Research Article

Comparative Study of the Photocatalytic Activity of Semiconductor Nanostructures and Their Hybrid Metal Nanocomposites on the Photodegradation of Malathion

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This work is devoted to synthesize different semiconductor nanoparticles and their metal-hybrid nanocomposites such as TiO_2, Au/TiO_2, ZnO, and Au/ZnO. The morphology and crystal structure of the prepared nanomaterials are characterized by the TEM and XRD, respectively. These materials are used as catalysts for the photodegradation of Malathion which is one of the most commonly used pesticides in the developing countries. The degradation of 10 ppm Malathion under ultraviolet (UV) and visible light in the presence of the different synthesized nanocomposites was analyzed with high-performance liquid chromatography (HPLC) and UV-Visible Spectra. A comprehensive study is carried out for the catalytic efficiency of the prepared nanoparticles. Different factors influencing the catalytic photodegradation are investigated, as different light source, surface coverage, and nature of the organic contaminants. The results indicate that hybrid nanocomposite of the semiconductor-metal hybrid serves as a better catalytic system compared with semiconductor nanoparticles themselves.

1. Introduction

Malathion, an organophosphorous pesticide with abroad range of target pests, has been widely used in agriculture. Malathion is suspected to cause child leukemia, anemia, and kidney failure and is widely used in developing countries [1, 2]; it can persist in the human body for at least two generations [3, 4]. However, due to its chemical stability and high toxicity, Malathion resists to biodegrade [5]. Therefore, it was important to explore a new methodology for reducing the contamination of water with Malathion. Photocatalysis is considered to be one of the most potential pollution remediation technologies in recent decades [6, 7]. In recent years, semiconductor photocatalysis has become more and more attractive and important since it has a great potential to contribute to such environmental problems. One of the most important aspects of environmental photocatalysis is the selection of the semiconductor material. Semiconductor

photocatalyst generates electron and hole pair (e^--h^+) upon irradiation of light energy that could be utilized in initiating oxidation and reduction reactions of the pesticide, respectively. Guillard et al. [8] reported that the number of photons striking the photocatalyst actually controls the rate of the reaction which is an indication that the reaction takes place only on the adsorbed phase of the semiconductor particle. Surface morphology, namely, the particle size and shape is a very important parameter influencing the performance of photocatalyst in photocatalytic oxidation [9]. TiO_2 is one of the most commonly studied photocatalyst for it is easily available, relatively inexpensive, and chemically stable [10, 11]. However, TiO_2 is incompetent due to the wide band gap, it can only be triggered by near UV radiation, the photo generated electron and hole pairs are liable to recombination, leading to low quantum yields [12, 13]. ZnO has received much attention in the degradation of environmental pollutants since it has almost the same band

gap energy (3.2 eV) as TiO$_2$. However, photo-corrosion frequently occurs with illumination of UV light and is considered as one of the main reasons for the decrease of ZnO photocatalytic activity.

Nanosized Gold particle possesses many excellent properties, such as easy reductive preparation, water solubility, high chemical stability, and significant biocompatibility and affinity [14]. Surface plasmon resonance absorption is a unique property of gold which is the ability of showing a strong absorption band in the visible region when the frequency of the electromagnetic field is resonant with the coherent electron motion [15]. Combining the semiconductor and metallic character in the same nanomaterial could enhance the catalytic activity due to the increase of the photo-absorption resulting from the plasmonic effect and also increases the rate of charge separation at the interface.

The prospect of developing new multifunctional nanocomposites of metal gold hybridized with inorganic components has become of great importance [16–18]. Bimetallic colloids are interesting from a number of perspectives, such as their unique electronic, catalytic, and optical properties [19–21]; photodegradation of Malathion has been studied in aqueous solution using an Au-Pd-TiO$_2$ nanotubes film [22].

