

Research Article

Effect of Pd and Au Sensitization of Bath Deposited Flowerlike TiO₂ Thin Films on CO Sensing and Photocatalytic Properties

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TiO₂ thin films having flower structure with nanopetals are deposited by chemical bath deposition (CBD) method. Deposited TiO₂ films are formed in pure anatase phase as confirmed by X-ray diffraction (XRD) analysis. Deposited films are used for detection of environmental hazardous carbon monoxide (CO) gas and photocatalytic (PC) degradation of malachite green (MG) dye. Effect of Pd and Au catalysts sensitization on gas sensing as well as PC degradation properties is investigated. The use of catalyst led to enhancement in the gas sensitivity and reduction in the operating temperature as well as response and recovery times. The Au sensitized film showed better CO sensing performance and PC efficiency in comparison to unsensitized and Pd sensitized TiO₂ thin films. For Au sensitized film, gas sensitivity, response time, and recovery time are found to be 32% (14% for TiO₂), 80 s, and 100 s, respectively, and PC efficiency is found to be 26.6% (16.9% for TiO₂).

1. Introduction

TiO₂ is one of the transition metal oxides, having excellent optical, electrical, and PC properties. It is photochemically stable, optically transparent, nontoxic, wide band gap and sensitive to UV radiations. Apart from the high photoactivity, TiO₂ is biologically and chemically inert, abundantly available, and cheap. It is a native oxygen-deficient metal oxide containing donor-like oxygen vacancies and therefore is an n-type semiconductor. It can present in three different crystalline phases: brookite, anatase, and rutile. TiO₂ with anatase phase is mostly being used for gas sensors and PC degradation of organic pollutants [1–3]. It has potential applications in the fields of gas sensors, supercapacitors, cosmetics, dye sensitized solar cells, and PC activity. Nowadays, organic pollutant and greenhouse gas emission are becoming serious health problems. Nanostructured materials with controlled composition are of increasing interest in the field of gas sensors and PC degradation because nanostructures provide high surface area which effectively enhances performance of both properties [4].

CO detection and monitoring are of particular importance because of its impact on environmental pollution. TiO₂ has received much attention for its stability and its specific response towards CO sensing [5]. More recently Park et al. [6] have reported CO (as low as 1 ppm) sensing at 546 K by electrospun TiO₂ nanofibers. Wang et al. [7] have reported the synthesis of low temperature tunable mesoporous TiO₂ as an effective support for Au catalyst for CO oxidation.

For the purification of water from contaminants, catalytic approach plays a vital role, which is based on the feature that the TiO₂ is able to photocatalyze many organic substances under UV irradiation (Honda-Fujishima effect). MG and its reduced form leucomalachite green are potential human health hazards [8]. Under normal atmospheric conditions and UV-Vis light, organic pollutants that are virulent and hard to be decomposed can be thoroughly oxidized to molecules, such as H₂O and CO₂ by using anatase TiO₂ under UV irradiation. PC reaction in the presence of TiO₂ consists of a free radical reaction initiated by absorption of the photon with energy equal to or greater than the band gap of TiO₂. To avoid the use of powder, which is to be separated from

the water in a slurry system after PC reaction [9], thin film coating of TiO₂ can be thought of as a good substitute. Moreover, in case of TiO₂ nanoparticles, PC rate initially increases with its loading and then decreases at high dosage because of light scattering and screening effects. However, there is no loading limit for TiO₂ thin films [10] and can be suitable for easy recycling application. Use of thin film coatings for PC applications has been investigated by Neppolian et al. [11] and has proposed that thin films can be upgraded to large volume of textile wastes of low concentration. Efficiency may depend on ability of the degraded compound to be adsorbed on the surface of catalyst [10].

The catalytic additives such as Pd, Au, Pt, and are widely being used in the field of gas sensors and PC to improve characteristics even at milder operation conditions [12–14]. Noble metals are high-effective oxidation catalysts and this ability can be used to enhance the reactions on surfaces. A wide diversity of methods, including impregnation, sol-gel, sputtering, and thermal evaporation, has been used for introducing noble metal additives into oxide semiconductors.

Among the various methods, CBD method is the most simple and effective in preparing nanostructured TiO₂ films at relatively low temperature [15]. Besides, it is a low temperature method which makes it very attractive and growth of different nanostructures is possible by controlling the deposition parameters [16, 17]. In the present endeavor, thin films of TiO₂ flowers are deposited by bath deposition method and are used for CO sensing and PC degradation of MG dye. The effect of Pd and Au sensitization on both properties is studied and discussed.

