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Photodegradation of pesticides using core-shell nanocomposites in wastewater

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ABSTRACT

In our study nanocomposites of TiO_2-Au and ZnO-Au core-shell nanoparticles have been prepared via colloidal chemical method. The particle size, shape and chemical composition have been determined via high resolution transmission electron microscope (TEM) and X-ray diffraction (XRD) analysis. These nanomaterials have been used as a photocalalysts for photodegradation of organic waste for water purification. Primicarb is one of the most commonly used pesticides in Egypt, the degradation of 20 ppm primicarb under ultraviolet (UV) and visible light in the presence and absence of TiO_2, TiO_2-Au, and ZnO-Au nanocomposite was analyzed with high performance liquid chromatography (HPLC) and UV-Visible Spectra. The rate of the photodegradation and the catalytic activity of these nanomaterials have been determined and compared. The results indicate that the core-shell nanoparticles is much more active catalyst in presence of sun light than pure TiO_2 nanomaterials which has absorption maximum at 370nm.

KEYWORDS

Photodegradation;
Pesticides;
Nanoparticals.

INTRODUCTION

Different pesticides of different chemical nature have been extensively used in agriculture all over the world, due to their human toxicity and persistence in soil and drinking water they should be continuously monitored. Even when present in small quantities, they have an adverse effect on ecological systems[1]. Migration of the pesticides to ground and surface water has played an important role in contamination especially in developing Countries[2]. Safe removal or degradation of pesticides has become an issue of great concern therefore many physicochemical methods have been employed for this task.

Many different semiconductor have been used as photocatalysts for degradation of organic pollutants such as TiO_2 which has been extensively stidied due to its chemical stability, and high safety and activity[3]. It was reported that the addition of noble metal to a photocatalytic semiconductor can change the semiconductor surface properties[4]. Nano particles are promising for their unique properties due to their small particle size and large surface to volume ratio[5, 6] and the ease with which they are anchored to the pesticides for water treatment.

Primicarb is one of the often used pesticides in Egypt, it is one the most important class of substituted N- dimethylcarbamate insecticides Figure 1. Kinetic degradation studies with primicarb on lettuce and asparagus in the field showed that primicarb broke down within few days[7, 8]. This study is concerned with experimental conditions influencing and enhancing the phodegardation of primicarb using different synthesized nanoparticals such as Au- TiO_2,Au-ZnO, TiO_2. Different investigations have been carried out to compare the optimal conditions influencing the rate of degradation in presence of UV-visible and natural sunlight. Identification and quantitative analysis of the starting material and its photoproducts was carried out in aqueous samples using high performance liquid chromatography HPLC, UV and GC-MS to monitor the rate of degradation.

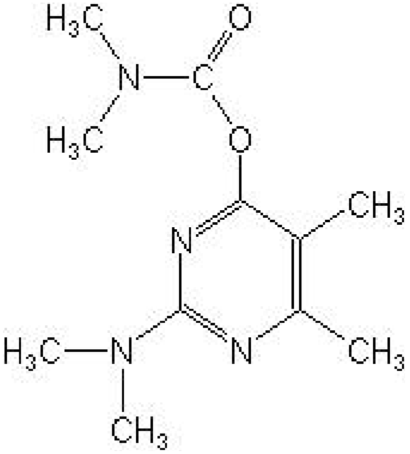

Figure 1 : Structure of primicarb

EXPERIMENTAL

Materials

Primicarb was obtained from Fluka (99% HPLC grade) and used as received. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4.3H_2O$). (Sigma-Aldrich, 99.9%), Polyvinyl pyrrolidone, PVP-K30. (Fluka, Av. Wt. 22000), Trisodium citrate (Sigma – Aldrich, 99%), Sterile sodium chloride physiological saline 0.9% (ADWIC) - Sodium borohydride (Sigma, 98%),Sodium carbonate (Sigma, 99%), L-Ascorbic acid (Sigma-Aldrich). TiO_2, ZnO, HPLC grade solvents (purity 99%) such as methanol, ethanol were purchased from Aldrich and high purity water are used in the experiments purified with the milli-Q system. All chemicals were used without any further purification.

