Research Article

Photo-Oxidation of Rhodamine-6-G via TiO_2 and Au/ TiO_2 -Bound Polythene Beads

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It is very important to improve the efficiency of water detoxification techniques. In this study, TiO_2 or gold- TiO_2 (Au/ TiO_2) nanocomposite-bound polythene beads were used for the photo-oxidation of rhodamine 6G (R6G) as a model of water organic pollutants. Simple thermal procedures were employed for anchoring TiO_2 or Au/ TiO_2 nanocomposites to polythene beads. The results revealed that the synthesized Au/ TiO_2 composites exhibited both considerably higher absorption capability of organic pollutants and better photocatalytic activity for the photo-oxidation of R-6G than pure titania. The better photocatalytic activity of the synthesized Au/ TiO_2 composites film than that of the pure titania film was attributed to high capacity of light absorption intensity and easy diffusion of absorbed pollutants on the absorption sites to photogenerated oxidizing radicals on the photoactive sites.

1. Introduction

Waste water from industrial effluents having organic dyes is of great environmental and aesthetic concern [1]. Because of the potential toxicity of these dyes, the removal or degradation of this waste water has been a topic of significant interest [2]. TiO_2 has been known as the ideal photocatalyst for the destruction of common organic pollutants in the textile industry because of its biological and chemical inertness, stability towards photochemical and chemical corrosion, and an electronic band gap that upon photoexcitation creates highly oxidizing holes and highly reducing electrons [3]. The process depends upon the absorption of TiO_2 at a light wavelength less than 388 nm; the photocatalytic processes only occur in this region; approximately 5% of the solar energy could be used for driving this process. When UV light illuminates TiO_2 , electron and hole pairs are generated; they reduce and oxidize adsorbates on the surface, respectively, thereby producing radical species such as $\text{OH}^\cdot$ radicals and $^\cdot\text{O}_2^-$. These radicals can decompose most organic compounds [4–6];

various classes of potentially hazardous compounds have been tested; the results have confirmed the wide applicability of TiO_2 -based photocatalysis [7–10]. However, a practical limitation of the method is the separation of the catalyst, once the process is completed. Several authors [11–14] have shown that the problem can be circumvented by supporting the catalyst on a suitable substrate. The first reported study on the use of polymer supports for anchoring a photocatalyst was by Tennakone et al. [15]. Polythene is a thermoplastic polymer and is particularly useful as a catalyst-supporting material because its storage and handling properties are excellent. Polythene is also resistant to caking, abrasion, moisture, and crushing [16] in addition to being low cost. Previous studies show that the composite film with TiO_2 nanoparticles can be used with reasonable stability and consistency. The observed behavior of the film has been attributed to the transportation of charge through TiO_2 nanoparticles enhancing the conduction with the cross-linked polymers. Thereby the composite polymer film that works for more than 100 days with consistent efficiency suggests its mechanical stability at longer range of humidity [17].

FIGURE 1: (a) Absorption spectra of synthesized Au nanoparticles (0.025 mg/mL), (b) absorption spectra of TiO₂ nanoparticles and (c) absorption spectra of the synthesized Au/TiO₂ nanocomposite.

Many trials have been carried out to use polymers as substrates. Some of them found that the polythene polymer is an effective and cheap substrate for binding TiO₂ particles [15], and the others found that an efficient charge separation can be obtained by coupling two semiconductor particles [18–20]. These are usually acquired by mixing semiconductor powders [21] or by depositing semiconductor films on the substrates [22, 23]. The general view illustrated that there is a growing interest in the use of the thin films of TiO₂ for generating a self-cleaning surface presently. Hence, the design of TiO₂ films to improve the textural properties by reducing the time and cost is strongly desired. This principle was recently demonstrated by us for the photocatalytic decomposition of Trypan Blue over nanocomposite thin films [24]. In the present study, TiO₂ or TiO₂ with gold nanoparticles can be embedded in the surface of polythene beads by a simple method using a thermal attachment procedure. The dried polythene beads were used for investigating the photochemical decomposition of R-6G as a pollutant under irradiation with natural sunlight. R-6G is used because it has a remarkably high molar absorptivity, high photostability, and high quantum yield [25]. Its quantum efficiency exceeds 0.9 [26]; hence, it is an ideal substance for a UV-visible detection and photo-oxidation study.

