photodegradation of dye pollutants in a Rayonet type Photoreactor (Associate Technica, India) having 16 UV tubes of 8W (HITACHI F8T5 8 WATT Hittach, Ltd., Tokyo, Japan) capacity. In a typical experiment, 50 mL of 10 mg/L of MO was placed in a quartz tube containing 3 g/L of catalyst and was irradiated with UV light under continuous stirring by air flow for 1 h. The above mentioned conditions were used in all experiments unless otherwise mentioned. The MO concentration was analyzed using a Varian, Cary spectrophotometer by absorbance measurements at the wavelength of maximum absorption of MO (464 nm) before and after degradation. The reaction conditions such as catalyst weight (1 to 5 g/L), dye concentration (5 to 20 mg/L), irradiation time (30 to 120 min under sunlight and 15 to 90 min under UV light irradiation), weight percentage of gold over TiO$_2$, and so forth were varied to find out the best condition for maximum photodegradation. The degradation studies were also conducted under different pH. Performance of 2%Au/TiO$_2$ in degrading different dyes in the selected conditions was also evaluated. Activity studies under sunlight were investigated using 1.5%Au/TiO$_2$.

3. Results and Discussion

3.1. Catalyst Characterization. XRD patterns of the undoped and AuNP doped samples in Figure 1 showed anatase as the only phase (major peak at $2\theta = 25.5°$), which is reported as the most photocatalytically active crystalline state of TiO$_2$ [24]. No peaks for gold are found to be present, indicating efficient dispersion of the inserted metal with dimensions lower than 5 nm [25]. TEM images shown in Figure 2 supported the
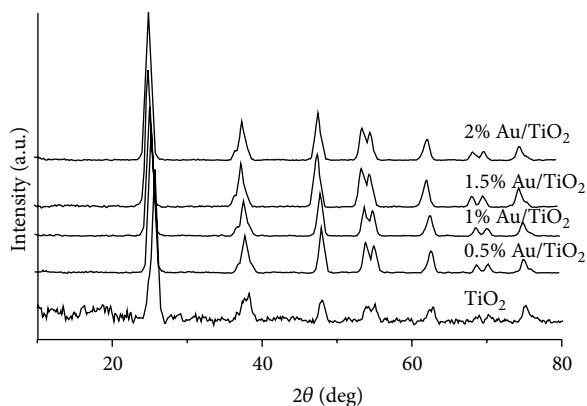
FIGURE 1: XRD patterns of the prepared photocatalysts.

above supposition. Well-dispersed gold nanoparticles, in the range of 2-3 nm diameters, appeared as black spots over the gray-coloured spherical particles of TiO_2. Since AuNP over TiO_2 is having diameter less than 5 nm, it lies in the size range required for effective use of nanogold in catalysis [26]. The spherical shaped titania particles have diameters in the range of 15–25 nm. Anatase lattice fringes are visible, and the micrograms demonstrate that the particles are connected to each other to form a mesoporous crystalline framework [27].

The XPS spectrum of the representative sample, 1.5%Au/TiO_2, was measured to elucidate the chemical state of Au and other species in the prepared samples. Figure 3 shows the wide scan spectra of the sample, and the spectra corresponding to Ti 2p, O 1s and Au 4f. From the high resolution spectra, it can be seen that the Ti 2p peaks appeared at binding energies (B.E.) of 458.7 ($2p_{3/2}$) and 464.4 ($2p_{1/2}$). The peak at 458.7 corresponds to titanium in pure anatase. Here, the energy splitting between Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is 5.7 eV, which confirms the existence of titanium as Ti^{4+} [28]. It is also reported that the position of the Ti $2p_{3/2}$ component at 458.7 eV corresponds to the oxidation state of +4 of Ti in titanium dioxide [29, 30]. The O 1s B.E. of the sample is located at 530.0 eV, which is assigned to bulk oxide (O^{2-}) in the TiO_2 lattice. Therefore, it can be concluded that no obvious changes on the chemical state of Ti and O were caused by doped and deposited Au.