Synthesis of semiconductor nanoparticles

Synthesis of TiO_2 nano-particles

The precursor of 5 ml Titanium isopropoxide is added to a mixture of 5 ml of isopropyl alcohol and 3 ml glacial acetic acid drop-wise 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 structure is determined using XRD. The optical absorption is measured using UV-Visible PerkinElmer Lambda 40 double beam spectrophotometer.

Synthesis of ZnO nanoparticles

1.48 g (10 mmol) of $Zn(CH_3COO)_2.2H_2O$ 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 $Zn(CH_3COO)_2.2H_2O$ is converted to ZnO nanoparticles, while the $NaHCO_3$ is converted to CH_3COONa 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.

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 prevents aggregation and further growth of the particles. 5 ml of 1% sodium citrate solution was added to 40 ml chlorouric acid ($HAuCl_4$) 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.

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 micro-waved for 12 minutes. The particle size and shape is determined using TEM and the crystal structure is determined using XRD.

RESULTS

Characterization of the synthesized nano composites

Different metal oxide nano-particles 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 2-5 shows 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[9, 10].

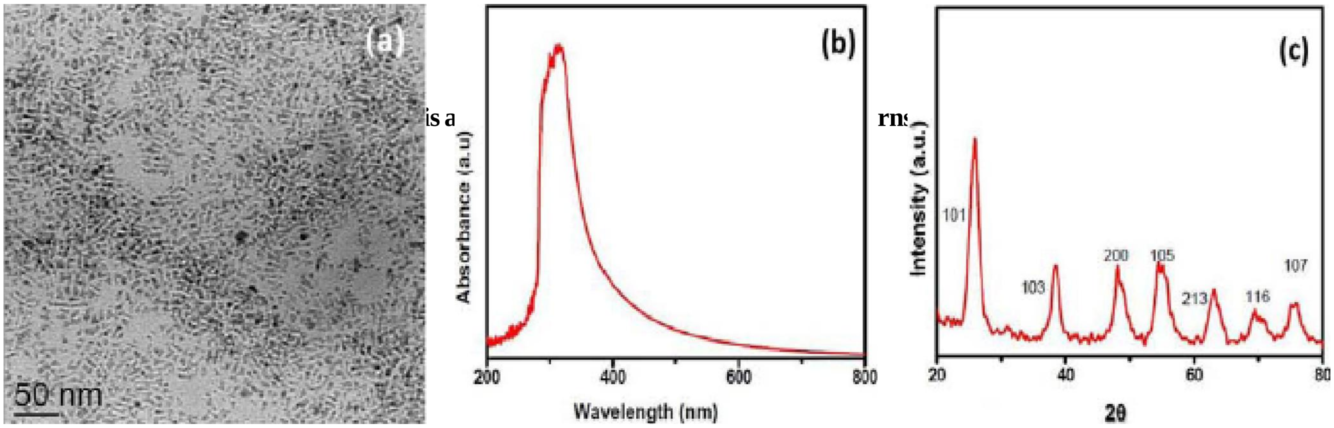

Figure 2 : Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared TiO_2 nanoparrticles.

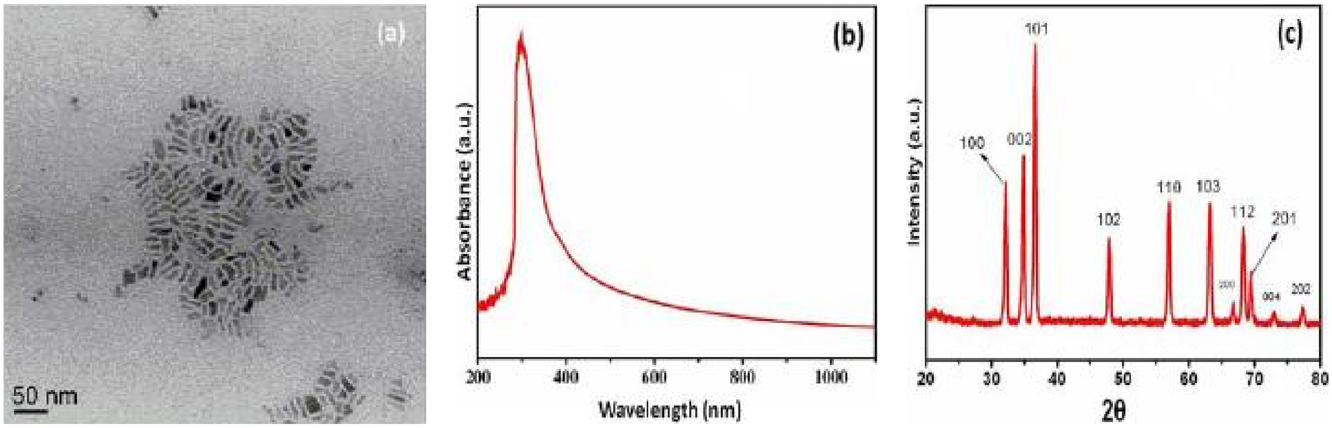

Figure 3 : Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared ZnO nanoparrticles.