2. Experimental

Chemicals. P25 TiO₂ (ca. 80% anatase, ca. 20% rutile) was supplied by Degussa. The typical surface area was $50 \pm 15 \text{ m}^2/\text{g}$; average primary particle size, 21 nm; and band gap, 3.03 eV for rutile and 3.18 for anatase. High-density polyethylene (HDPE) having a density of 0.95 g/mL at 25°C and average Mw of $\sim 125,000$ was used in the form of beads. It was obtained from Sigma Aldrich.

2.1. Preparation of Gold Nanoparticles. Gold nanoparticles were prepared by the chemical reduction of HAuCl₄, according to Turkevich's method [27]. 95 mL of chlorauric acid (HAuCl₄, Sigma Aldrich) solution containing 2.5 mg of Au was refluxed, and 5 mL of 1% sodium citrate solution was

added to the boiling solution. The solution was further boiled for 30 min and then left to cool to room temperature.

2.2. Preparation of TiO₂ and Au/TiO₂-Bound HDPE. The thermal attachment procedure was used for anchoring the titanium dioxide onto the polythene beads. TiO₂ (0.08 g) was simply sprinkled onto ultra-high-molecular-weight polyethylene (HDPE, 0.16 g) in the ratio of 1 : 2 and stirred in 10 mL of ethanol by sonication. The mixture was agitated onto a Pyrex glass Petri dish. After drying overnight at room temperature, the mixture was gently heated at a temperature higher than the melting point of the polymer in an oven. As the temperature increased, the polythene beads reached their melting point ($\sim 145^\circ\text{C}$), at which TiO₂ particles adhered to the soft-melted surface of the polythene beads. After being in the oven for 25 min (oven temperature: $\sim 160^\circ\text{C}$), the Petri dish containing the TiO₂-polythene mixture was allowed to cool down at a rate of $5^\circ\text{C}/\text{h}$. The resulting beads were semitransparent, and the thickness of the coating was approximately 1 mm. This method was repeated; 2 mL of the prepared aqueous gold nanoparticles were used, and the resulting polymer sheet became light wine red in color.

2.3. Photocatalysis Experiment. The photocatalysis experiment was carried out by exposing 100 mL of the aqueous R-6G samples over the HDPE thin film in a Petri dish to outdoor sunlight. The HDPE thin film was maintained at the bottom of the Pyrex glass Petri dish (diameter: 100 mm) by holding large-lipped paper clips vertically across the dish boundary. The values of natural sunlight irradiance were measured by using the three-channel Eldonet dosimeter (Germany), and the concentration of R-6G was $1 \times 10^{-5} \text{ mol dm}^{-3}$. Three control experiments were carried out: first, the R-6G solution over the HDPE blank thin film was kept in the dark, and second, a similar solution was exposed to sunlight. In the third experiment, only the R-6G solution was exposed to sunlight without using the TiO₂-HDPE thin film. The temperature was maintained at 22°C – 25°C by using an ice-water bath. Airing by oxygen was done in all experiments (to enhance the formation of the $\cdot\text{O}_2^-$

FIGURE 2: Scanning electron microscopic photograph of (a) synthesized Au nanoparticles, (b) TiO_2 nanoparticles, (c) Au/ TiO_2 nanocomposite, (d) microporous layer of the fused polycrystalline polythene film, (e) TiO_2 nanoparticles embedded in the microporous layer, and (f) Au/ TiO_2 nanocomposite embedded in the microporous layer of the fused polycrystalline polythene film.

radical) using a battery-powered (3 V) portable aquarium fish tank air pump (R-104). Samples (3 mL) were taken out at regular time intervals for analysis using a Perkin Elmer λ_{40} spectrophotometer (USA). Data acquisition and manipulation were performed using UV-winlab λ_{40} and origin 7 computer-based programs.

2.4. Imaging. A scanning electron microscope (JEOL JSM-T330A) having an acceleration voltage of 30 kV was used for studying the physical characteristics by applying the thin beads of each control sample and experimental sample on the platinum grid.