In the present work, we tested the suitability of using semiconductor nanocomposites (TiO$_2$, ZnO) and metal semiconductors nanocomposite (Au/TiO$_2$, Au/ZnO) for the photodegradation of Malathion. The photocatalytic activities of the different synthesized nanoparticles are compared, and the influence of different parameters is studied, such as surface coverage and light source irradiation. The efficiency of the catalytic activity showed dependence on source of light irradiation, particle size, crystalline, surface coverage of the nanocomposite, and nature of the organic contaminate.

2. Materials and Methods

2.1. Chemicals. Malathion (99% HPLC grade) was purchased from Fluka and used as received. Hydrogen tetrachloroaurate trihydrate (HAuCl$_4$.3H$_2$O) (99.9%) was purchased from Sigma-Aldrich, and Polyvinyl pyrrolidone PVP-K30 (Av. Wt. 22000) was purchased from Fluka. Tri-sodium citrate (99%) was purchased from (Sigma-Aldrich), sterile sodium chloride physiological saline (0.9%) (ADWIC). TiO$_2$, ZnO and HPLC grade solvents (purity 99%) such as methanol and ethanol were purchased from Aldrich. High purity water used in the experiments was purified with the milli-Q system. All chemicals were used without any further purification.

2.2. Synthesis of Semiconductor Nanoparticles

2.2.1. Synthesis of TiO$_2$ Nanoparticles. The precursor of 5 mL Titanium isopropoxide is added to a mixture of 5 mL of isopropyl alcohol and 3 mL glacial acetic acid dropwise with constant stirring. The prepared particles are separated with centrifuge and dried for further characterization. The particle size and shape is determined using TEM and the crystal
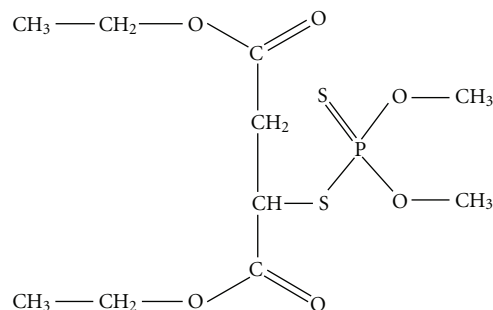

Figure 1: Chemical structure of Malathion.

structure is determined using XRD. The optical absorption is measured using UV-Visible PerkinElmer Lambda 40 double beam spectrophotometer.

2.2.2. Synthesis of ZnO Nanoparticles. 1.48 g (10 mmoL) of Zn(CH$_3$COO)$_2$2H$_2$O and 1.38 g (23.8 mmoL) of NaHCO$_3$ are mixed at room temperature. The mixture is ignited at 300°C for 3 hours. The Zn(CH$_3$COO)$_2$2H$_2$O is converted to ZnO nanoparticles, while the NaHCO$_3$ is converted to CH$_3$COONa and eventually washed away with deionized water until the formation of white ZnO nanoparticles. The particle size and shape is determined using TEM, and the crystal structure is determined using XRD.

2.2.3. Synthesis of Gold Nanoparticles by Citrate Method. Spherical gold nanoparticles (GNPs) were prepared in aqueous solution according to a method described by Turkevich. Simply, the method is a chemical reduction of gold ions by sodium citrate in aqueous solution. Sodium citrate serves also as a capping material which prevents aggregation and further growth of the particles. 5 mL of 1% sodium citrate solution was added to 40 mL chloroauric acid (HAuCl4) boiling solution containing 5 mg of gold ions. The solution was boiled for 30 minutes and was then left to cool down to room temperature. The particle size and shape is determined using TEM, and the crystal structure is determined using XRD.

2.2.4. Synthesis Au/TiO$_2$ and Au/ZnO Nanoparticles. Gold nanoparticles are prepared by citrate method as shown above, and the obtained particles are used as a seed to grow TiO$_2$ or ZnO nanoshell. The reaction mixture is microwaved for 12 minutes. The particle size and shape is determined using TEM, and the crystal structure is determined using XRD.

