Photodegradation of Methylene Blue Solution via Au Doped TiO_2 Nanocomposite Catalysts Prepared Using Novel Photolysis Method

Zaid Hamid Mahmoud*[+]

Department of Chemistry, Collage of Science, Diyala University, Baqubah, IRAQ

ABSTRACT: *Gold doped TiO_2 has been successfully synthesized via photolysis method and it characterized by different techniques. NPs of gold doped TiO_2 were utilized for the degradation of methylene blue as a material pigmentation pollutant. The substitution of Au on TiO_2 surface was established via XRD, EDX, TEM, and FT-IR techniques. The TEM and SEM results appeared that the particles in the nano range and its size below 15nm. Without catalyst, the degradation of dye under visible light in acid and nature medium gives humble results but good results at pH 11 while it gives excellent results at all conditions when using catalyst.*

KEYWORDS: *Doped; Methylene blue; Nanoparticles; Photodegradation; Photolysis*.

INTRODUCTION

In the last years, semiconductor photocatalytic treatment for organic pollutants has received much interest. These reactions are of special attention due to their capacity to utilize solar energy. TiO_2 constantly remains as first choice photocatalyst due its biological and chemical stability, low cost, relatively high photocatalytic activity, long stable life and non-poisonous [1–3]. Using TiO_2 semiconductors is good method for the removal of dangerous ecological pollutants [4–9], particularly for the degradation of bio recalcitrant organic contaminants. The mixture of two titanium oxide mineral (anatase and rutile) appears optimal photocatalytic efficiency. TiO_2 has a large band gap (3.20 eV) and thus used small portion of visible solar spectrum [10]. Visible light catalysts have attracted much interest in the last years because the visible light is substantial clean energy and facilely used. So as to utilize visible energy efficiently, the essential step is to scout new materials as visible photo catalysts. Many trials have been made so as to increase the visible light adsorption ability of titanium dioxide, such as sensitized 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 Au into TiO_2 was newly found to be more affectivity than the traditional technique to accommodate catalyst with high catalytic action under visible source. The activity action of catalyst depended on the state of matels but the photocatalytic action still boosts in any case of the oxidation state. The present study was assumed to produce Au doped TiO_2 powder by photolysis method. photolysis is an effective process for preparing matel oxides nanoparticles from its complex or salt (bottom to top method). The main concentration is on converting the absorption of TiO_2 to visible region

* *To whom correspondence should be addressed.*

+ E-mail: zaidhamid@sciences.uodiyala.edu.iq

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by introducing Au into the TiO_2 lattice structure. The advanced photocatalysts have been used for the photocatalytic degradation of Methylene Blue (MB) so as to explore the relationship between different percentages of Au doped TiO_2 and additionally exploit for their dielectric properties. The present study concentricity on the resolve of catalyst material appearing possibility in photocatalysis, with the ability of demolition of pollutants under visible light and carrying out other selective catalytic processes.

EXPERIMENTAL SECTION

Materials

Titanium tri chloride and Chloroauric acid were supplied from Sigma Aldrich company and used without purification.

Characterization

The structure of Au-TiO_2 catalyst was recorded by Shimadzu XRD-6000 operating at 40 kV and 30 mA (Cu Ka 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 MB showed using UV–visible spectrophotometer (PerkinElmer) in the range of 200–800nm while the analysis of Energy dispersive carried with a Hitachi S-3400.

Synthesis of Au-TiO_2 catalyst

The preparation of Au-TiO_2 catalyst occurred in two steps: (a) initially, 5gm of titanium chloride dissolved in 100mL distilled water. Then, it irradiated with continuously stirring until brown precipitate appeared using irradiation system as shown in Fig. 1. After that, 10mL of chloroauric acid added to freshly brown precipitate solution with stirring. Then, 5mL of (0.1N) NaOH added drop wise drop to the fresh solution until appeared mixture of brown yellow precipitate. Finally, it isolated, washed 3 times with acetone and distilled water, dried and calcined at 400.

Photocatalytic activity tests

Photocatalytic rendering of synthesized photocatalysts has been carried via the decomposition of Methylene Blue (MB) using optical absorption spectroscopy. The reaction of photocatalytic was executed in a beaker, that includes 150 mL of MB dye solution and 50 mg of catalyst. Irradiation was occurred using 125 W visible lamps put horizontally over a beaker. 5mL of samples were collected at orderly times through the irradiation and MB solution was isolated from the photocatalyst via centrifugation before analysis. The degradation was checked by measuring the absorbance of solution using UV–Vis spectrophotometer at 663 nm wavelength.