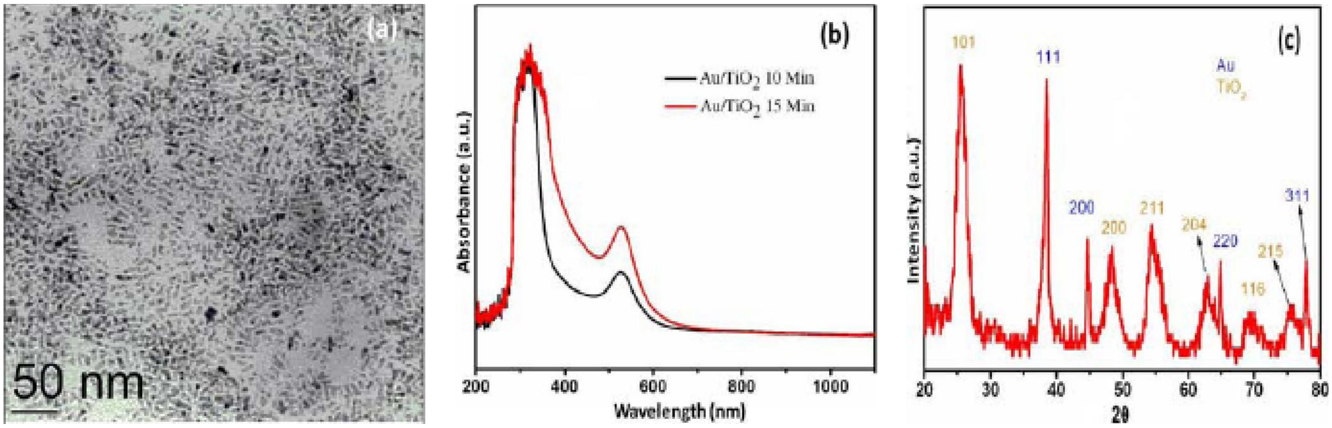

Figure 4 : Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared Au/TiO_2 nanoparrticles.

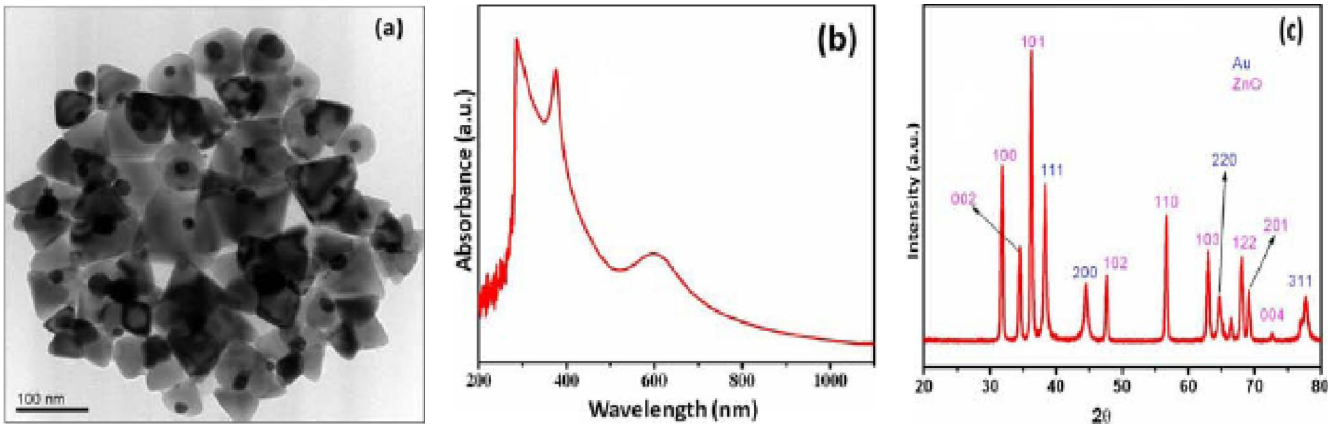

Figure 5 : Shows TEM image (a), UV-Vis absorption spectrum (b), and XRD patterns (c) of prepared Au/ZnO nanoparrticles.