Au 4f XPS spectrum of 1.5%Au/TiO_2 sample exhibited peaks at the B.E. values of 83.6 and 87.1 eV for $4f_{7/2}$ and $4f_{5/2}$ electrons, corresponding to Au in the metallic state [31]. In addition, peaks arising from Au^{+1} are observed at 84.8 eV ($4f_{7/2}$) and 88.6 ($4f_{5/2}$). It is depicted that 92% of Au exists in Au^0 state and 8% exists in its ionic state, Au^+. This confirms the formation of nanogold, Au^0 on the TiO_2 surface. As per the reported data [32, 33], the doublet of Au^0 was centered at 84.0 and 87.7 eV. The decrease in the binding energies of Au 4f peaks in the present Au doped TiO_2 system may be due to the negative charge of the Au nanoparticles as a result of the charge transfer from the TiO_2 substrate as already reported [34]. The formation of negative charge of the Au nanoparticles may be due to the large difference in the work function of Au and TiO_2 which facilitates the

electron transfer from TiO_2 to Au [34]. The negative shift in comparison with bulk gold thus suggests the formation of a strong metal-support interaction [35] over the present catalyst. XPS analysis also confirmed the absence of any contamination from sodium and chlorine species (NaOH and $HAuCl_4$), which were used during the doping process.

Two bands are observed in the UV-visible diffuse reflectance spectra of Au doped TiO_2 samples (Figure 4). The intense band with absorption maxima around 320 to 350 nm is associated to the O^{2-}-Ti^{4+} charge-transfer, corresponding to the electronic excitation from the valence band to the conduction band [36]. In the case of undoped TiO_2, this band is found to be highly intense, which may be a result of the presence of greater number of Ti^{4+} ions and consequently a greater number of Ti^{4+}-O^{2-} bonds [37]. Gold doping decreases the intensity of this band, which can be due to the interaction between Au nanoparticles with the TiO_2 support [38]. The metal-support interaction is already suggested from the interpretation of XPS results. A slight red shift of the above band is observed upon gold doping. The shift may be due to the insertion of metal ions into the TiO_2 at substitutional sites [39]. XPS analysis revealed the presence of a minor percentage of Au^+ in the representative sample, 1.5%Au/TiO_2, supporting this possibility. Nanogold doped samples show the presence of a comparatively less intense band with λ_{max} in the region of 540–570 nm. This band can be attributed to the surface plasmon resonance of Au, which arises from the collective oscillations of the free conduction band electrons that are induced by the incident electromagnetic radiation [40, 41].

The elemental analysis results of representative samples, 1%Au/TiO_2, 1.5%Au/TiO_2, and 2%Au/TiO_2, reveals the inserted Au contents as 0.074 wt%, 0.182 wt%, and 0.225 wt%, respectively. Increase in the amount of gold precursor in the preparation showed an increase in the amount of metal incorporated over TiO_2. The incorporated amount was less than the amount of gold taken, which may be due to the loss of unbound nanogold while washing the catalysts with distilled water during the preparation.

3.2. Photocatalytic Activity. The activity of the different systems under visible light was investigated, and it was found that the photocatalysts were not active under visible light. But the experiments under UV irradiation were satisfactory in the degradation of MO. The reaction parameters were varied to get best results.