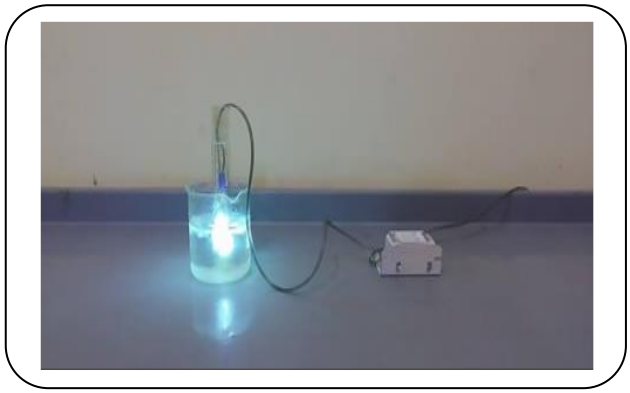

Fig. 1: The system of irradiation.

ESULTS AND DISCUSSION

The phase of crystals for Au-TiO_2 catalyst was examined by x-ray diffraction as shown in Fig. 2. The diffraction peaks corresponding 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 agreement with JCPDS card (21-1272) and the comparatively sharp peaks that appeared indicate to the sample is composed of highly crystalline TiO_2. The comparatively weak peaks at 2θ 44.34, 64.64, and 77.52 agree to FCC gold (200), (220) and (311), respectively, signalizing the low content of gold in the Au-TiO_2 and the result in agreement with JCPDS card (02-1095).

The morphology image of the Au doped TiO_2 catalyst was recorded utilizing SEM as shown in Fig. 3. The particles are found to be regular, spherical and a bit agglomerated. Moreover, the result signalizes that morphology of the particles is very gruff and may be beneficial to boosting the adsorption of reactants due to its high surface area and great surface grossness.

The TEM analysis occurred to confirm the distribution of the crystallites and size of the particles and it appeared the doping of gold particles on the surface of

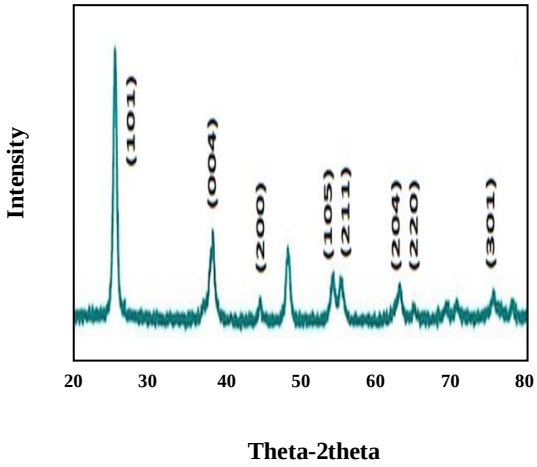

Fig. 2: XRD spectrum of Au-TiO_2.

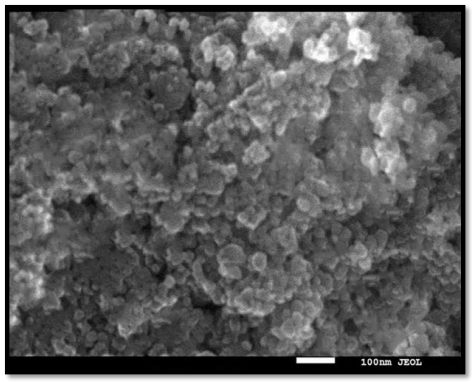

Fig. 3: SEM image of Au-TiO_2.

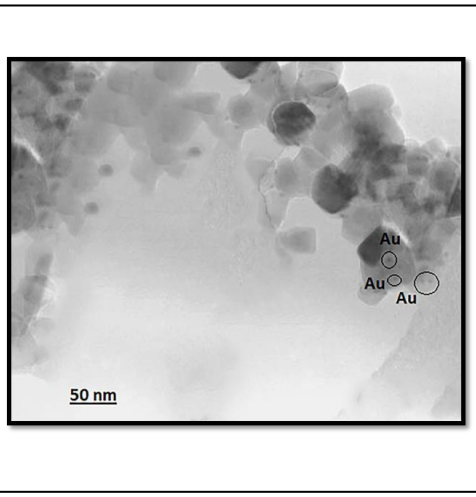

Fig. 4: TEM image of Au-TiO_2.

TiO_2 and the particles in the nano scale with average 9nm and are well distributed with aggregates as shown in Fig. 4.

The FTIR spectrum of doping gold atom on the surface of TiO_2 appeared in Fig. 5. The broad band showed at 3440cm^{-1} assigned to O-H stretching vibration and another band at 1636cm^{-1} back to bending vibration of O-H [30]. Many board bands below 1900cm^{-1} were showed unsymmetrically, it back to Ti-O-Ti and Ti-O-Au [31].