3. Result and Discussion

3.1. Morphological Studies of Au/ TiO_2 -Bound Polythene Beads. The spectrum of the gold nanospheres had an intense band at 521 nm (Figure 1(a)) assignable to the plasmon absorption of gold particle diameter: 22 nm [28, 29].

Figure 1(b) illustrates the absorption spectrum of TiO_2 nanoparticles at λ_{max} 315 nm arising from one resonance system of the whole molecule. In Figure 1(c) nanocomposite exhibits two absorption bands arising from each component of Nanogold and TiO_2 nanoparticles.

The shapes of the Au, TiO_2 , Au/ TiO_2 , HDPE, and TiO_2 entrenched in HDPE and the combination of Au/ TiO_2 ingrained in HDPE beads have been observed with SEM. The results are shown in Figure 2. It can be seen that the synthesized Au nanoparticles were homogenous, dispersed, and almost spherically shaped (Figure 2(a)). Figure 2(b) shows TiO_2 nanoparticles. The core-shell Au/ TiO_2 nanocomposite is clearly confirmed in Figure 2(c). Figure 2(d) illustrates the particle shape of the fused HDPE control sample. In

FIGURE 3: Normalized absorption spectra of R6G (1×10^{-5} mol dm^{-3} ; exposure time: 210 min; sunlight intensity: 500–600 W/m^2); sun blank 1: sunlight irradiation to R6G without HDPE; dark blank 2: dark adsorption of R6G over HDPE beads in the dark; sun blank 3: sunlight irradiation of R6G over HDPE beads; dark adsorption 1: adsorption of R6G over TiO_2 -bound HDPE beads in the dark; dark adsorption 2: adsorption of R6G over Au/ TiO_2 -bound HDPE beads in the dark.

Figure 2(e), the TiO_2 was appended to the surface of the fused HDPE beads. Figure 2(f) illustrates the presence of gold as dispersed black dots on the mingled HDPE beads. It was evident from these pictures that the Au and TiO_2 nanoparticles were tagged onto the surface of the fused HDPE polymer beads.

FIGURE 4: (a) Absorption spectra showing the photobleaching of 1×10^{-5} mole dm^{-3} R6G irradiated with sunlight at (500–600 W/m^2) in polymer-TiO₂. (b) Absorption spectra showing the photobleaching of 1×10^{-5} mol dm^{-3} R6G irradiated with sunlight at (500–600 W/m^2) in polymer-TiO₂-gold.

3.2. Adsorption and Photocatalytic Decomposition of R6G. The photocatalytic activity of TiO₂ and Au/TiO₂ bound to polythene beads was evaluated by the photocatalytic degradation of rhodamine 6G. One of the most important criteria for an efficient charge transfer is to adsorb the dyes strongly on the semiconductor surface [30, 31].

Figure 3 shows the normalized electronic absorption spectra and time courses (210 min) of the photoinduced degradation of R6G (1×10^{-5} mol dm^{-3}). There was approximately no effect either when R6G was exposed alone to the sun (sun blank 1) or incubated over HDPE in the dark (dark blank 2). Also, polythene beads without nanoparticles (sun blank 3) resulted in negligible photodegradation yields ($\sim 0.06\%$) after irradiation in the sun. About 48% of R6G was adsorbed on TiO₂-HDPE beads (dark adsorption 1) after incubation in dark. Considerable adsorption of R6G ($\sim 72\%$) was observed on Au/TiO₂-bound polythene beads (dark adsorption 2) after incubation in dark. It was confirmed that a better adsorption of organics on the surface of TiO₂ had an advantage with respect to their photocatalytic degradation [32].

In the dark, a gradual decrease in the R6G concentration with time was due to the adsorption of R6G into the surfaces of TiO₂ or Au/TiO₂-bound polythene beads. From the above results, relatively high photocatalytic activity under UV-visible light irradiation can be expected. It was suggested that the electron transfer between the dye and TiO₂ was promoted because of the adsorption enhancement of the dye on the surface of TiO₂ [33]. The dependence of R6G degradation on the irradiation time is shown in Figure 4(a). As can be seen from the figure, the maximum absorption peak at 526 nm gradually decreased during the illumination, which was reasonably supposed to be due to both the adsorption of R6G into TiO₂ particles and the decomposition of R6G