2. Experimental Details

CBD method was used to deposit nanostructured TiO₂ thin films on commercially available glass microslides (Blue Star) substrate. For deposition, bath was prepared by adding 2 mL titanium(III) chloride (15% in HCL, Loba Chemie, India) in 50 mL de-ionized (DI) water (18.2 MΩ·cm resistivity) and the pH of the bath was adjusted in the range of 0.5–0.8 using urea (NH₂CONH₂) solution with constant stirring. A homogeneous violet solution was observed after 1 hr of constant stirring at room temperature. Precleaned amorphous glass substrates were then immersed vertically in the bath and then bath was heated. Precipitation was observed in the bath after 353 K temperature. During the precipitation, heterogeneous reaction occurred and deposition of TiO₂ took place on the substrate. Substrates coated with TiO₂ thin films were removed after 2 h and washed thoroughly with DI water until heterogeneities are removed and then air dried. Before use amorphous glass substrates were cleaned with laboline detergent, thoroughly washed with DI water, and boiled in dilute chromic acid. Finally these substrates were sonicated in water bath for 15 minutes.

The as-deposited films were then air annealed at 723 K for 2 hrs. Air annealed thin films were then used for sensitization by Pd and Au. The Pd and Au sensitization was done by impregnation method. For this, separate methanolic solutions of 5 mM PdCl₂ and 5 mM HAuCl₄ were used. Two different air annealed TiO₂ films were then dipped in separate

solutions of Pd and Au precursors for 5 s and then dried in air. The Pd and Au sensitized TiO₂ films were heat treated at 473 K for 30 min to remove chlorine from the deposits.

Crystallographic study was carried out using Bruker AXS, Germany (Model D8 Advanced) diffractometer in the scanning range of 20–80° (2θ) using Cu Kα radiations of wavelength 1.5406 Å. JEOL ASM 6360A scanning electron microscope (SEM) was used to study the morphology of the films and the elemental analysis.

A laboratory set up [18] comprising an electric heater plate, a K type thermocouple, a temperature controller, gas flow meter, and a gas chamber was used to investigate the CO sensing properties of both unsensitized and sensitized TiO₂ thin films. The dc electrical resistance of all the samples in air atmosphere and in presence of CO was measured. Silver paste was applied to ensure good ohmic contacts with the films and the area of the films was defined (1 cm²). The dc electrical resistances of the samples in air (R_a) and in presence of CO gas (R_g) were measured to evaluate the gas sensitivity, S , defined as follows [13]:

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100. \quad (1)$$

For PC degradation of MG dye, 40 mL solution of MG of 0.025 g mL⁻¹ used and TiO₂ thin film (area 2 cm²) immersed in solution. This solution stirred for 10 minutes in dark for equilibrium of adsorption and desorption process of MG with TiO₂ thin film. After stirring, solution was irradiated by UV lamp (Blue Wave 50 AS, DYMAX Corporation) medium intensity spot lamp under radiation range of 200–600 nm with nominal intensity 1000–2000 mW cm⁻². UV-visible spectra of MG dye solution were recorded initially and after every 5 minutes irradiation of UV light. Concentrations of MG were estimated at 618 nm wavelength (being characteristic absorbance peak for MG dye) from UV-Vis spectra. All PC experiments were performed at room temperature in the dark. The apparent rate constant for degradation of dye was obtained by calculating the correlation between the length of time of visible-light irradiation and the decreasing ratio of dye, determined using the following equation [19]:

$$\ln\left(\frac{C_0}{C}\right) = K_{app}.t. \quad (2)$$

The percentage efficiency of photo degradation of dyes (also known as decolourizing ratio) was determined using following equation [19]

$$X = \frac{C_0 - C}{C_0} \times 100, \quad (3)$$

where C_0 and C are the solution concentration before and after degradation.