Figure 5 describes the effect of reaction conditions on the performance of the catalyst. Initial steep rise in photodegradation capacity is observed with increase in the amount of catalyst weight, which then attains saturation at a catalyst dosage of 3 g/L. Thus a catalyst weight of 3 g/L (0.15 g) was selected for further studies. The dye concentration is varied, and from the results, it is observed that the catalyst showed 100% degradation of the dye pollutant at low concentrations. The activity decreased from an increased dye concentration of 15 mg/L onwards as seen from the data shown in Figure 5(b). We also varied the pH of the solution, since the dye pollutant effluent from the industry may be of different pH. The
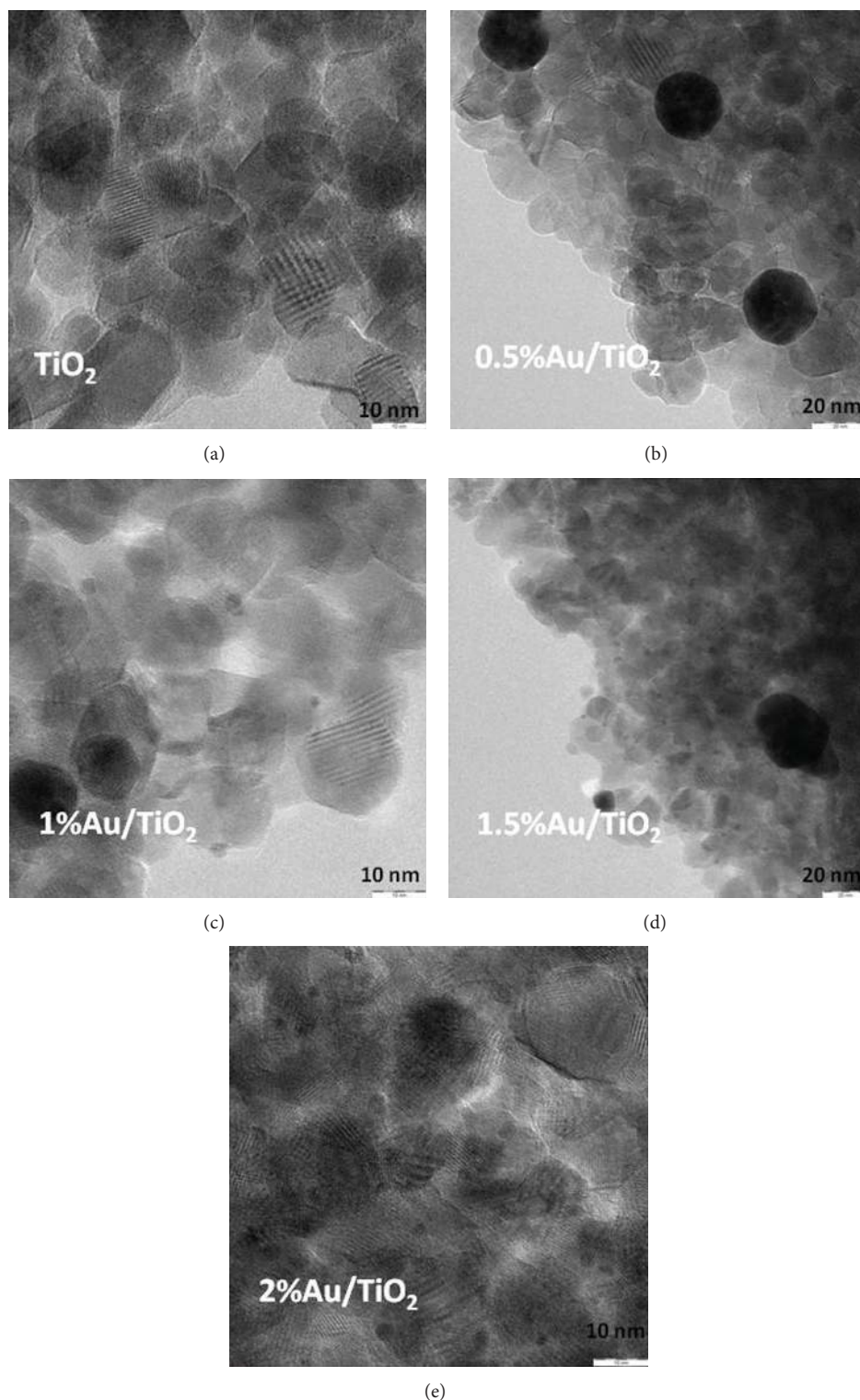
(a)

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(d)

(e)

FIGURE 2: TEM image of TiO_2 and AuNP loaded TiO_2 photocatalysts.

catalysts worked well in lower pH values till the natural pH of the solution. Under basic pH, activity is reduced and the percentage dye degradation decreased to 84.9% at a high pH value of 11. Still, the activity is better since the percentage

dye degradation is more than 80% as observed in the results shown in Figure 5(c).