Presence of gold with the nanocomposite enhances its absorption coeffecient and increases the photocatalytic acitivity due to the increase in the charge separation rate[11-13].

Also the gold-semicondutor composite has absorption at visible region due the surface plasomon of the gold particle, this means that the photocatalytic activity of gold could be intiated by irradiation with both UV and visible light[14-16].

Photodegradation on Rh6G using different synthesed nanocomposites

The photocatalytic activity efficiency of the different prepared nanocrystals was investigated by monitoring the photo degradation of organic dye such as R6G which has strong absorption in the visible range as shown in Figure 6

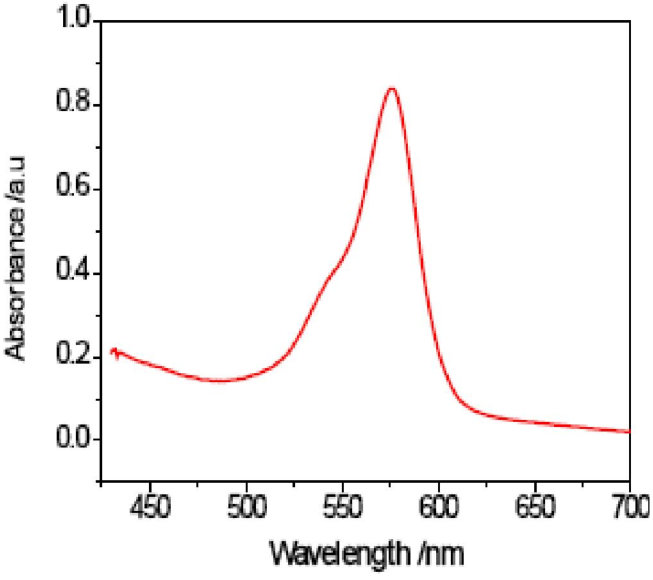

Figure 6 : Absorption Spectra of Rhodamine 6G

Before studying the effect of the photocatalyst on the photodegradation rate of the dye, it was important to determine the photodegradation of the organic dye without any catalyst by exposure to direct sun light and examine their absorption spectra at different time intervals. The absorption spectra of Rh6G after exposure to the sun light at different time intervals is shown in Figure 7

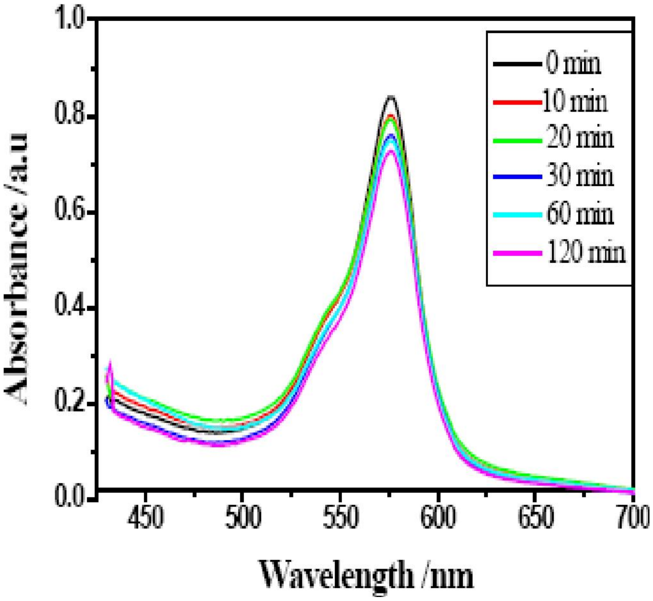

Figure 7 : The absorption spectra of Rh6G at different time a) 10 min, b) 20 min, c) 30 min, d) 60 min, e) 90 min and f) 120 min

Changes of the absorption spectra during the photodegradation process of the R6G dye over TiO_2, Au-TiO_2 and Au-ZnO sheet under sun irradiation are illustrated in Figure 8. As shown in Figure 8 adding layer of gold over the nanoparticls [TiO_2-ZnO] increase its catalytic activity, whereas, 93% of the dye decomposes only in 50 minutes.