2.3. Photodegradation of Malathion. Photodegradation radiation rate of Malathion was carried out using Bischof HPLC system (Mainz, Germany), C18, reversed Colum (250 × 4.6 mm), and UV-detector with variable wave length 250 nm was used. Methanol/water (70/30) was used as an eluent at flow rate of 1 mL/min at retention times 12 min. 20 μL was injected to the HPLC at periodic interval 20 minutes. The adsorption of the pesticides on the nanoparticles resulted
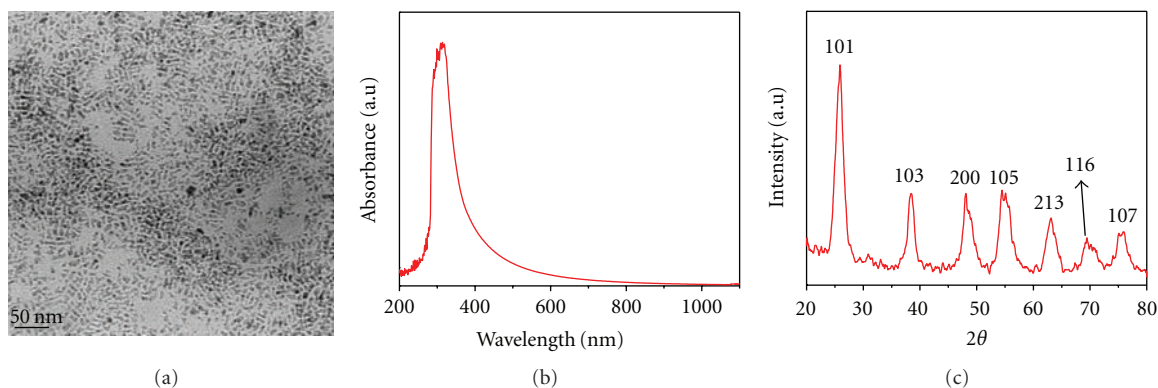
FIGURE 2: Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared TiO$_2$ nanoparticles.
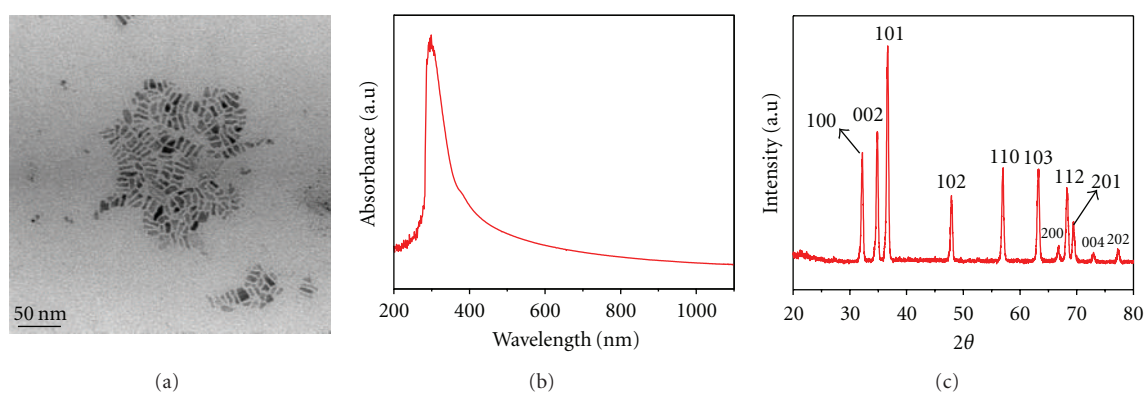

FIGURE 3: Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared ZnO nanoparticles.

in the gradual decrease in the peak area and area percent in comparison to the peak area and area percent of the standard solution of the Malathion. An interaction was carried out between 10 ppm of Malathion (Figure 1) with the different synthesised nanoparticles (TiO$_2$, ZnO, Au/ZnO, and Au/TiO$_2$) of three different concentrations (10^{-4}, 3×10^{-5}, 10^{-5} M) ; the different aliquots were subjected to UV lamp, natural sunlight and investigated at equal time intervals 30 min and analyzed by using Perkin Elemer 240 spectrophotometer. Data acquisition and manipulation were performed using computer-based program.