The percentage of gold doping over TiO_2 is varied to attain maximum photoactivity, and the dye degradation is
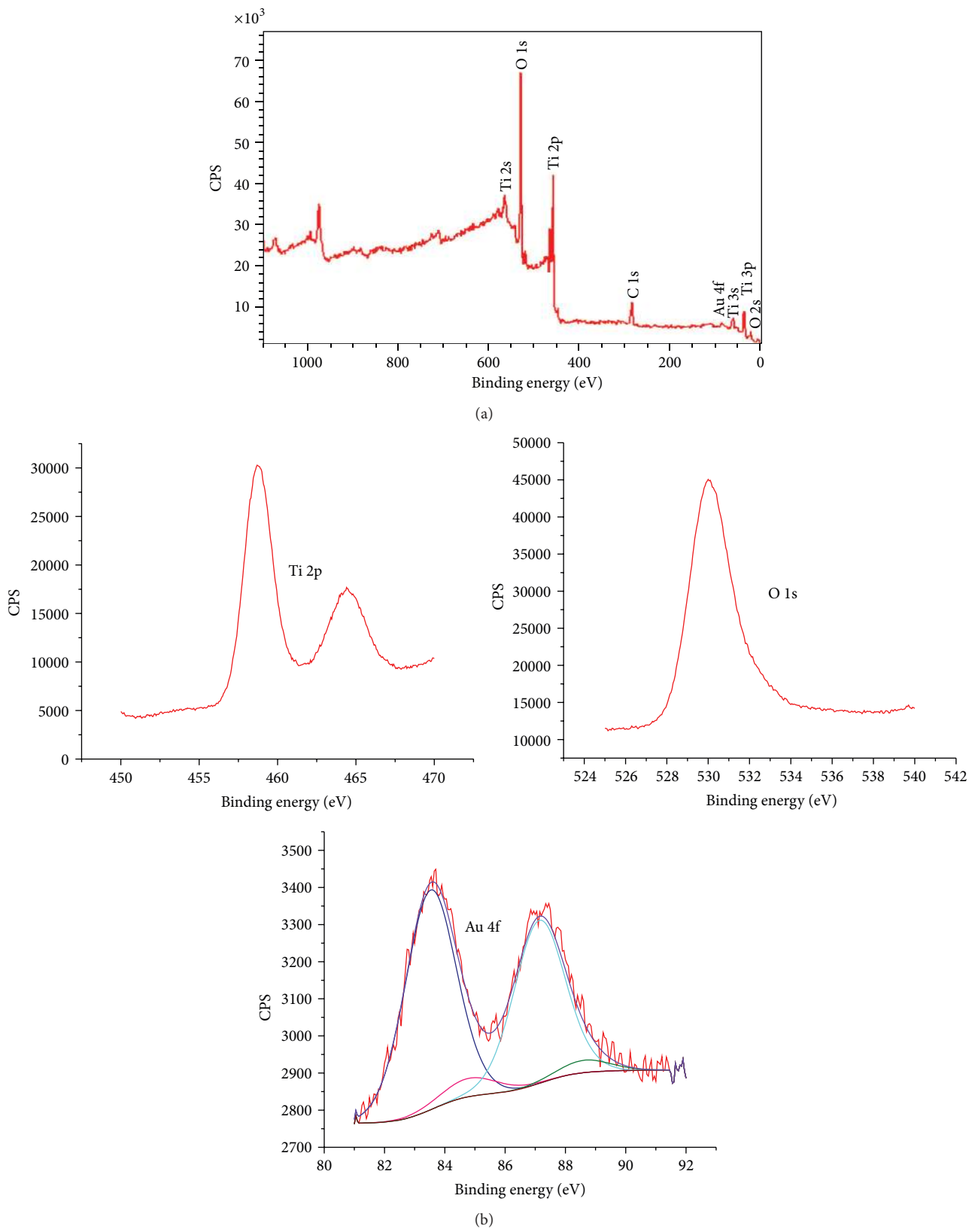
(a)