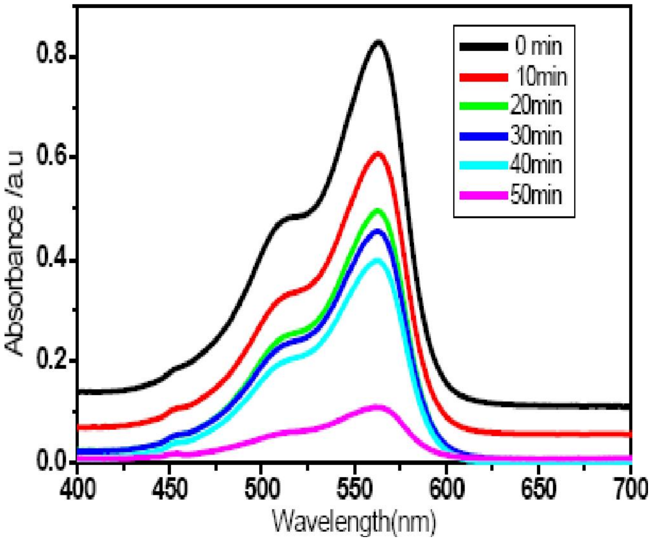

Figure 8 : Photodegradation of Rh 6G in presence of Au-TiO$_2$ core shell nanoparticles. 93% of the dye decomposes in 50 minutes of visible irradiation.

Photodegradation on primicarb using different synthesed nanoparticals

The photodegradation of primicarb was investigated using the three different synthesized nanoparticls Au-TiO$_2$, Au-ZnO$_2$, TiO$_2$ and the rates of decomposition were monitored using HPLC and UV spectra. The results indicate that primicarb photo degradation efficiency was enhanced using Au-TiO$_2$ and Au-ZnO$_2$ compared with TiO$_2$ when irradiation to UV-visible lamp and natural sun light as shown Figure 9 which presents the HPLC chromatograms obtained for primicarb alone and after the addition of the different nanoparticls, primicarb showed a sharp peak at retention time 4.6 min Figure 9a, a marked decrease in the peak area and the integration area percentage was obtained on addition of the Au-TiO$_2$ and Au-ZnO nanoparticls to primicarb in comparison to the phodegradation using TiO$_2$ and splitting of the peaks indicate the formation of photo degraded species Figure 9 b-d, this was further stated by using GC-MS techniques, where two by products where identified such as m/z 168 and m/z 225 which adopts the ability of using new synthesized nanoparticls in the degradation of primicarb. Figure 8 represents the UV-visible spectra of primicarb, changes in the absorption of 20 ppm primicarb on addition of Au-TiO$_2$ and Au-ZnO in a time dependent manner were presented in Figure 10-12. The absorption spectra was taken after 20 minutes of addition of the nanoparticls to the 20 ppm primicarb, the progressive decrease in the absorption UV of primicarb after irradiation for 3 hours was obtained, but still a complete degradation was difficult to obtain[17]. The small differences in the degradation is dependent on the practical size, crystalline structure increasing the efficiency of the different nanoparticls in photodegradation could be achieved by modulating the crystalline structure of the different nanoparticls which will give a wide range of specifity and selectivity. It could be concluded that the photocatalytic activity of the TiO$_2$ is markedly enhanced by the doping of small amounts of metals specially Au as shown in TABLE. 1[18-20].

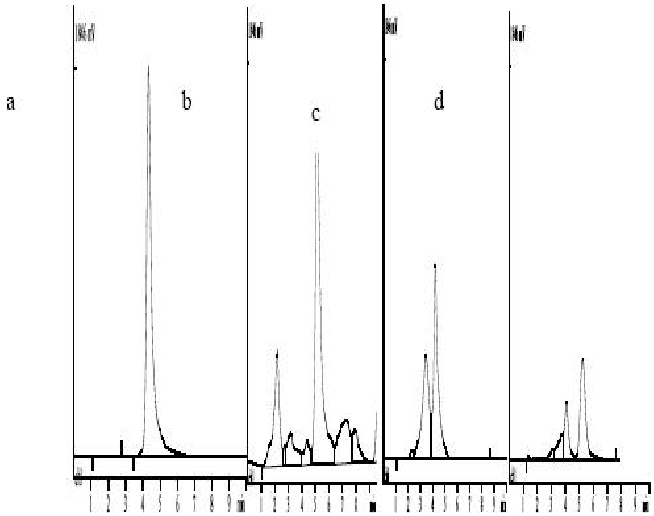

Figure 9 : HPLC chromatograms for the photodegradation of 20mg/l^{-1} primicarb using the three different synthesized nanoparticals a) primicarb b) primcarb+TiO$_2$ c) primicarb+TiO$_2$–Au d) primicarb+ZnO - Au