3. Results and Discussion

3.1. Crystallographic Studies. To confirm the formation of TiO₂, XRD pattern of the air annealed thin film was recorded and is shown in Figure 1. The diffraction pattern shows that

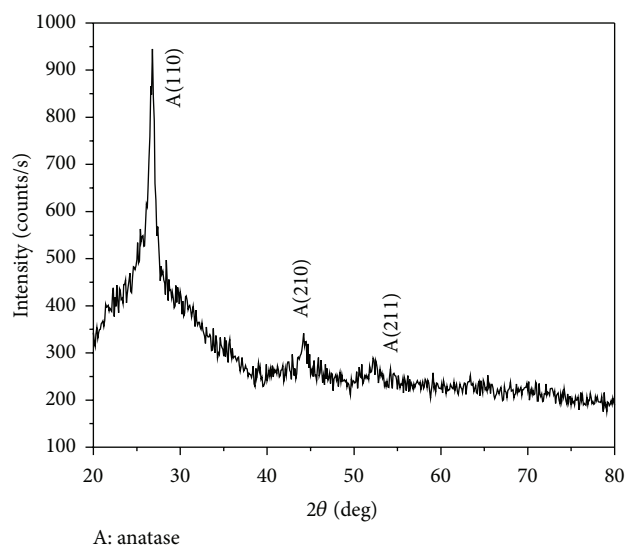


FIGURE 1: XRD pattern of TiO_2 thin film.

film crystallized in the pure anatase phase and highly oriented along plane (110) (JCPDS file 84-1284). The crystallite size, calculated using Scherrer formula, is around 12 nm. For the phase transformation from anatase to more stable rutile, it requires temperature of around 1023 K [20]. It shows good relevance with earlier reports on TiO_2 crystallized in anatase phase after annealing [21, 22]. Dutta et al. [5] have intentionally maintained TiO_2 anatase phase to enhance the CO sensitivity. Enhancement in the CO sensitivity with increasing crystallinity to anatase phase has been reported by Seeley et al. [23, 24]. Observed initial broad hump ($20\text{--}40^\circ$) can be attributed to glass substrate.

3.2. Elemental Analysis. The sensitization of TiO_2 thin films by noble metals Pd and Au as catalysts, using impregnation method, was confirmed by recording EDAX spectra and is depicted in Figure 2. Emission peaks such as OKa, TiKa, and TiKb observed in the EDAX spectrum confirmed the stoichiometry of films. Presence of various emission peaks such as PdM, PdL1, PdLa, PdLb and, arose due to various transitions between energy states of Pd and proves the presence of Pd on the TiO_2 surface. Similarly, AuMz, AuMa, AuMr, and so forth, emission peaks are observed in case of Au sensitized TiO_2 film. Presence of SiKa emission peak is due to the amorphous glass substrate.

3.3. Morphological Studies. Morphological investigation of air annealed TiO_2 film was carried out by SEM and is shown in Figure 3. The surface morphological characterization highlighted importance of film preparation in maintaining the nanostructured phase. It is clear from Figure 3(a) that films are uniformly deposited over the substrate surface. In the higher magnified image, as can be seen from Figure 3(b), the flowerlike morphology with broad size distribution is revealed. Particularly, maximum size of the petals is found to be around 100 nm. For similar deposition procedure, More et al. [15] have obtained nanorod morphology for TiO_2

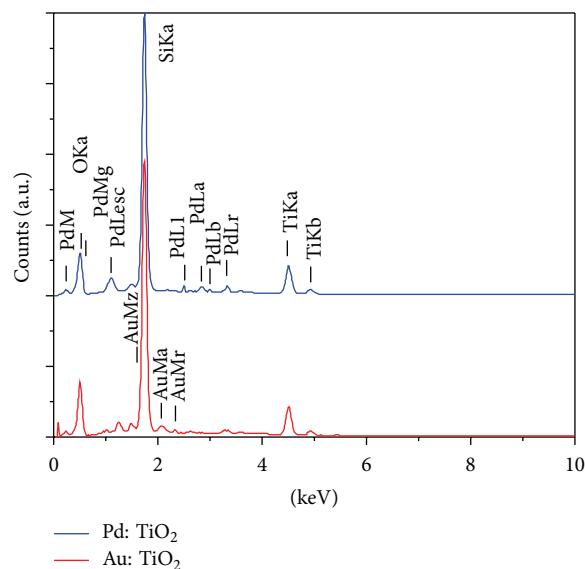


FIGURE 2: EDAX spectra of Pd and Au sensitized TiO_2 thin films.

thin films deposited over fluorine doped Tin Oxide (FTO) substrates. Difference in the morphology can be attributed to different substrates used because nucleation and growth process in the CBD depends on the nature of substrate [25]. Larger surface area due to flower morphology is beneficial for the gas sensing as well as PC degradation both being surface phenomenon [13].