3. Results and Discussion

3.1. Characterization of the Synthesized Nanocomposites. Different metal oxide nanoparticles such as TiO$_2$, ZnO, and their core-shell gold nanocomposites has been synthesized chemically as shown in the experimental part and characterized using absorption spectra, TEM and XRD. Figures 2, 3, 4, and 5 show the absorption spectra associated with TEM images for all the particles prepared. As shown in Figures 2–5, the prepared nanoparticles have monodispersed size and shapes and their size is less than 100 nm and a band gap absorption in the UV region; accordingly irradiation with UV light only creates (e$^-$-h$^+$) pair and activates the material

to be a photocatalyst. Presence of gold with the nanocomposite enhances its absorption coefficient and increases the photocatalytic activity due to the increase in the charge separation rate. Also the gold-semiconductor composite has absorption at visible region due to the surface plasmon of the gold particle; this means that the photocatalytic activity of gold could be initiated by irradiation with both UV and visible lights.

3.2. Effect of Different Light Sources. Malathion has a characteristic absorption band at 260 nm; however, the rate of photodegradation is followed using the decay of this band. The degradation of Malathion was carried out under the irradiation of light from two different sources, sun light (which is mainly visible light) and UV lamp which emits light around 254 nm (Table 1). It has been reported that the photodegradation rate increases as increasing the light intensity during photocatalytic degradation reaction [22–25]. Our results clearly indicate that UV irradiation causes higher rate of degradation for Malathion than with sun light, due to high intensity of light which is suitable for the excitation of many electrons from the valence band of the metal oxide semiconductor as illustrated in Figure 6. The band gap for TiO$_2$ and ZnO lies in the UV region, thus, using UV light initiates the excitation of electrons from the conduction band into the valance band due to the
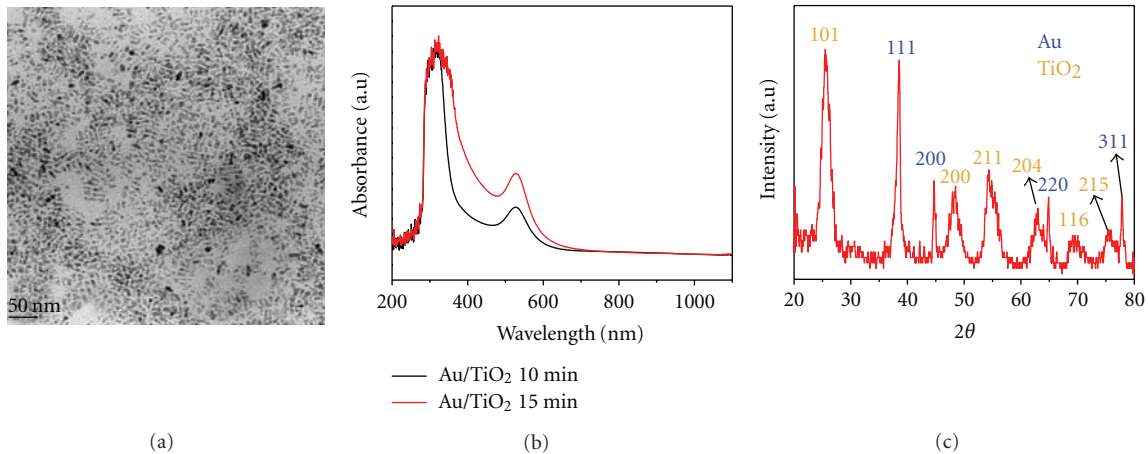
(a)

(b)

- Au/TiO$_2$ 10 min
- Au/TiO$_2$ 15 min

(c)