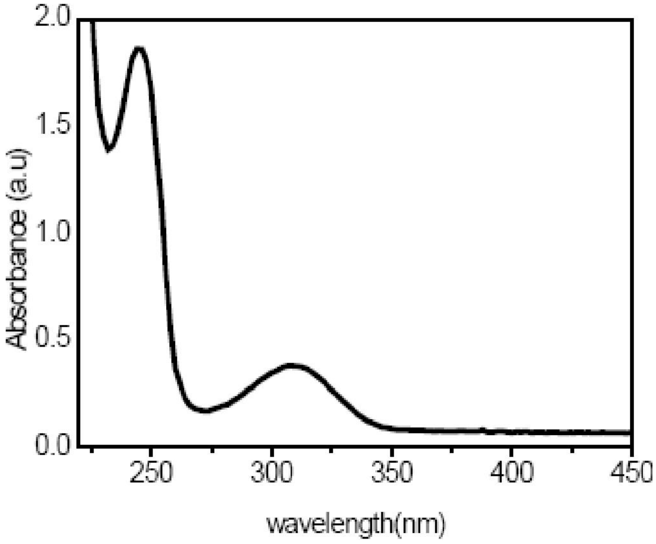

Figure 10 : UV spectrum for primicarb

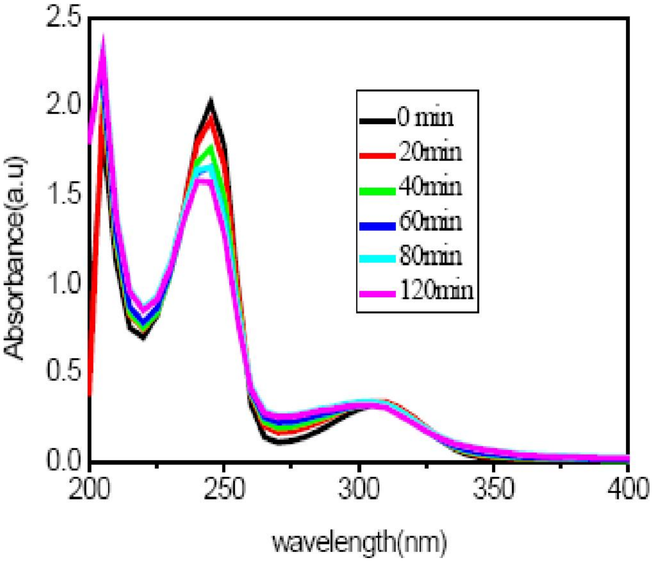

Figure 11 : Time dependent UV-visible spectra showing the adsorption of primicarb on TiO_2 – Au in 2 hours on irradiation to visible light

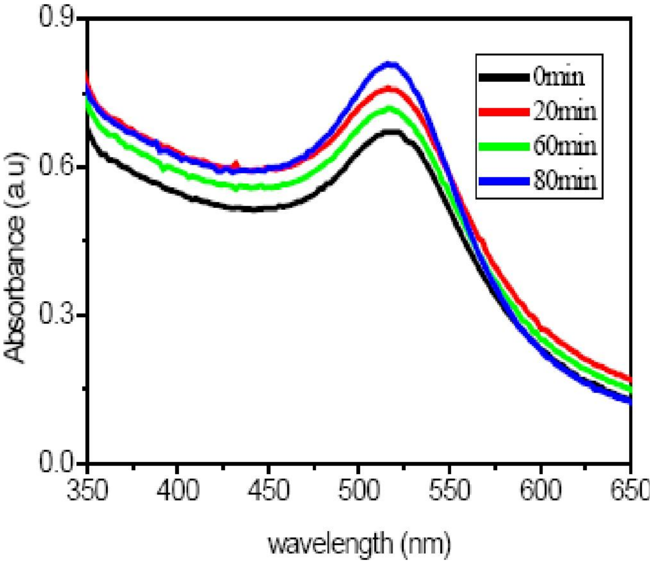

Figure 12 : Time dependent UV-visible spectra showing the adsorption of primicarb on TiO_2- Au in 2 hours on irradiation to visible light