3.4. CO Sensing Properties. Unsensitized air annealed TiO_2 , sensitized with Pd and Au TiO_2 thin films, respectively, termed as TiO_2 , Pd : TiO_2 and, Au : TiO_2 samples hereafter, were employed for CO sensing application. Before exposure to CO, all the samples were allowed to be stable for electrical resistance, for 30 min, and the stabilized resistance was taken as R_a . Initially, CO sensing response was studied as a function of operating temperature for all the samples with 0.02 vol.% of CO and is shown in Figure 4. From Figure 4, it is found that with increasing operating temperature CO sensitivity of TiO_2 sample increased, reached to maximum, that is, 14% at temperature 673 K, and decreased thereafter. Sensor response is restricted by the speed of chemical reaction at low operating temperatures and by speed of diffusion of gas molecules at higher operating temperatures. The speed values of these two processes become equal at some intermediate temperature, called an optimum operating temperature, and sensor response reaches its maximum value. Similar behavior is observed for Pd : TiO_2 and Au : TiO_2 samples but with decreasing optimum operating temperature and enhanced sensitivity, as can be seen from Figure 4. CO sensitivity is found to be increased up to 25% and an optimum operating temperature decreased to 548 K for Pd : TiO_2 sample. Similarly for Au : TiO_2 sample, CO sensitivity is found to be increased to 32% and an optimum operating temperature is further decreased to 498 K.

Response transient of all the samples to 0.02 vol.% of CO at an optimum operating temperature was studied and

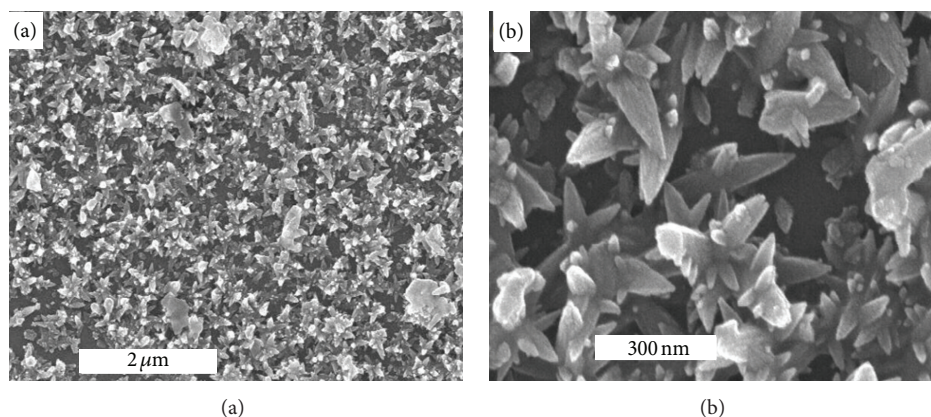


FIGURE 3: SEM micrographs of TiO₂ thin film at (a) 15,000 magnification, (b) 100,000 magnification.

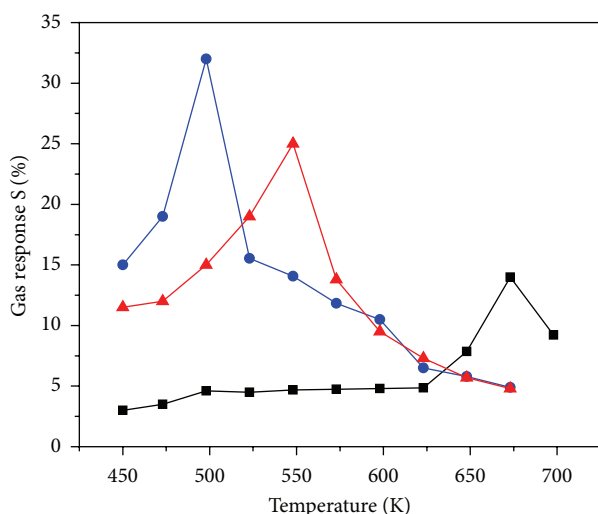


FIGURE 4: Plot of gas response as a function of temperature for TiO₂ (■), TiO₂: Pd (▲), and TiO₂: Au (●) under the exposure of 0.02 vol.% of CO.

