

Synthesis and Characterization of TiO₂/Au Nanocomposite Using UV-Irradiation Method and Its Photocatalytic Activity to Degradation of Methylene Blue

MOHAMMED ALWAN FARHAN^{1,*}, ZAID HAMID MAHMOUD^{1,*} and MARWA SABBAR FALIH²

¹Department of Chemistry, College of Science, University of Diyala, Baquba, Diyala Province, Iraq

²Department of Chemistry, College of Science, Al-Mustansiriya University, Baghdad, Iraq

*Corresponding authors: E-mail: mohammed.alwn@sciences.uodiyala.edu.iq; zaidhamid@sciences.uodiyala.edu.iq; zaidhameed_91@yahoo.com

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Gold doped TiO₂ has been successfully synthesized *via* photolysis method and is characterized by different techniques. Nanoparticles of gold doped TiO₂ were utilized for the degradation of methylene blue as a material pigmentation pollutant. The substitution of Au on TiO₂ surface was confirmed by XRD, EDX, TEM and FTIR techniques. The TEM and SEM results showed that the particles are in nano range and its size is below 15 nm. Without a catalyst, the degradation of the dye under visible light in acid and natural medium gives a modest result, but a better results at pH 11 while it gives an excellent result at all conditions when using a catalyst.

Keywords: Doped, Methylene blue, Nanoparticles, Photodegradation, Photolysis.

INTRODUCTION

In previous years, photocatalytic remediation of pollutants *via* semiconductor has received great interest. These processes are of special attention because of their capacity to utilize solar power. Titanium dioxide (TiO₂) remains a first select photocatalyst due to the biological and chemical constancy, low charge, relatively high photocatalytic activity, relatively rising photocatalytic vigor, long stable life and non-poisonous [1-3]. The use of TiO₂ semiconductors is a good technique to remove of dangerous ecological contaminants [4-9], particularly to degradation of bio recalcitrant organic contaminants. The mixture of two titanium oxide mineral (anatase and rutile) has optimal photocatalytic efficiency. Titanium dioxide owns a major band gap (3.20 eV) and consequently use a little fraction of the visible solar vision [10] and it has pulled extremely interest during the last years due to the visible light is a substantial neat power and facilely used. So as to utilize it efficiently, the essential stride is to scout novel materials as visible photocatalysts. Many trials have been done so as to rise the adsorption ability of TiO₂, like sensitized together with organic materials, doping with transition metals [11-23], nonmetal atoms [24-28] and precious metals [29]. Narrowing of band gap by inserting cation such as gold into TiO₂ was newly located to be more effective than the traditional way to accommodate catalyst together with the increase catalytic action down visible source. The action of the catalyst depends on the state of metals, but the photocatalytic action still boosts in any case the

oxidation. This paper reports the preparation of Au doped TiO₂ powder *via* photolysis method. Photolysis is an effective process for preparing metal oxides nanoparticles from its complex or salt (bottom to top method). The main objective is converting the absorption of TiO₂ to the visible region by introducing Au into the TiO₂ lattice structure.

EXPERIMENTAL

Titanium trichloride and chloroauric acid were supplied from Sigma Aldrich Company and used without purification.

Characterization: The structure of Au-TiO₂ catalyst was recorded by Shimadzu XRD-6000 operating at 40 kV and 30 mA (Cu K_α as the irradiation source). The morphology of catalyst was measured using a JEOL JSM-6700F field-emission SEM and TEM (JEOL JEM-2100 Japan). The spectra degradation of methylene blue was shown using UV-visible spectrophotometer (Perkin Elmer) in the range of 200-800 nm while the analysis of Energy dispersive was carried out with a Hitachi S-3400.

Synthesis of Au-TiO₂ catalyst: The preparation of Au-TiO₂ catalyst occurred in two steps: (a) initially, 5 g of titanium chloride was dissolved in 100 mL of distilled water. It was irradiated by continuously stirring until a brown precipitate appeared using irradiation system. 10 mL of chloroauric acid was added to the freshly brown precipitate solution with stirring. 5 mL of (0.1 N) NaOH was added drop-wise in a fresh solution until a mixture brown yellow precipitate appeared.