FIGURE 4: Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared Au/TiO$_2$ nanoparticles.
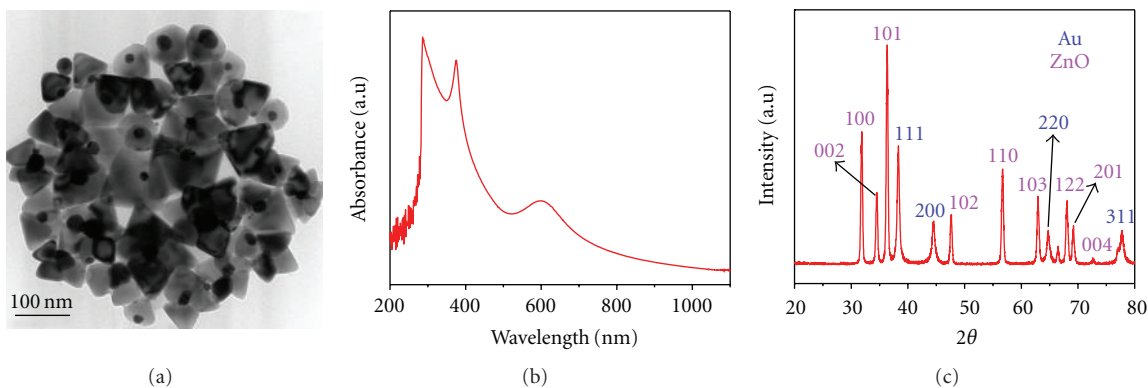

(a)

(b)

(c)

FIGURE 5: Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared Au/ZnO nanoparticles.
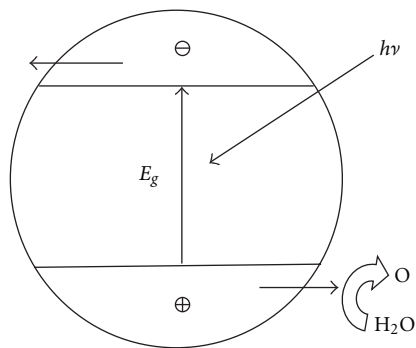

FIGURE 6: Scheme shows the roles of the Semiconductor metal oxide in photodegradation which creates active oxygen causing decomposition of water pollutants.

TABLE 1: Degradation of Malathion after 1 hour on irradiation to UV-lamp and natural sun light.

Photocatalysts	Degradation rate %	
	Irradiation to sun light	Irradiation to UV-C lamp
TiO$_2$	6	68
ZnO	5	60
Au/ZnO	62	79
Au/TiO$_2$	67	81