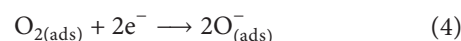
shown in Figure 5(a). For TiO₂ sample, the response transient was recorded at an optimum operating temperature of 673 K. It is discernible from Figure 5(a) that response time and recovery time for TiO₂ sample are 130 s and 160 s, respectively. For Pd:TiO₂ sample at 548 K, these values are found to be decreased, namely, 90 s of response time and 110 s of recovery time. Further decrement in the values of response and recovery times are observed for Au:TiO₂ sample kept at its optimum operating temperature, that is, 498 K, as can be seen from Figure 5(a). These values are found to be 80 s of response and 100 s of recovery time. The higher values of recovery times than response times can be attributed to strongly held carboxylates formed on the surface [5]. To check the persistency of the performance of sensor elements, they were repeatedly exposed to the 0.02 vol.% of CO at an operating temperature. The behavior of sensor elements to the cyclic exposure of target gas is presented in Figure 5(b). It is evident from Figure 5(b) that all the samples show

persistency in the gas sensing performance, when repeatedly exposed to CO gas.

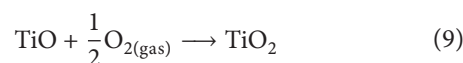
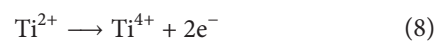
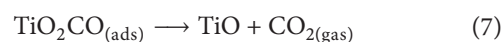
The CO sensing response as a function of gas concentration, at an optimum operating temperature, for all the samples was studied and is depicted in Figure 6. It is clear from Figure 6 that for TiO₂ sample kept at 673 K, CO sensitivity is increased with increasing gas concentration, reached maximum, that is, 16.5% for 0.03 vol.% of CO, and saturated thereafter. Whereas similar behavior is observed for Pd:TiO₂ sample kept at 548 K, but CO sensitivity is found to be saturated to 30% for 0.04 vol.% of CO, and this can be attributed to increased reaction sites due to sensitization. Similar to Pd:TiO₂, Au:TiO₂ sample kept at 498 K showed increment in the saturation value, 37.8% of CO sensitivity, but at the same gas concentration, that is, 0.04 vol.% of CO. High catalytic activity of Au over TiO₂ surface for CO oxidation, reported by Wang et al. [7], supports these results. Moreover, Ruiz et al. [12] have sensitized TiO₂ nanoparticles using hydrothermal treatment by different catalysts for CO sensing and have also observed that Au catalyst gave better sensing performance than other catalysts, for the samples annealed at 800°C. All gas sensing performance parameters are presented in Table 1.

CO sensing behavior of TiO₂ flowers based thin film sensor can be explained on the basis of mechanisms reported by Dutta et al. [5] as follows.