Finally, it is isolated, washed for 3 times with acetone and distilled water, dried and calcined at 400 °C.

Photocatalytic activity: Photocatalytic rendering of synthesized photocatalysts was carried *via* the decomposition of methylene blue using optical absorption spectroscopy. The photocatalytic reaction was executed in a beaker, that include 150 mL of methylene blue dye solution and 50 mg of catalyst. Irradiation was done using 125 W visible lamps placed horizontally over the beaker. 5 mL of samples were collected at orderly times through irradiation and methylene blue sol. was isolated from the photocatalyst *via* centrifugation before analysis. The degradation was checked by gauging the Ads of the methylene blue sol utilizing UV-visible spectrophotometer at 663 nm wavelength.

RESULTS AND DISCUSSION

The phase of crystals for Au-TiO₂ catalyst was examined by X-ray diffraction as shown in Fig. 1. The diffraction peaks correspond to (101), (004), (200), (105), (211), (204), (220) and (301) reflections can be found at 2θ (25.30), (37.78), (48.07), (53.86), (55.02), (62.71), (70.34) and (76.06), respectively and 'it's in agreement with JCPDS card (21-1272) and the comparatively sharp peaks that indicate the sample is composed of highly crystalline TiO₂. The comparatively weak peaks at 2θ 44.34, 64.64 and 77.52 agree with the FCC gold (200), (220) and (311), respectively, signaling low content of gold in the Au-TiO₂ and the result is in agreement with JCPDS card (02-1095).

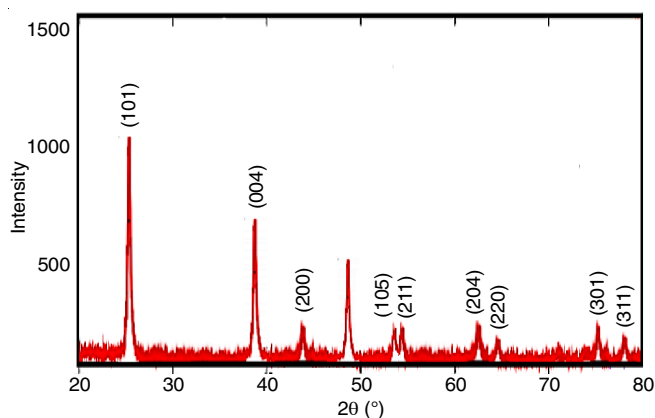


Fig. 1. XRD spectrum of Au-TiO₂

The morphology image of Au doped TiO₂ catalyst was recorded using SEM (Fig. 2). The particles are found to be regular, spherical and a bit agglomerated. Moreover, the result signalizes that the morphology of the particles is very gruff and may be beneficial to boosting the adsorption of reactants due to its high surface area and greater surface grossness.

The TEM analysis was to confirm the distribution of the crystallites and size of the particles and it appeared the doping of gold particles on the surface of TiO₂ and the particles in nanoscale with an average of 9 nm and are well distributed with aggregates as shown in Fig. 3.

The FTIR spectrum of the doping gold atom on the surface of TiO₂ is shown in Fig. 4. Broadband showed at 3440 cm⁻¹ assigned to O-H stretching vibration and another band at 1636