The amount of Au loading on the TiO_2 surface showed using EDX spectrum as shown in Fig. 6. The EDX spectra were measured from a single structure of TiO_2 crystal. From the mensuration, it is counted that the loading of Au on TiO_2 NPs are nearly stoichiometric.

Degradation of MB

photo-degradation without Au-TiO_2

Methylene blue solutions without TiO_2-Au in different values of pH from 3 to 11 were left in a dark site for 1hr. The dye elimination efficiency was modest in all pH values. Then, the solutions of MB dye were exposed to irradiation of sunlight and various drain were observed as shown in Fig. 7. At acidic and natural medium, the concentration of dye was no decrease and this mentions that the forthright photolysis of MB by irradiation of solar was humble at these mediums. It denotes that the provocation of dye molecules via photon and scuttle of the excitation energy had no role on the decolorization of the dye as following:

The UV-Vis spectrum of Methylene blue in aqueous solution at pH 11 in different time (0, 30, 60 and 90min) was appeared at Fig. 8 and showed two absorption peaks at 292nm back to aromatic rings [32] and peak between 600 and 700 nm can be referred to a chromophore including a long conjugated system. When the time of irradiation increased, the concentration of MB decreased as shown in Fig. 8 due to the subsequent proton producing reactions, formation of NO^{-3} and SO_4^{-2} ions as following reaction [33]:

$$C_{16}H_{18}N_3S^+ + 15.2O_2 \rightarrow$$

$$16CO_2 + 3NO_3^{-1} + SO_4^{2-} + 6H^+ + 6H_2O$$

Several trials occurred without Au-TiO_2 at pH=11 to explore the mechanism of photolysis. The pigmentation elimination efficiency after 90 min at dark place at 35 °C was unassuming as shown in Fig. 9A while

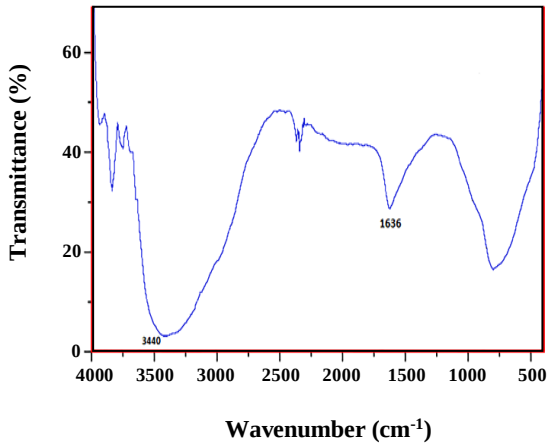

Fig. 5: FTIR spectrum of Au-TiO₂.

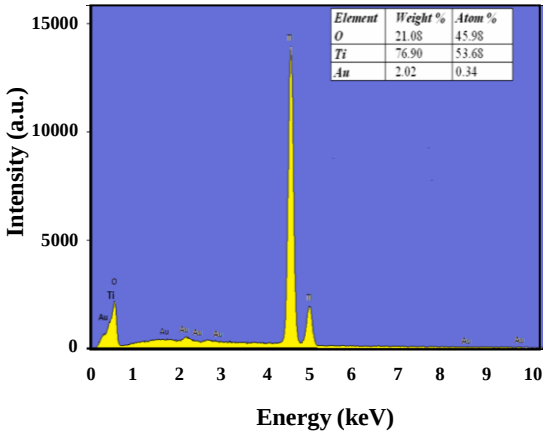

Fig. 6: EDX spectrum of Au-TiO₂.

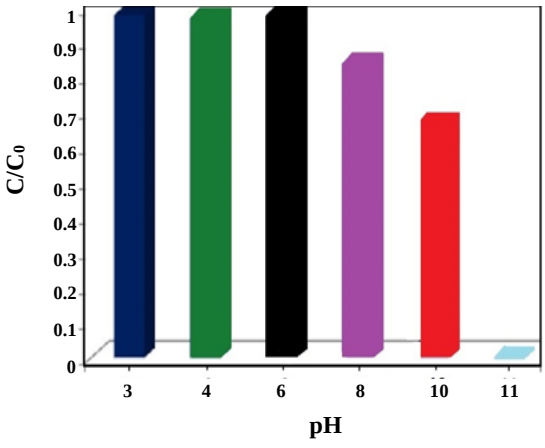

Fig. 7: Photolysis of MB at different pH (Co = 50 mg/L, time of irradiation= 90 min).

in another trial, the temperature was raised to 45 °C and the different variables stayed constant. Consequently, the temperature has no fundamental part in the photolysis of MB but the photolysis was complete under the irradiation of sun after 90min as shown in Fig. 9C.