Mechanism I



Mechanism II



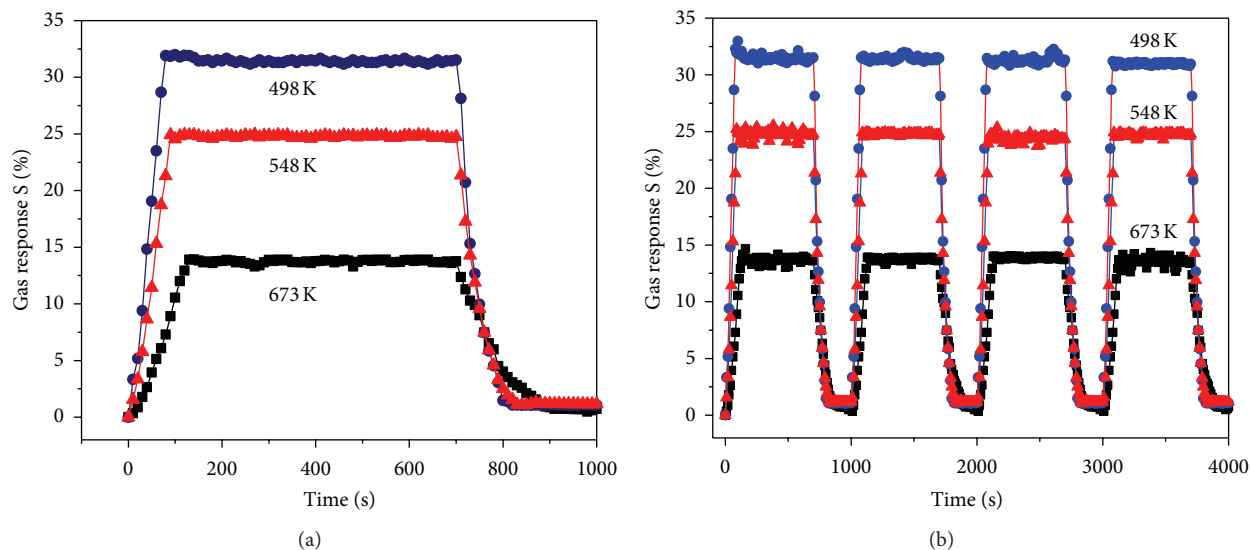


FIGURE 5: (a) Response transient curve of TiO_2 (■), TiO_2 : Pd (▲), and TiO_2 : Au (●) for 0.02 vol.% of CO at an operating temperature. (b) Response transient curve of TiO_2 (■), TiO_2 : Pd (▲), and TiO_2 : Au (●) for alternating CO of 0.02 vol.% at an operating temperature.

TABLE 1: CO gas sensing and PC degradation of MG dye performance parameters of all the samples.

Sample	S (%)	Operat. temp. (K)	Resp. time (s)	Recov. time (s)	$K_{\text{app.}} \times 10^{-2}$	$X_{(25 \text{ min})}$ (%)
TiO_2	14	673	130	160	0.70	16.9
Au: TiO_2	32	498	80	100	1.33	26.6
Pd: TiO_2	25	548	90	110	1.31	23.4

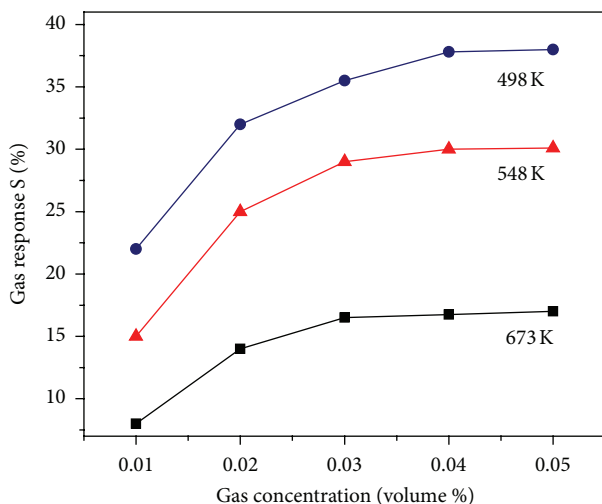


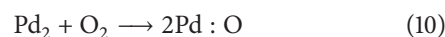
FIGURE 6: Variation of gas response of TiO_2 (■), TiO_2 : Pd (▲), and TiO_2 : Au (●) as a function of gas concentration at an operating temperature.

TiO_2 is an n-type semiconducting oxide because of the existence of appreciable concentration of oxygen vacancies which acts as surface defects. There are two possible mechanisms by which CO can interact with surface of TiO_2 . Mechanism I involves that adsorption of oxygen at the surface defects leads to formation of species O^- (4) by capturing

the electron from the conduction band (CB) of TiO_2 . This increases the resistance of the TiO_2 . When these TiO_2 film exposed to CO, reducing gas, it reacts with the O^- to form CO_2 and which leads to liberation of an electron back to the CB of TiO_2 (4) leading to reduction in the resistance of TiO_2 . Mechanism II suggests that the CO directly reduces the Ti(IV) on the anatase surface to form CO_2 (7). After CO_2 desorbs, the extra electrons associated with the reduced Ti are distributed through the lattice, resulting in a decrease in resistance (8). Oxygen can reoxidize the site, resulting in generation of the starting material (9).

O^- is believed to be dominant at the operating temperature of 473–723 K [26] which is the working temperature for most metal oxide gas sensors. An optimum operating temperature lies in between this range. At an optimum operating temperature the thermal energy for reaction (mechanisms I and II) to occur and diffusion of the CO gas molecules becomes optimal and the sensor response reaches to its maximum value.