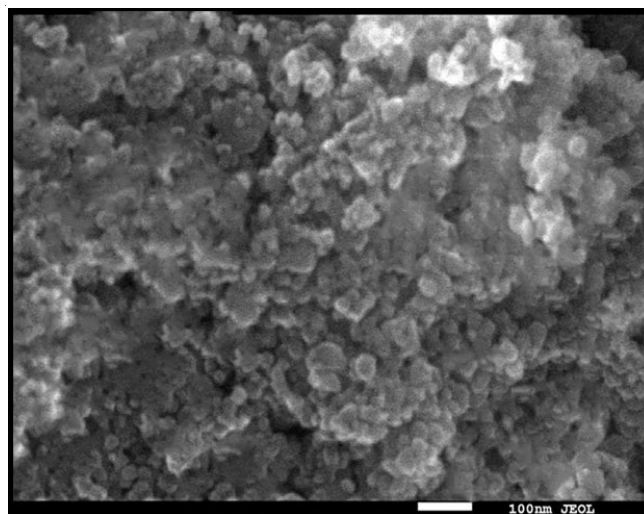


Fig. 2. SEM image of Au-TiO₂

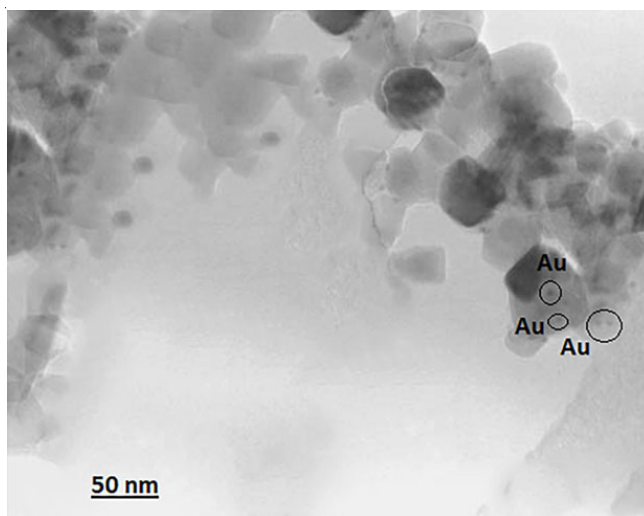


Fig. 3. TEM image of Au-TiO₂

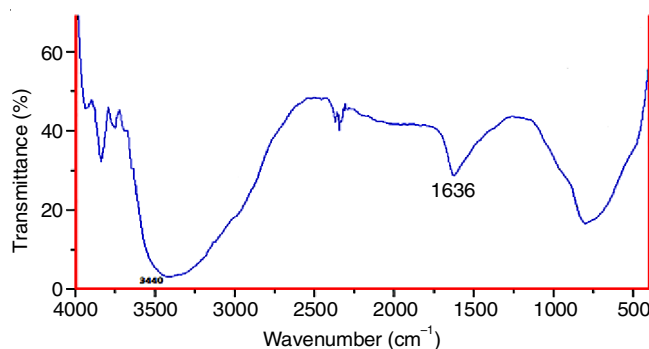
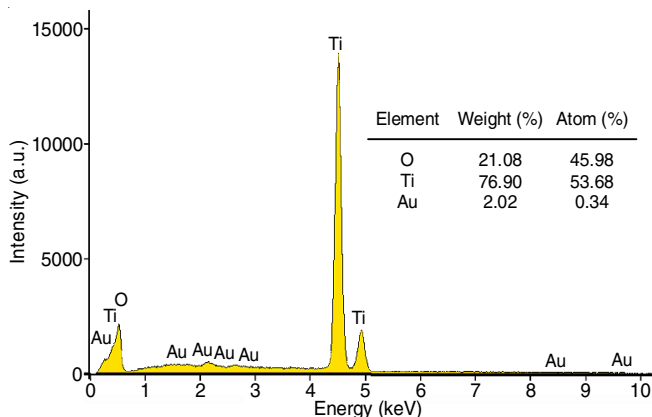


Fig. 4. FTIR spectrum of Au-TiO₂

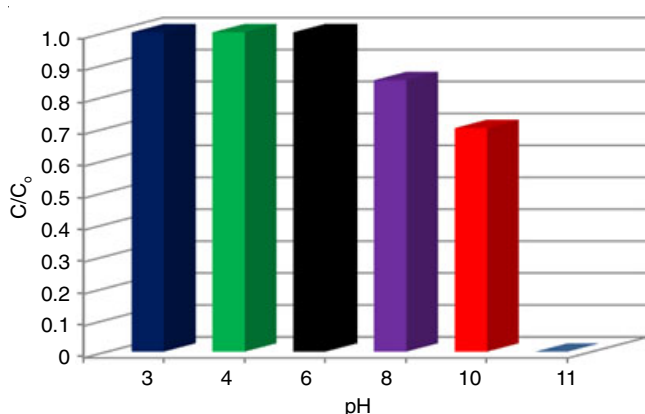
cm⁻¹ back to bending vibration of O-H [30]. Many board bands below 1900 cm⁻¹ were shown unsymmetrical, it's back to Ti-O-Ti and Ti-O-Au [31].