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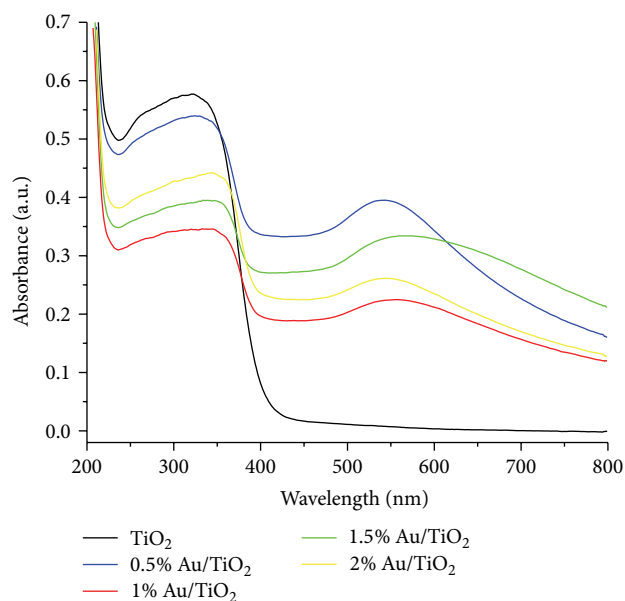FIGURE 3: XPS spectra of 1.5%Au/TiO$_2$: (a) wide scan spectra, (b) high resolution spectra corresponding to Ti 2p, O 1s, and Au 4f.

FIGURE 4: UV-visible diffuse reflectance spectra of Au doped TiO_2 samples.

TABLE 1: Photodegradation of aquatic dye pollutants over Au NP doped TiO_2.

Dyes	% Degradation
Methylorange	100.00
Crystal violet	98.63
Methylene blue	95.30
Malachite green	100.00
Orange II	99.05
Acid blue	94.69

Reaction conditions: 50 mL of 10 mg/L dye solution, 0.15 g catalyst, 1 h, 2% Au/TiO_2.

monitored. Incorporation of gold increases the activity of TiO_2 drastically, which again moves up with increase in the amount of gold. Both 1.5% and 2 wt% AuNP doped systems gave 100% degradation of 50 mL, 10 mg/L MO dye over 3 g/L catalyst for 2 h exposure to UV light. In order to recognize the best Au doping, the time of UV irradiation was changed to 1 h, where 2%Au/TiO_2 provided the complete dye degradation. The results given in Figure 5(d) suggest 2%Au/TiO_2 as the best photocatalyst of the present investigation.

Reusability of the catalyst is one of the most projected attractions of any heterogeneous catalyzed reaction, but only limited experiments are there on the reusability studies of powder photocatalysts [42, 43]. This may be due to the difficulties in separation of the catalyst powder after pollutant degradation and may also be due to the low reusability of the catalysts. Present catalysts are easily separable from the solution and also well dispersible under stirring. It is simple to detach the catalyst from the cleaned solution either by filtration or by centrifugation. There was no permanent adsorption of dye over the catalyst, and the cleaning merely arises from photodegradation. Regeneration of the best catalyst, 2%Au/TiO_2, was done after each reaction, by centrifugation, washing with water, and further treatment at the calcination temperature of the catalyst, that is, at 200°C, for 1 h. The photocatalytic activity of the nanogold doped titania remains intact even up to ten consecutive experiments under the selected reaction conditions (Figure 6). The performance of the 2% Au/TiO_2 in the degradation of a number of dye pollutants was also tested where the activity is found to be admirable. The results are given in Table 1.

The excellent activity of the present nanogold loaded TiO_2 photocatalysts under UV light pinched us to test its ability to harvest the UV present in the sunlight. The photoactivity was also evaluated by the direct use of sunlight that may

immediately turn the attention of industries for pollutant treatment. Akbarzadeh et al. had reported vanadium doped TiO_2 systems that are effective under sunlight where the catalyst used both UV and visible spectra of the sunlight for photoactivity [44]. The 0.5% vanadium doped TiO_2 showed 53.99% degradation of methyleneblue after 1 h irradiation. Present AuNP doped TiO_2 displayed very good activity under sunlight where more than 80% of the methylorange dye is degraded within 1 h and degradation reached around 93% by 2 h exposure to sunlight over 1.5%Au/TiO_2. The use of UV radiation of sunlight for the photocatalytic degradation is investigated in our experiments. When the reaction is conducted under sunlight using glass tubes instead of quartz tubes, the activity dropped drastically. Glass is opaque to UV light and that may be the reason for decreased activity which suggests the use of UV light for degradation. The degradation data of MO under sunlight over 1.5%Au/TiO_2 with time is presented in Figure 7(a). The degradation results under UV lamps are also offered for comparison in Figure 7(b).