Enhanced response of the sensitized TiO_2 films can be attributed to highly effective dissociation catalytic ability of Au and Pd. The dissociation of molecular oxygen by Au/Pd is as follows:

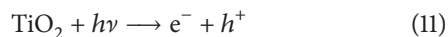


Au and Pd are better oxygen dissociation catalysts than pristine TiO_2 ; they capture; molecular oxygen from the surrounding and form weak bond with the oxygen, as shown

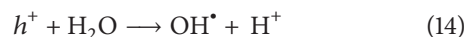
in (10). Resulting complex is readily dissociated at relatively low temperature and the oxygen atoms are produced. Then atomic products diffuse to the TiO_2 . Moreover, it is not necessary for molecular oxygen to dissociate on Au/Pd surface only. It is considered that oxygen molecules can reside briefly on TiO_2 support and diffuse to a catalyst particle before it has had an opportunity to desorb. This is called as the spillover effect [27]. If the whole surface of TiO_2 covered by this oxygen, the net result is enhancement in the probability of oxygen ionosorption, that is, formation of O^- on TiO_2 and hence the sensitivity (by mechanism I). As there are more numbers of oxygen species, there will be enhanced sensitivity at low temperature. Thus, with Au/Pd sensitizer layer, it is possible to obtain high sensitivity at relatively low operating temperature.

3.5. PC Degradation of MG Dye. Figure 7 shows the PC degradation of MG dye using TiO_2 , Pd : TiO_2 , and Au : TiO_2 thin films with time at wavelength 618 nm which is the characteristic absorption peak of MG dye. From Figure 7, it can be seen that the absorbance intensity of MG is decreased with time. Au : TiO_2 thin film shows the highest catalytic activity followed by Pd : TiO_2 and TiO_2 . Figure 8 shows the apparent rate constant for MG dye as estimated from (2). The slope of this plot is the apparent rate constant for degradation of dye and the apparent rate constant for degradation of MG are 0.70×10^{-2} , 1.31×10^{-2} , and 1.33×10^{-2} , respectively, for TiO_2 , Pd : TiO_2 , and Au : TiO_2 thin films. The percentage efficiency of photo degradation of MG dye was calculated using (3) and is depicted in Figure 9 with irradiation time. Figure 9 reveals that the photo degradation efficiency increases with increasing irradiation time and is 26.6% for Au : TiO_2 , 23.4% for Pd : TiO_2 and 16.9% for TiO_2 after 25 min. Au : TiO_2 and Pd : TiO_2 show efficiency enhancement of 57.3% and 38.4%, respectively, as compared to plain TiO_2 . Performance parameters of PC degradation of MG dye are listed in Table 1.

Mechanism for PC degradation of MG dye can be explained as follows. Illumination of catalyst surface with enough energy leads to the formation of a hole (h^+) in the valence band and an electron (e^-) in the conduction band. The hole oxidizes either pollutant directly or water to produce OH^* radicals, whereas the electron in the conduction band reduces the oxygen adsorbed on the catalyst. The activation of TiO_2 by UV light can be represented by the following steps:



In this reaction, h^+ and e^- are powerful oxidizing and reductive agents, respectively. The oxidative and reductive reaction steps are expressed as follows:



The effect of sensitization on PC activity can be explained on the basis of enhancement in redox processes [28] on

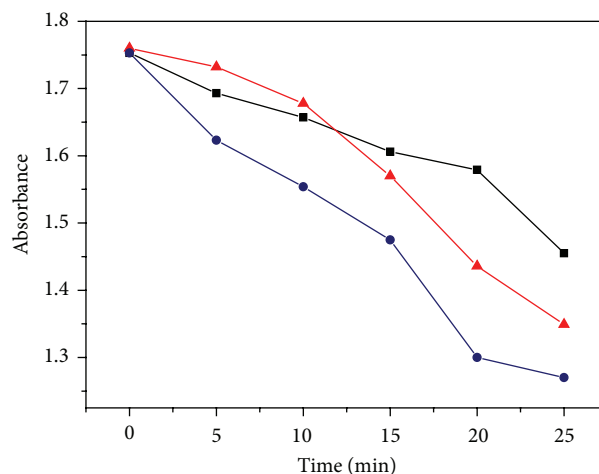


FIGURE 7: Reduction of UV absorbance at 618 nm with MG dye for TiO_2 (■), $\text{TiO}_2 : \text{Pd}$ (▲), and $\text{TiO}_2 : \text{Au}$ (●).