by TiO₂ on polythene beads. Under sunlight irradiation, electrons on the conductive band and holes on the valence band of TiO₂ were subsequently generated and reacted with the surface OH group and preadsorbed species (water and dioxygen molecule) on the surface of TiO₂ to produce active oxidative species. The active oxidative species then attacked and further degraded R6G [34]. The possible reaction mechanisms for the light-driven decomposition of R6G are illustrated in Scheme 1. The photocatalytic system of Au/TiO₂ nanocomposite is shown in Scheme 2. When Au nanoparticles were bespoken on the surface of TiO₂, the photoinduced electrons can relocate to the surface of gold nanoparticles and diminish the dissolved O₂ easily. Also the photogenerated holes on the TiO₂ surface can react with water to create powerful oxidative radicals OH $\cdot$ and HO₂ $\cdot$. This process inhibited the recombination rate of the photo-produced electrons and holes; so the photocatalytic activity of TiO₂ nanoparticles was improved obviously by the modification of Au, as suggested in [35].

Since there were no shifts in the absorption maxima and no additional peaks appearing in the course of the experiments using titania nanoparticles or Au on TiO₂, the dye was completely degraded and not only photobleached [36–39].

It was shown that the photocatalytic electron transfer process at the semiconductor interface could be enhanced by depositing a noble metal on the semiconductor nanoparticles [40]. In the absence of Au, the degradation of R6G proceeded slowly, and R6G was degraded after irradiation for 210 min. In the presence of Au (Figure 4(b)), however, R6G degraded after 105 min (half time). The data provided evidence of good photocatalytic activity in the photodegradation of R6G because of the high surface area, narrow distribution with average pore sizes, crystalline bead framework, and accessible diffusion pathways. This means that the presence

SCHEME 1: R6G photocatalytic degradation process.

SCHEME 2: Interfacial charge transfer process of gold-TiO₂ nanocomposites under the irradiation of UV light. SCHEME 3: Influence of surface charges upon adsorption of R6G on the surface of TiO₂ and Au.

TABLE 1: Photodegradation rate and yields of R6G (1×10^{-5} mol dm^{-3}) in the photocatalytic experiments under dark and sun- light irradiation (the exposure or incubation time was 210 for all experiments except for no. 7. The irradiation time was 105 min) at $\lambda_{\text{max}} = 526$ nm.

Samples	Photodegradation or adsorption yield % = $(A_0 - A_t/A_0)100$	Photodegradation or adsorption rate $(A_0 - A_t/t)$ $\text{mol dm}^{-3} \text{sec}^{-1}$
(1) Photodegradation Blank 1 [Sun]	0	0
(2) Adsorption Blank 2 (HDPE + R6G [Dark])	2	1.6×10^{-6}
(3) Photodegradation Blank 3 (HDPE + R6G [Sun])	6	3.4×10^{-6}
(4) Adsorption (HDPE + TiO_2 + R6G [Dark])	48	2.7×10^{-5}
(5) Adsorption (HDPE + Au/ TiO_2 + R6G [Dark])	72	5.3×10^{-5}
(6) Photodegradation (HDPE + TiO_2 + R6G [Sun])	89	5.1×10^{-5}
(7) Photodegradation (HDPE + Au/ TiO_2 + R6G [Sun])	86	9.8×10^{-5}

of Au nanoparticles together with TiO_2 increases the rate of photobleaching to approximately two times more than that of TiO_2 alone by increasing the efficiency of the charge separation of the light-generated electron-hole pairs [41–45]. The influence of surface charges on the adsorption of R6G on the surface of TiO_2 and Au/ TiO_2 is shown in Scheme 3.

The summary of photodegradation and adsorption yields and rate in the photocatalytic experiments in dark and under sunlight irradiation is given in Table 1. The rate (see [24]), and yield (see [46]) were calculated according to the following equations:

$$\begin{aligned} \text{Rate} &= \frac{(A_0 - A_t)}{t}, \\ \text{Yield} &= 100 \left(A_0 - \frac{A_t}{A_0} \right), \end{aligned} \quad (1)$$

where A_0 is the absorption spectra ($\lambda_{\text{max}} = 526$ nm) at zero time, A_t is the absorption spectra ($\lambda_{\text{max}} = 526$ nm) at time t , and t is the irradiation or incubation time in seconds.