3.3. Proposed Mechanism of Photodegradation. The plausible reaction mechanism for the photodegradation of dyes over nanogold doped TiO_2 under UV irradiation is suggested here. Upon UV irradiation, the electrons present in the valance band (VB) get promoted to the conduction band (CB) since the band gap of TiO_2 lies in the UV region [45–47]. In the CB, the electrons can be further transferred to the adsorbed O_2 on the surface of TiO_2 to form the superoxide radical anions, $O_2{}^{\bullet-}$ [48, 49]. In addition, in the case of metal nanoparticle doped TiO_2, the metal nanoparticles can be considered as an electron sink, where the electrons in the conduction band can migrate to the noble metal surface, thereby preventing the recombination of electron-hole ($e^- \text{-} h^+$) pairs [40, 45]. Thus the migration of electrons from the interior of the photocatalyst to the metal surface results in increased photoquantum efficiency, which can be the reason for the excellent photoactivity for the present nanogold doped systems even by using low intensity UV present in the sunlight. The transferred electrons in the metal surface facilitate the formation of oxygen superoxide radical anion. In the VB, the holes interact with water molecules, resulting in the formation of hydroxyl radical ($^\bullet OH$) and proton. Protonation of the superoxide anion, $O_2{}^{\bullet-}$, creates $^\bullet OOH$ radicals which leads to the formation of H_2O_2 and
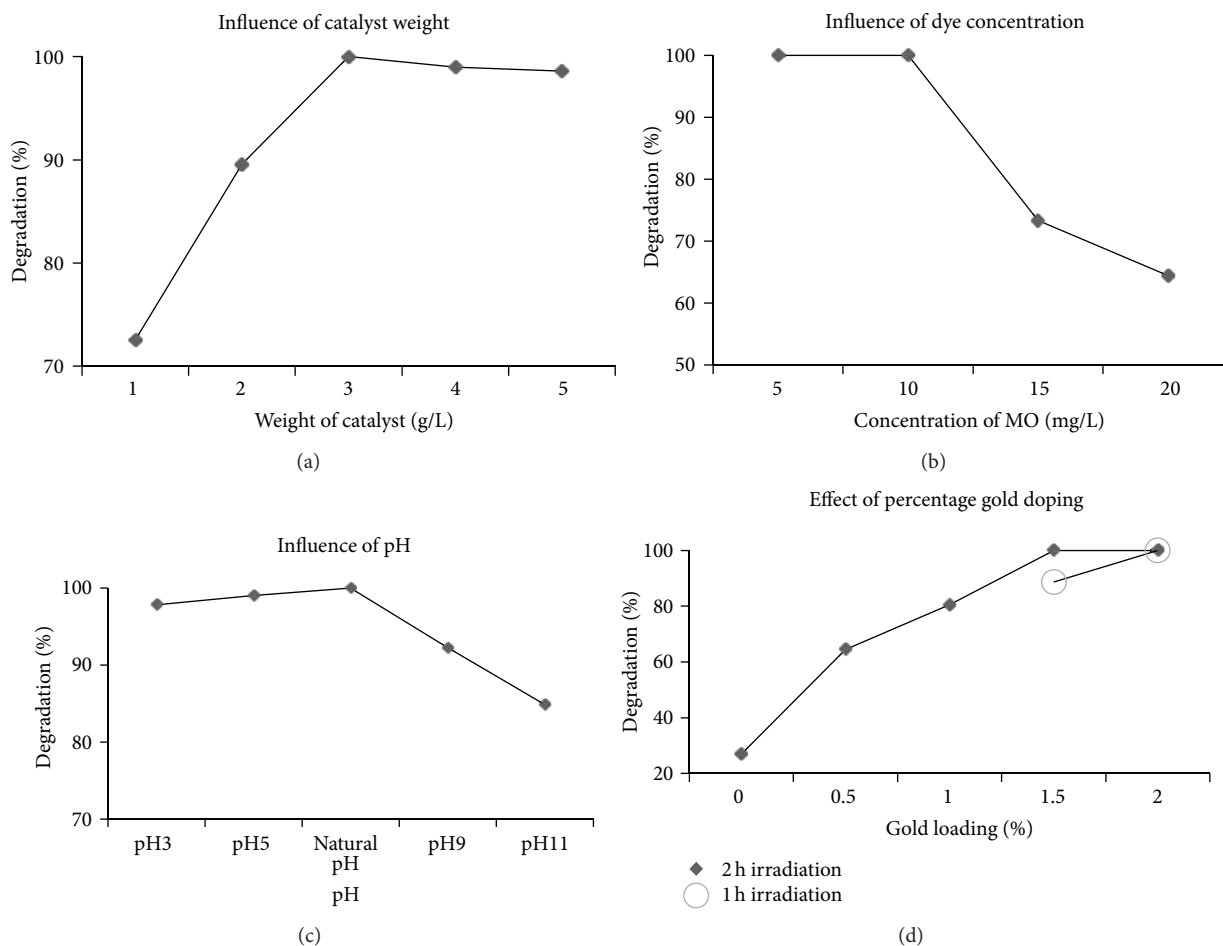
(a)