The amount of Au loading on the TiO₂ surface was shown using EDX spectrum as shown in Fig. 5. The EDX spectra were measured from a single structure of TiO₂ crystal. From the mensuration, it is counted that the loading of Au on TiO₂ nanoparticles is nearly stoichiometries.

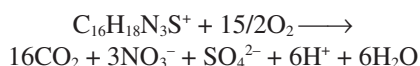
Fig. 5. EDX spectrum of Au-TiO₂

Degradation of methylene blue

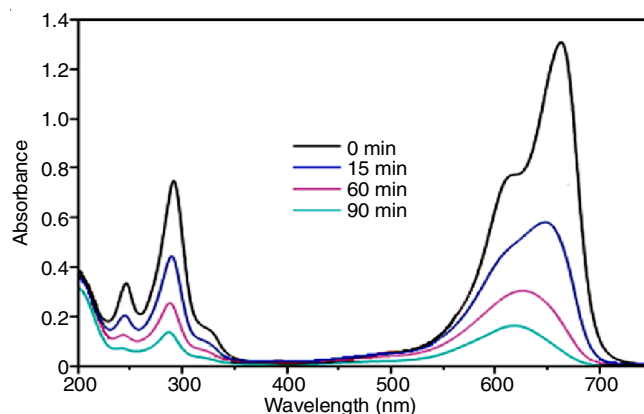
Photo-degradation without Au-TiO₂: Methylene blue solutions without TiO₂-Au with different values of pH ranging from 3 to 11 were left in a dark site for 1 h. The dye elimination efficiency was modest in all pH value. The solutions of methylene blue dye were exposed to sunlight irradiation and the various drain was observed as shown in Fig. 6. At acidic and natural medium, the concentration of dye did not decrease and this shows that the forthright photolysis of methylene blue by sunlight irradiation was modest at these mediums. It indicates that the provocation of dye molecules *via* photon and scuttle of the excitation energy had no role on the decolourization of the dye as follows:

Fig. 6. Photolysis of methylene blue at different pH ($C_0 = 50$ mg/L, time of irradiation = 90 min)

The UV-visible spectrum of methylene blue in aqueous solution at pH 11 in different time (0, 30, 60 and 90 min) as shown in Fig. 7 showed two absorption peaks at 292 nm back to aromatic rings [32] and peak between 600 and 700 nm can be referred to as chromophore including a long conjugated system. When the time of irradiation increased, the concentration of methylene blue decreased as shown in Fig. 7 due to the subsequent proton producing reactions, the formation of NO₃⁻ and SO₄²⁻ ions is shown in the reaction [33]:



Several trials were occurring without Au-TiO₂ at pH11 to explore the mechanism of photolysis. The pigmentation

Fig. 7. UV-visible spectrum of methylene blue without Au-TiO₂ at pH = 11

elimination efficiency after 90 min at a dark place at 35 °C was unassuming as shown in Fig. 8(1) while in another trial, the temperature was raised to 45 °C and the different variables stayed constant. Consequently, the temperature has no fundamental part on the photolysis of methylene blue but the photolysis was completed under the irradiation of sun after 90 min as shown in Fig. 8(3).

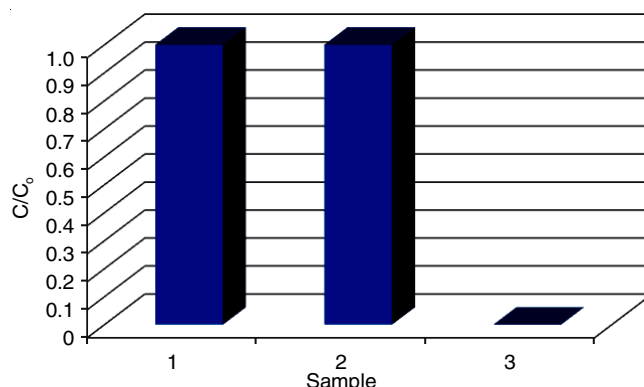


Fig. 8. Photolysis of methylene blue at pH = 11.0: (1) original dye, (2) dye in dark for 90 min and (3) dye in light for 90 min