formed electron or active oxygen which are responsible for the degradation of the Malathion. Presence of the gold in the photocatalyst permits the photodegradation of Malathion in natural sun light since it is a visible light responsive catalyst having an absorption band around 520 nm; this explains the marked increase in photodegradation of Malathion with Au/ZnO and Au/TiO$_2$. The catalytic activity is markedly enhanced by doping small amounts of metals such as Au which prevents the electron hole recombination and accelerates the photocatalytic degradation with UV light to a greater extent as shown in (Table 1). Figure 7 presents the HPLC chromatograms for Malathion alone, and after the addition of the different nanoparticles, Malathion showed a marked decrease in the peak height and the integration area percentage in addition to the Au/TiO$_2$ and Au/ZnO nanoparticles to Malathion in comparison to the photodegradation using TiO$_2$ and ZnO as presented in (Table 2), which adopts the idea that the presence of gold effectively scavenged the holes, thus competing with the charge recombination which in terms accelerates the photodegradation.
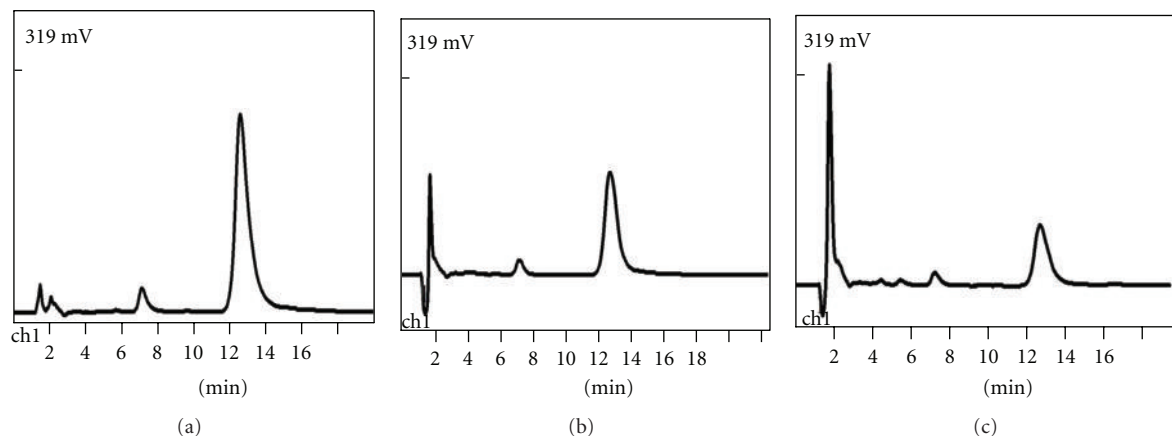
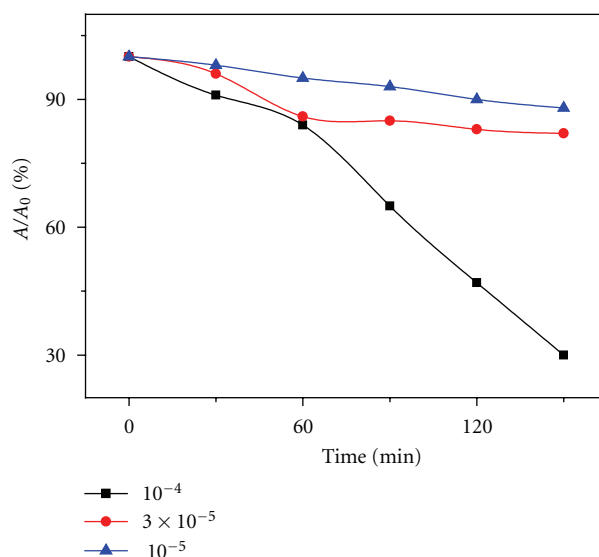FIGURE 7: Shows HPLC chromatogram for Malathion (a), Malathion + Au/ZnO (b), and Malathion Au/TiO$_2$ (c).

FIGURE 8: Shows the effect of different concentrations of TiO$_2$ nanoparticle on the degradation of Malathion.

TABLE 2: HPLC integration area for Malathion on irradiation to UV.

Photocatalyst	Integration area (%)	
	At once	After an hour
TiO$_2$	83	40
Au/TiO$_2$	75	19
Au/ZnO	85	27