Table 1 illustrates that the rate and yield increased when Au/ TiO_2 was used. The time required for mineralization in the case of TiO_2 was longer than that in the case of Au/ TiO_2 . This may be due to the presence of gold nanoparticles that decrease the recombination rate between electron-hole pairs and consequently increase the radicals produced in the medium and enhance the efficiency of the photodegradation and adsorption processes.

4. Conclusion

Photocatalyst TiO_2 and Au/ TiO_2 particles were successfully anchored on the beads of HDPE, under a thermal treatment. TiO_2 -Au/ TiO_2 -particle-mounted HDPE beads showed both adsorptivity and photocatalytic activities, which were evaluated through the measurements of the concentration change of R6G in the water in the dark and under sunlight irradiation, respectively. The deposition of Au nanoparticles on the surface of TiO_2 -polythene polymer beads improved the photocatalytic decomposition of R6G. The improvement of the efficiency resulted mainly from the increase in the rate of adsorption on the TiO_2 -Au polymer beads due to the electrostatic attraction between the R6G and the gold nanoparticles. In addition, the presence of Au nanoparticles enhanced the interfacial charge-transfer process.

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References

- [1] B. Gözmen, M. Turabik, and A. Hesenov, "Photocatalytic degradation of basic red 46 and basic yellow 28 in single and binary mixture by UV/ TiO_2 /periodate system," *Journal of Hazardous Materials*, vol. 164, no. 2-3, pp. 1487–1495, 2009.
- [2] F. Han, V. S. R. Kambala, M. Srinivasan, D. Rajarathnam, and R. Naidu, "Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: a review," *Applied Catalysis A*, vol. 359, no. 1-2, pp. 25–40, 2009.
- [3] M. A. Fox and M. T. Dulay, "Heterogeneous photocatalysis," *Chemical Reviews*, vol. 93, no. 1, pp. 341–357, 1993.
- [4] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [5] T. Kawai and T. Sakata, "Conversion of carbohydrate into hydrogen fuel by a photocatalytic process," *Nature*, vol. 286, no. 5772, pp. 474–476, 1980.
- [6] I. Rosenberg, J. R. Brock, and A. Heller, "Collection optics of TiO_2 photocatalyst on hollow glass microbeads floating on oil slicks," *Journal of Physical Chemistry*, vol. 96, p. 3523, 1992.
- [7] R. W. Matthews, "Photo-oxidation of organic material in aqueous suspensions of titanium dioxide," *Water Research*, vol. 20, no. 5, pp. 569–578, 1986.
- [8] C. K. Grätzel, M. Jirousek, and M. Grätzel, "Accelerated decomposition of active phosphates on TiO_2 surfaces," *Journal of Molecular Catalysis*, vol. 39, no. 3, pp. 347–353, 1987.
- [9] E. Pelizzetti, V. Maurino, C. Minero, O. Zerbini, and E. Borgarello, "Photocatalytic degradation of bentazon by TiO_2 particles," *Chemosphere*, vol. 18, no. 7-8, pp. 1437–1445, 1989.
- [10] R. W. Matthews, "Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide," *Journal of Catalysis*, vol. 111, no. 2, pp. 264–272, 1988.
- [11] R. W. Matthews, "Photooxidation of organic impurities in water using thin films of titanium dioxide," *Journal of Physical Chemistry*, vol. 91, no. 12, pp. 3328–3333, 1987.
- [12] H. Al-Ekabi and N. Serpone, "Kinetic studies in heterogeneous photocatalysis. 1. Photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TiO_2 supported on