It illustrates that O_2 has a major part in the degradation of MB. 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 the radiation of solar light in basic aqueous solutions as following reaction [34]:

$$MB^{+} + OH^{-} \rightarrow MB^{\bullet} + OH^{\bullet}$$

The radical species of hydroxyl can interact with any others and creating H_2O_2 that is a substantial active species in photolysis processes [35]

$$2OH^{\bullet} \rightarrow H_2O_2$$

O_2 as a radical lover can interact with $MB^{\bullet}$ radical and create $O_2^{-\bullet}$ as other substantial intermediate species as the following the reaction [36]:

$$MB^{\bullet} + O_2 \rightarrow MB^{+} + O_2^{-\bullet}$$

Consequently, the degradation of MB at a basic medium could be preceded by immediate reactions of MB with highly reactive radical species that created in the existence of sun irradiation.

Photo degradation of MB with Au-TiO₂

The intensity of absorption decreased after irradiation of a solution of methylene blue in the existence prepared photocatalyst. The degradation of the pigmentation under light irradiation was determined via gauging the spectra of absorption employing a UV-Vis spectrophotometer. The information showed through the lighting of the Au doped TiO_2 photocatalysts with visible light are shown in Fig 10. Fig. 10 appears the modification in spectra of absorption for the degradation of methylene blue dye as a function for the time of irradiation under Vis light in the existence of Au doped TiO_2. The bands of methylene blue that located at 663 and 291 nm decreased with increasing irradiation times and this trial clearly appears that the decoloration of methylene blue can be completed under visible-light irradiation when the methylene blue solutio is lay in contact with Au-TiO_2. The decolorization of methylene blue solution can occurs either by the oxidative

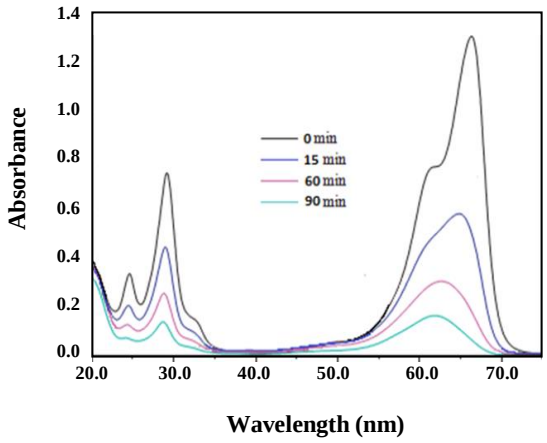

Fig. 8: UV-Vis spectrum of MB without Au-TiO_2 at pH = 11.

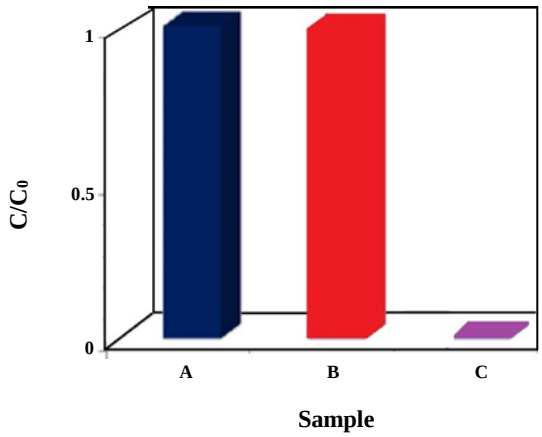

Fig. 9: Photolysis of MB at pH = 11.0: (A) original dye, (B) dye in dark for 90 min, and (D) dye in light for 90 min.

degradation of the pigmentation or by the reduction of two-electron to its colorless form [37] and we could discover a small peak of the distinguishing absorption band of leuco MB at 256 nm. Hence, the decoloration of MB is referred to the oxidative degradation of the pigmentation.

CONCLUSIONS

In summary, pure Au-TiO_2 NPs as an active photocatalyst for the degradation of methylene blue solution under the light of sun irradiation, have been successfully fabricated by photolysis method. The nanoparticles of Au-TiO_2 with tiny crystallite size and strong for 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 MB and the Au-TiO_2 catalyst appeared elevated adsorption in acidic medium that is suitable for the perfect photocatalytic degradation at low pH. According to UV–Vis spectrum, after 90 min of the light of sun irradiation in acidic medium, peaks vanish and no new peaks showed. While in basic medium, the degradation of methylene blue occurred via only photolysis of pigmentation in the existence the light of sun irradiation. In high pH (11), full photolysis occurs in 90 min of irradiation.

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