3.3. Effect of the Nature of Photocatalyst. A direct correlation exists between the removal of the organic pollutant and the surface coverage of TiO$_2$ photocatalyst [26]. Heterogeneous photocatalytic reactions are known to show a proportional increase in the photodegradation with catalyst loading [27]. Generally, in any given photocatalytic application, the optimum catalyst concentration must be determined, in order to avoid the excess catalyst and ensure the total absorption of the efficient photons [28]. This is because the scattering of an unfavorable light and reduction of light penetration into the solution is observed with excess photocatalyst loading [29]. During photocatalytic oxidation process, the concentration of organic substrate over time is dependent upon photonic efficiency [30]. At high-substrate concentrations, however, the photonic efficiency diminishes and the titanium dioxide surface becomes saturated leading to catalyst deactivation [31]. Different concentrations of the nanoparticles were investigated to select the optimal concentration for efficient photodegradation. As presented in Figure 8, it is concluded that 10^{-4} M is the optimum concentration for efficient degradation of Malathion using the different nanoparticles; about 69% was achieved in 1 hour using TiO$_2$; at lower concentrations (3×10^{-5}, 10^{-4}) free radical production rate is limited which suppresses the rate of the degradation reaction to (10–20%). The same trend was obtained for the prepared nanoparticles as presented in Figures 9-10; an increase of the degradation percentage was observed on using Au/ZnO and Au/TiO$_2$ and also a reduction of the radiation rate time, which is due to the presence of
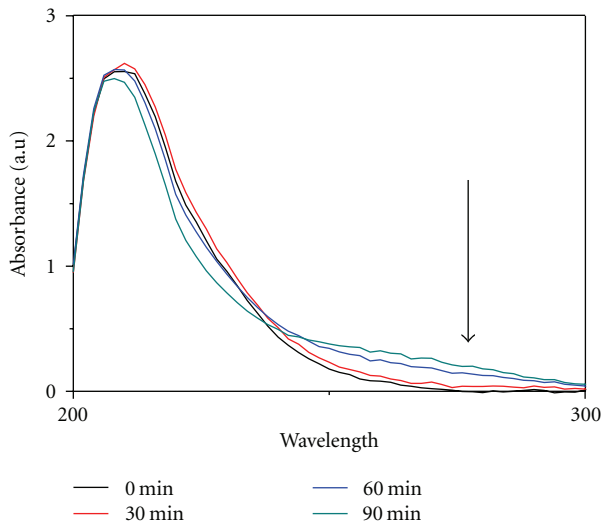
FIGURE 9: Shows time-dependent degradation of Malathion using TiO$_2$ in UV lamp.

(a)

(b)

FIGURE 11: Shows time-dependent photodegradation of cholridazon in UV lamp after addition of 10^{-4} TiO$_2$/Au (a) and ZnO/Au (b).
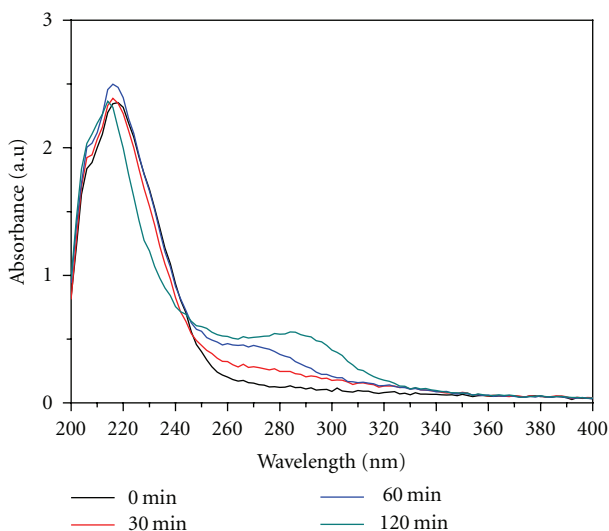

FIGURE 10: Shows time-dependent degradation of Malathion using Au/ZnO in UV lamp.

the gold which prevents the electron hole recombination and accelerates the photodegradation.