- a glass matrix," *Journal of Physical Chemistry*, vol. 92, no. 20, pp. 5726–5731, 1988.
- [13] H. Yoneyama, S. Haga, and S. Yamanaka, "Photocatalytic activities of microcrystalline TiO_2 incorporated in sheet silicates of clay," *Journal of Physical Chemistry*, vol. 93, no. 12, pp. 4833–4837, 1989.
- [14] B. Ohtani, S. Adzuma, S. I. Nishimoto, and T. Kagiya, "Photocatalytic degradation of polyethylene film by incorporated extra-fine particles of titanium dioxide," *Polymer Degradation and Stability*, vol. 35, no. 1, pp. 53–60, 1992.
- [15] K. Tennakone, C. T. K. Tilakaratne, and I. R. M. Kottegoda, "Photocatalytic degradation of organic contaminants in water with TiO_2 supported on polythene films," *Journal of Photochemistry and Photobiology A*, vol. 87, no. 2, pp. 177–179, 1995.
- [16] A. S. Omar, "Polyethylene-Coated Urea. 1. Improved Storage and Handling Properties," *Industrial & Engineering Chemistry Research*, vol. 28, no. 5, pp. 630–632, 1989.
- [17] J. Monika and R. P. Singh, "Cross linking polymers (PVA & PEG) with TiO_2 nanoparticles for humidity sensing," *Sensors & Transducers Journal*, vol. 110, no. 11, p. 105, 2009.
- [18] L. Spanhel, H. Weller, and A. Henglein, "Photochemistry of semiconductor colloids. 22. Electron injection from illuminated CdS into attached TiO_2 and ZnO particles," *Journal of the American Chemical Society*, vol. 109, no. 22, pp. 6632–6635, 1987.
- [19] K. R. Gopidas, M. Bohorquez, and P. V. Kamat, "Photophysical and photochemical aspects of coupled semiconductors. Charge-transfer processes in colloidal CdS- TiO_2 and CdS-AgI systems," *Journal of Physical Chemistry*, vol. 94, no. 16, pp. 6435–6440, 1990.
- [20] A. Di Paola, L. Palmisano, A. M. Venezia, and V. Augugliaro, "Coupled semiconductor systems for photocatalysis. preparation and characterization of polycrystalline mixed WO_3/WS_2 powders," *Journal of Physical Chemistry B*, vol. 103, no. 39, pp. 8236–8244, 1999.
- [21] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, and H. Hidaka, "Exploiting the interparticle electron transfer process in the photocatalysed oxidation of phenol, 2-chlorophenol and pentachlorophenol: chemical evidence for electron and hole transfer between coupled semiconductors," *Journal of Photochemistry and Photobiology A*, vol. 85, no. 3, pp. 247–255, 1995.
- [22] D. Lui and P. V. Kamat, "Photoelectrochemical behavior of thin cadmium selenide and coupled titania/cadmium selenide semiconductor films," *Journal of Physical Chemistry*, vol. 97, no. 41, pp. 10769–10773, 1993.
- [23] Y. Ma, J. B. Qiu, Y. A. Cao, Z. S. Guan, and J. N. Yao, "Photocatalytic activity of TiO_2 films grown on different substrates," *Chemosphere*, vol. 44, no. 5, pp. 1087–1092, 2001.
- [24] S. A. Elfeky and A.-S. A. Al-Sherbini, "Photocatalytic decomposition of Trypan Blue over nanocomposite thin films," *Kinetics and Catalysis*, vol. 52, no. 3, pp. 391–396, 2011.
- [25] R. F. Kubin and A. N. Fletcher, "Fluorescence quantum yields of some rhodamine dyes," *Journal of Luminescence*, vol. 27, no. 4, pp. 455–462, 1982.
- [26] K. H. Drexhage, "Structure and properties of laser dyes," in *Dye Lasers*, F. P. Schafer, Ed., pp. 155–200, Springer, Berlin, Germany, 1973.
- [27] J. Turkevich, "Colloidal gold. Part I," *Gold Bulletin*, vol. 18, no. 3, pp. 86–91, 1985.
- [28] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, New York, NY, USA, 1983.
- [29] S. Link and M. A. El-Sayed, "Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles," *Journal of Physical Chemistry B*, vol. 103, no. 21, pp. 4212–4217, 1999.
- [30] M. Bideau, B. Claudel, C. Dubien, L. Faure, and H. Kazouan, "On the "immobilization" of titanium dioxide in the photocatalytic oxidation of spent waters," *Journal of Photochemistry and Photobiology A*, vol. 91, no. 2, pp. 137–144, 1995.