TABLE 1 : Effect of different nanoparticls on the degradation of primicarb on irradiation to visible light

Catalyst primicarb degradation (8hr)	%
TiO_2	60
Au-TiO_2	90
Au-ZnO	87

Effect of different light sources

The irradiation intensity and time plays an important role in the photocatalytic degradation of primicarb[21, 22]. In this study a comparison between the photodegradation of primicarb in presence and in absence of sun light was carried out and was compared with the results obtained on irradiation to UV lamp. UV irradiation has limited the use of solar energy our task is to investigate the ability of using a photocatalyt that degrades primicarb with visible light since it is the major spectra of the solar light. Primicarb treated with the three synthesized nanoparticls (TiO_2, Au-ZnO-, AuTiO_2) was irradiated with natural sunlight and UV lamp separately in an identical experimental condition and the results were compared with the results obtained in absence of the irradiation to light and are illustrated in Figure 13. As shown in Figure 13, primicarb was undecomposed in absence of sun light and presence of either photocatalysts only 5% was decomposed after 8 hours while complete degradation is known to occur after 180 min on irradiation to UV lamp[17]. Figure 13 showed that the rate of decomposition increased to 87-90% in presence of Au-TiO_2 and Au-ZnO on irradiation with natural sun light. While no obvious photo degradation was observed for nano TiO_2 under the same conditions Figure 12. since TiO_2 is not a visible responsive catalyst the neat TiO_2 with band gap 3.2eV is well suitable for only UV light source around 300 nm, Which adopts the idea that the catalytic activity of a semiconductor (TiO_2, ZnO) is markedly enhanced by doping

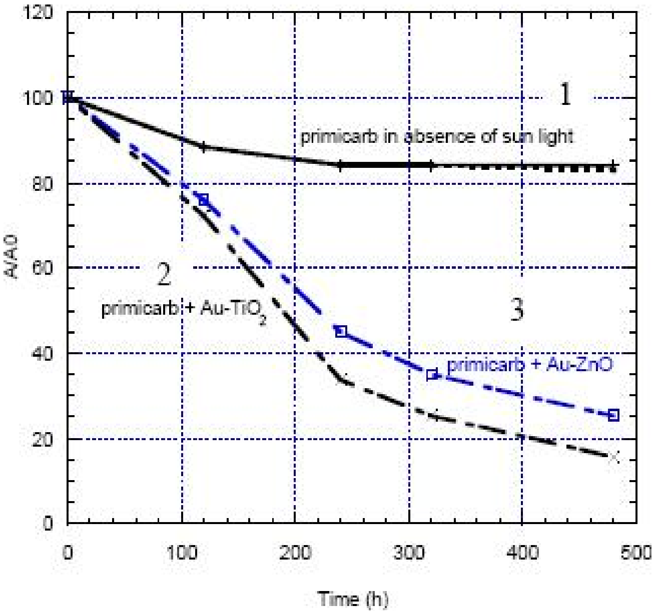

Figure 13 : Normalized curve for photo catalytic degradation pf primicarb 20ppm 1) Absence of sunlight using nanoparticls 2) in presence of sun light using TiO_2 - Au 3) in presence of sunlight using ZnO- Au

small amount of metals such as (Au), due to the easy transfer of electrons which are formed to the doped metal particles, which prevents the electron hole recombination accelerating the photocatalytic degradation reaction to a greater extent.

High energy of the UV source would excite more electrons from valence band to conduction band, simultaneously the quantum efficiency of the nano-particls is therefore increased as illustrated in Figure 14 where the rate of photo decomposition was about 87-90 % in about 1 hours.