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FIGURE 5: Influence of reaction conditions on photodegradation of methylorange over different photocatalysts.
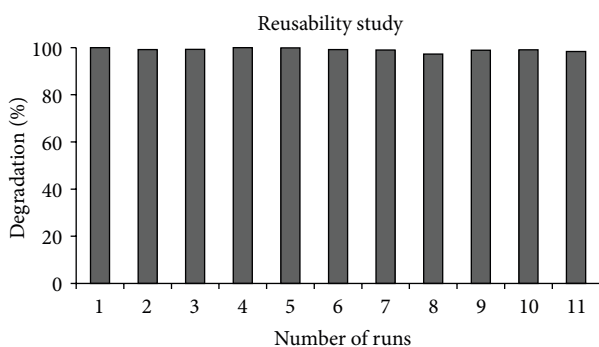

FIGURE 6: Reusability data over 2%Au/TiO$_2$ in the degradation of 50 mL of 10 mg/L MO, over 3 g/L catalyst, for 1 h irradiation under UV.

finally $^\bullet$OH radical [50]. These $^\bullet$OH radicals are responsible for the degradation of dye molecules. The presence of $^\bullet$OH radicals for photoactivity is already confirmed in previous reports [50–53]. Thus it can be understood that insertion of AuNP as well as increase in the amount of inserted nanogold particles can increase the photoactivity of TiO$_2$ significantly. Increase in the number of AuNPs over the support can lead

to the enhanced migration of electrons from the CB of TiO$_2$ to the Au surfaces which promotes the electron transfer to the adsorbed O$_2$ molecules [54, 55]. This will facilitate the formation of more number of O$_2$$^{\bullet-}$ and finally can lead to the formation of more number of $^\bullet$OH which is responsible for dye degradation. This explains the observed increase in the dye degradation over the present photocatalysts with an increase in the percentage gold doping. The mechanism of photodegradation is schematically represented in Figure 8.