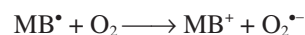
It shows that O₂ has the major part of the degradation of methylene blue. So, light, oxygen and hydroxyl ions have considerable effects on the degradations as it can be stopped with reduction of any of them. Highly reactive OH radicals were created under sunlight radiation in basic aqueous solutions as shown in the reaction [34]:



The radical species of hydroxyl can interact with any others and create H₂O₂ that is a substantial active species in photolysis processes [35]:



O₂ as a radical lover can interact with MB^{*} radical and create O₂^{•-} as other substantial intermediate species as shown in the following reaction [36]:



Consequently, the degradation of methylene blue at basic medium could be preceded by immediate reactions of methylene blue with highly reactive radical species that is created by the existence of solar irradiation.

Photodegradation of methylene blue with Au-TiO₂: The intensity of absorption decreased after irradiation of a solution of methylene blue in the presence of a prepared photocatalyst. The degradation of the pigmentation under light irradiation was determined *via* gauging the spectra of absorption employing a UV-visible spectrophotometer. The result showed through the lighting of the Au doped TiO₂ photocatalysts with visible light are shown in Fig. 9. Fig. 9 shows the modification in the spectra of absorption for the degradation of methylene blue dye as a function of time of irradiation under visible light in the existence of Au doped TiO₂. The bands of methylene blue located at 663 and 291 nm decreased with increasing irradiation times and this trial clearly shows that the decolouration of methylene blue can be completed under visible-light irradiation when the methylene blue solution lies in contact with Au-TiO₂. The decolourization of methylene blue solution can occur either by the oxidative degradation of the pigmentation or by the reduction of two-electron to its colourless form [37] and we could discover a small peak of the distinguishing absorption band of methylene blue at 256 nm. Hence, the decolouration of methylene blue refers to the oxidative degradation of the pigmentation.

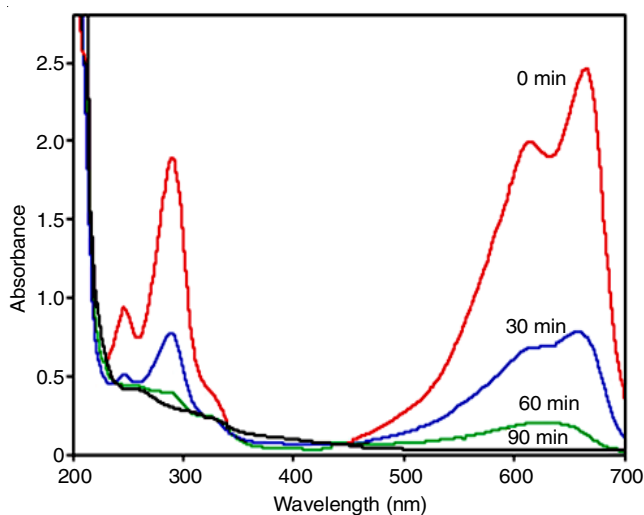


Fig. 9. UV-visible spectrum of methylene blue with Au-TiO₂ in acidic medium

Conclusion

In summary, pure Au-TiO₂ nanoparticles are an active photocatalyst for the degradation of methylene blue solution under sunlight irradiation and have been successfully fabricated by photolysis method. The nanoparticles of Au-TiO₂ with tiny crystalline size and strong visible-light were suitable for the photocatalytic degradation of methylene blue. The influence of pH was studied in specifics on the photolysis and photocatalysis of the methylene blue and the Au-TiO₂ catalyst showed elevated adsorption in an acidic medium and is suitable for the perfect photocatalytic degradation at low pH. According to UV-visible spectrum, after 90 min of UV light irradiation in acidic medium, peaks vanish and no new peaks are shown. While in a basic medium, the degradation of methylene blue occurred *via* photolysis of pigmentation in the presence of sunlight irradiation. In high pH (11), full photolysis occurs in 90 min of irradiation.

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