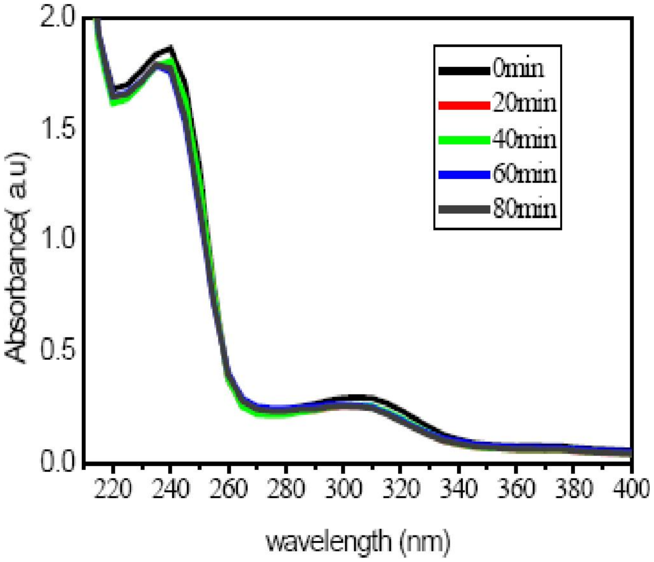

Figure 14 : Time dependent UV-visible spectra showing the adsorption of primicarb on TiO_2 in 80 mn on irradiation to visible light

Effect of different concentrations of reactants

Optimising the different amounts of primicarb and nanoparticals used is important for the photocatalytic degradation to avoid unnecessary interferences of the excess amount of nanoparticls[23-25]. Different concentration of nano- particals were investigated for their effect on the primicarb degradation results were illustrated in Figure 13 the mixtures were made 1:10 nano: Primicarb (V/V%) which showed that concentrations down to 10^{-5} M.

Nanoparticals were able to degrade the primicarb and the rate of degradation increases with the increase in the concentration of the nanoparticals (Au-ZnO, Au-TiO_2, TiO_2). Degradation becomes faster to a certain limit since the excess in the concentration of the nano partical might cause the scattering of light which occurs due to the turbidity and accordingly fewer particles can undergo excitation and also recombination of photo-formed electrons-holes facilitate to a greater extent, when applying high amount of the different nanoparticals. Hence, only 57% of degradation of primicarb was noted with 10^{-3} M nanoparticle whereas at low amount of catalysts $5x10^{-5}$ will accelerate the rate of degradation reactions (63%) Figure 15.

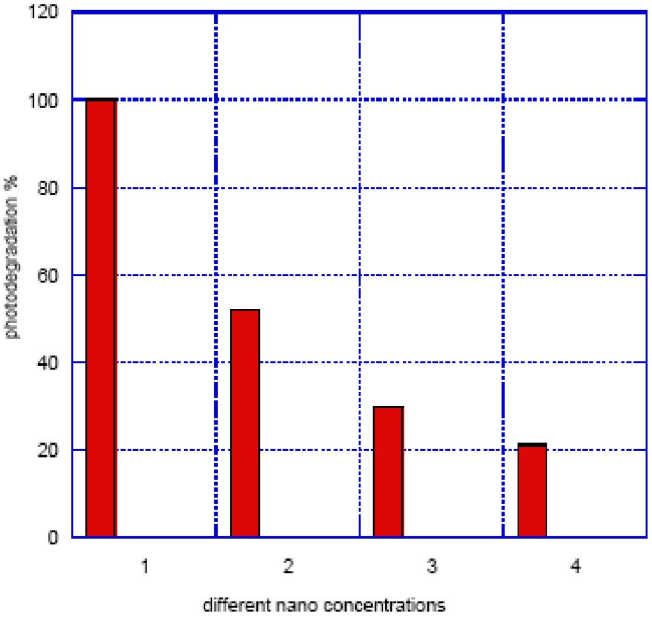

Figure15 : Effect of different concentrations of nanoparticals on the phodegradation of primicarb 1) primicarb 2) primicarb+ 10^{-3}M ZnO-Au3) primicarb+ 10^{-4} ZnO -Au 4) primicarb+ 10^{-5}ZnO-Au

CONCLUSION

The synthesized nanoparticls Au-TiO_2,Au-ZnO,TiO_2 are proved to be efficient for the photo-

Degradation of primicarb. Optimizing the parameters affecting the rate of degradation is an important task, such as intensity of different light sources, concentration of the nanocatalyts.

The study states the ability of using the different semiconductor doped with nanometals for the degradation of primicarb on irradiation to natural sun light as a easy and practical way for degradation of toxic compounds.

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