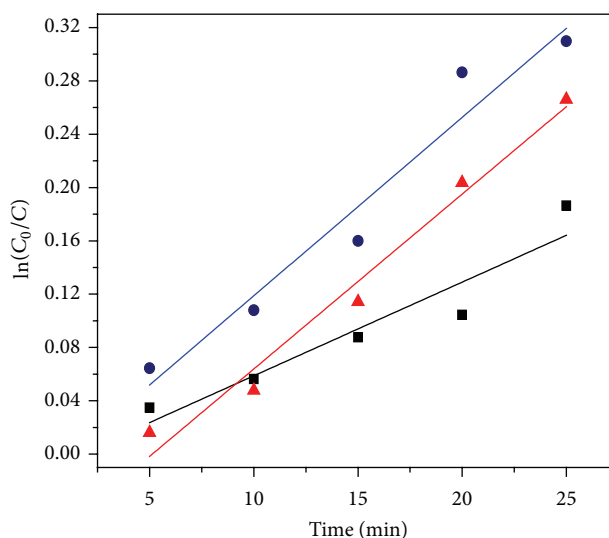


FIGURE 8: Plot of $\ln(C_0/C)$ versus time for wavelength 618 nm for TiO_2 (■), $\text{TiO}_2 : \text{Pd}$ (▲), and $\text{TiO}_2 : \text{Au}$ (●).

inclusion of metal nanoparticles on semiconductor surface. TiO_2 has both a high oxidation potential and a band gap that allows for absorption of the UV light. Both the reduction and oxidation sites are located on the TiO_2 surface, and the reduction of adsorbed oxygen molecules proceeds on the TiO_2 surface. Titanium dioxide forms highly oxidizing holes and photo generated electrons resulting in powerful oxidizing and reductive agents hydroxyl radicals and superoxides.

4. Conclusions

Thin films of TiO_2 flowers, with nanopetals, are deposited by simple and inexpensive technique and films are successfully employed for CO sensing and PC degradation of MG dye. Pure anatase phase of TiO_2 is achieved by CBD method which is effective in both applications. The sensitization of TiO_2 films by catalyst is effectively done by impregnation

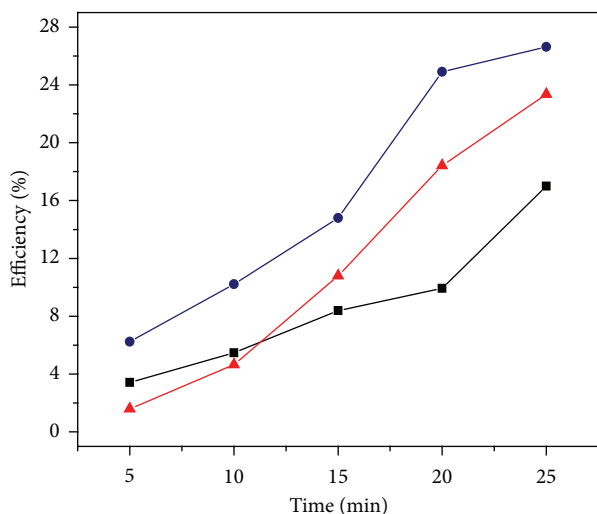


FIGURE 9: Percentage efficiency for PC degradation of MG dye at 618 nm for TiO₂ (■), TiO₂: Pd (▲), and TiO₂: Au (●).

method. The improvement in CO sensor characteristics, that is, enhancement in sensitivity and reduction in the optimum operating temperature as well as response and recovery times is observed by sensitization. Au sensitized TiO₂ film showed better CO sensor characteristics and PC degradation of MG dye than Pd sensitized and unsensitized TiO₂ sample.

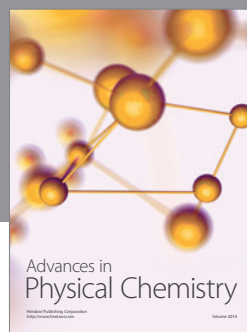
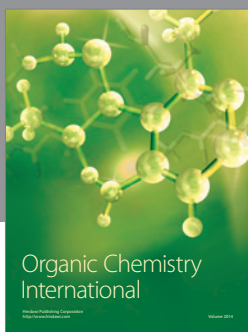
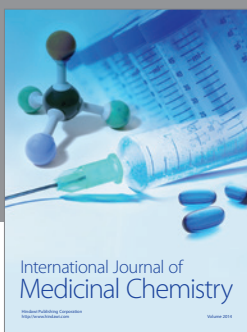
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