- [31] P. V. Kamat, "Photoelectrochemistry in particulate systems. 9. Photosensitized reduction in a colloidal TiO_2 system using anthracene-9-carboxylic acid as the sensitizer," *Journal of Physical Chemistry*, vol. 93, no. 2, pp. 859–864, 1989.
- [32] F. Chen, J. Zhao, and H. Hidaka, "Adsorption factor and photocatalytic degradation of dye-constituent aromatics on the surface of TiO_2 in the presence of phosphate anions," *Research on Chemical Intermediates*, vol. 29, no. 7–9, pp. 733–748, 2003.
- [33] Q. Ping, J. Zhao, L. Zang, T. Shen, and H. Hidaka, "Enhancement of the photoinduced electron transfer from cationic dyes to colloidal TiO_2 particles by addition of an anionic surfactant in acidic media," *Colloids and Surfaces A*, vol. 138, no. 1, pp. 39–50, 1998.
- [34] A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.
- [35] J. Xu, Y. Sun, Y. Zhao, J. Huang, C. Chen, and Z. Jiang, "Photocatalytic inactivation effect of gold-doped TiO_2 (Au/TiO_2) nanocomposites on human colon carcinoma LoVo cells," *International Journal of Photoenergy*, vol. 2007, Article ID 97308, 7 pages, 2007.
- [36] Y. Ma and J.-N. Yao, "Photodegradation of Rhodamine B catalyzed by TiO_2 thin films," *Journal of Photochemistry and Photobiology A*, vol. 116, no. 2, pp. 167–170, 1998.
- [37] J.-M. Wu and T.-W. Zhang, "Photodegradation of rhodamine B in water assisted by titania films prepared through a novel procedure," *Journal of Photochemistry and Photobiology A*, vol. 162, no. 1, pp. 171–177, 2004.
- [38] T. Watanabe, T. Takizawa, and K. Honda, "Photocatalysis through excitation of adsorbates. 1. Highly efficient N-deethylation of rhodamine B adsorbed to CdS," *Journal of Physical Chemistry*, vol. 81, no. 19, pp. 1845–1851, 1977.
- [39] P. Qu, J. Zhao, T. Shen, and H. Hidaka, " TiO_2 -assisted photodegradation of dyes: a study of two competitive primary processes in the degradation of RB in an aqueous TiO_2 colloidal solution," *Journal of Molecular Catalysis A*, vol. 129, no. 2–3, pp. 257–268, 1998.
- [40] N. Chandrasekharan and P. Y. Kainat, "Improving the photoelectrochemical performance of nanostructured TiO_2 films by adsorption of gold nanoparticles," *Journal of Physical Chemistry B*, vol. 104, no. 46, pp. 10851–10857, 2000.
- [41] M. Mrowetz, A. Villa, L. Prati, and E. Selli, "Effect of Au nanoparticles on TiO_2 in the photocatalytic degradation of an azo dye," *Gold Bulletin*, vol. 40, no. 2, pp. 154–160, 2007.
- [42] Y. Nakato, M. Shioji, and H. Tsubomura, "Photoeffects on the potentials of thin metal films on a n- TiO_2 crystal wafer. The mechanism of semiconductor photocatalysts," *Chemical Physics Letters*, vol. 90, no. 6, pp. 453–456, 1982.
- [43] Y. Nakato, K. Ueda, H. Yano, and H. Tsubomura, "Effect of microscopic discontinuity of metal overlayers on the photovoltages in metal-coated semiconductor-liquid junction photoelectrochemical cells for efficient solar energy conversion," *Journal of Physical Chemistry*, vol. 92, no. 8, pp. 2316–2324, 1988.
- [44] N. Chandrasekharan and P. Y. Kainat, "Improving the photoelectrochemical performance of nanostructured TiO_2 films by

- adsorption of gold nanoparticles,” *Journal of Physical Chemistry B*, vol. 104, no. 46, pp. 10851–10857, 2000.
- [45] V. Subramanian, E. Wolf, and P. V. Kamat, “Semiconductor-metal composite nanostructures. To what extent do metal nanoparticles improve the photocatalytic activity of TiO_2 films?” *Journal of Physical Chemistry B*, vol. 105, no. 46, pp. 11439–11446, 2001.
- [46] W.-J. Gong, H.-W. Tao, G.-L. Zi et al., “Visible light photodegradation of dyes over mesoporous titania prepared by using chrome azurol S as template,” *Research on Chemical Intermediates*, vol. 35, no. 6-7, pp. 751–760, 2009.