3.4. Effect of the Nature of the Contaminant. Organic molecules which adhere effectively to the surface of the photocatalyst are more susceptible to direct oxidation [32]. Thus the photocatalytic degradation of aromatics depends on the substituent group. It is reported that nitro-phenol is much stronger adsorbing substrate than phenol and therefore degrades faster [33]. In the degradation of chloroaromatics, Bhatkhande et al. [34] pointed out that monochlorinated phenol degrades faster than di- or tri-chlorinated member. In general, molecules with electron withdrawing groups such as nitrobenzene and benzoic acid were found to adsorb significantly in the dark compared to those with electron
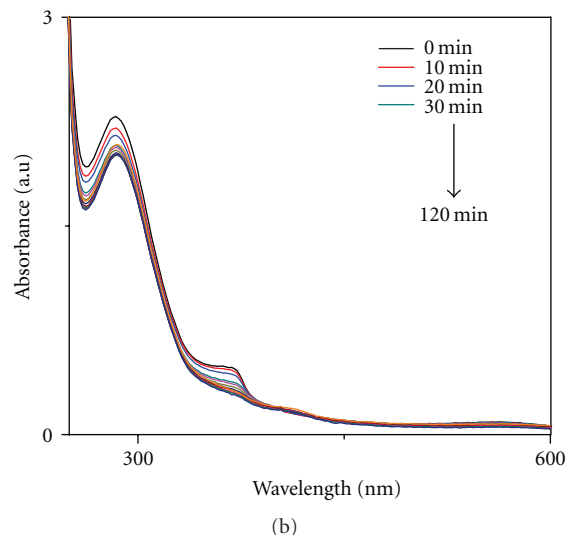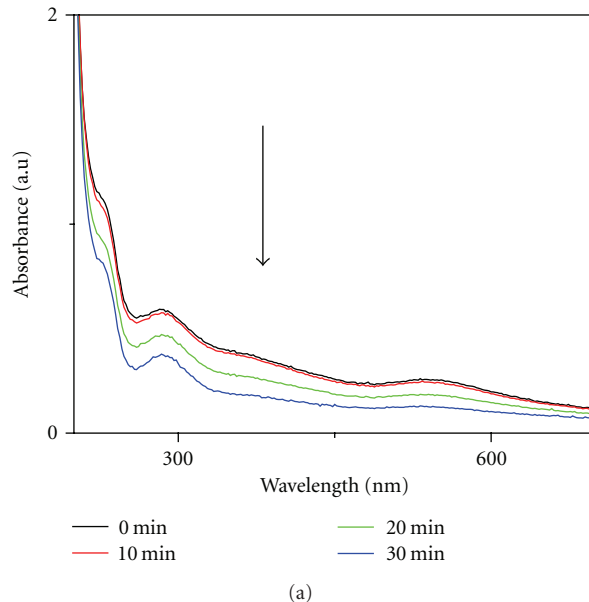
donating groups [35]. During photocatalytic oxidation process, the concentration of organic substrate over time is dependent upon photonic efficiency [36]. At high-substrate concentrations, however, the photonic efficiency diminishes and the titanium dioxide surface becomes saturated leading to catalyst deactivation [37]. In the present work, we compared the degradation of two different pesticides as a model for aliphatic (Malathion) and chloroaromatic (chloridazone) by subjecting them to the same concentration of different categories of nanoparticle Au/TiO$_2$ and Au/ZnO and for same period of time, about 1 hour. As indicated in Figure 11, it is clearly shown that the degradation of chloridazone is faster in comparison to Malathion; a similar trend of degradation was obtained for the both types of nanoparticles since after irradiation to UV lamp for 30 min the degradation

of Malathion was about 30%, while in case of chloridazone it was about 50%; this could be explained in terms of the presence of aromatic rings as well as the number and nature of substituent on the ring (like electron donating or electron withdrawing groups) which are known to affect the adsorption and consequently the degradation rate [38].
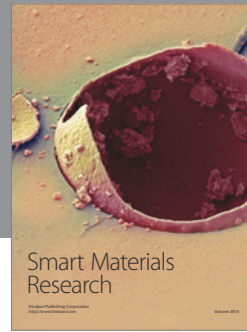
4. Conclusion

The ability to synthesize multicomponent nanocomposites is important to improve the electronic, optical, and magnetic functionality. According to our study, gold hybrid semiconductor-noble metal nanocrystals not only combine the unique properties of the metal and semiconductors but also generate collective new phenomena based on the intraparticles interaction between the metal and the semiconductor at their interface. The presence of metal-semiconductor interface promotes effective charge separation carrier transfers which subsequently enhance photocatalytic effect. Photodegradation of 10 ppm Malathion was enhanced in the presence of gold-semiconductor nanoparticle; other factors also influenced the degradation rate such as different light sources and nature of the catalyst.

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