4. Conclusions

Highly efficient photocatalysts were prepared by nanogold doping over sol-gel TiO$_2$. XRD patterns show the exclusive existence of anatase crystalline phase of TiO$_2$. Majority of the incorporated gold exists in its metallic state, where the particles have diameters less than 5 nm. The strong interaction between the Au and the support, as evident from the characterization of the materials, leads to enhanced photocatalytic activity. The gold nanoparticles act as effective trapping centres to prevent recombination of electron-hole pairs, making the catalysts even active under sunlight for the efficient degradation of pollutants. Another attractiveness of
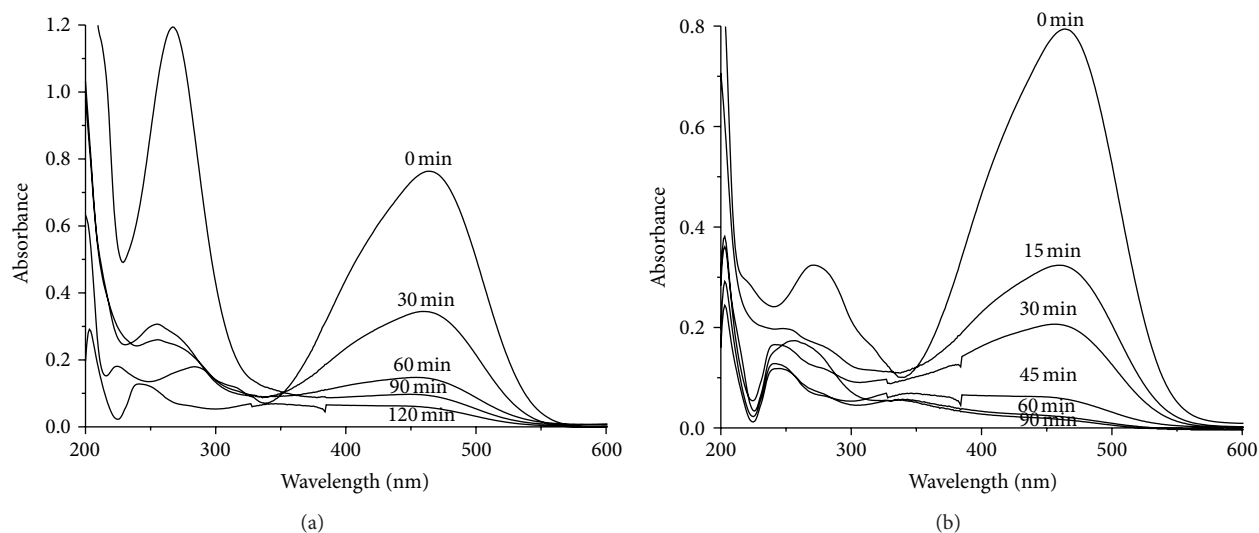
(a)

(b)

FIGURE 7: (a) Degradation of 10 mg/L MO under sunlight over 3 g/L of 1.5%Au/TiO$_2$. (b) Degradation of 10 mg/L MO under UV irradiation over 3 g/L of 2%Au/TiO$_2$.
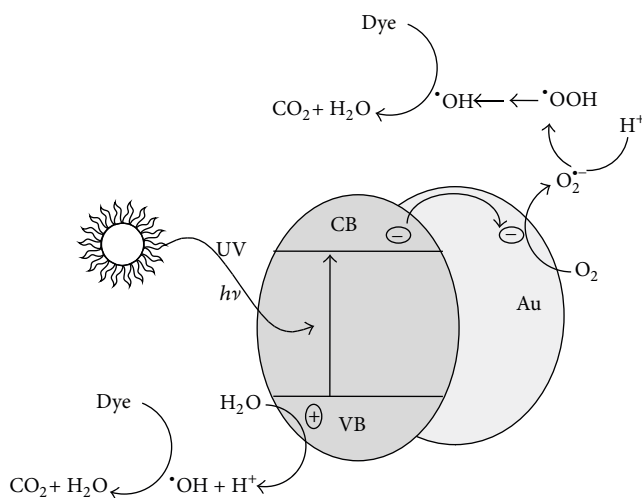

FIGURE 8: Plausible mechanism of photodegradation of dyes over AuNP doped TiO$_2$.

the present photocatalysts lies in their easy separation from the cleaned solution and reusability.
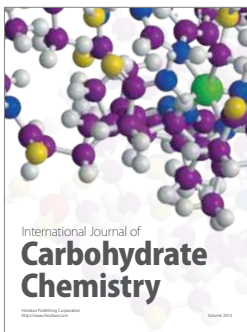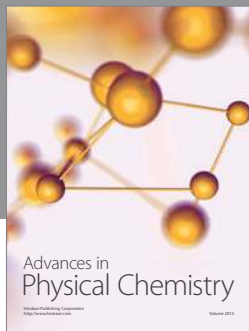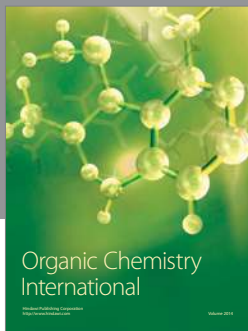
Acknowledgments

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