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PHOTOCATALYTIC AACTIVITY OF TiO_2 /Ag NANOPARTICLE ON DEGRADATION OF WATER POLLUTIONS

M. BEHPOUR*, S. M. GHOREISHI, F. S. RAZAVI
Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I. R. Iran

In different industries, especially in chemical ones environmental pollutants is a basic problem. In these days study about purification process that has functional properties such as high efficiency: low time and low cost is very noticeable. Use of photocatalysis is a suitable method for degradation of organic pollutants. Photocatalytic procedure based on titanium dioxide is widely used in many areas. In this work, the TiO_2 nano particles on the Ti metal surface sheet was immoblized by electrochemical method and then for enhance the photocatalytic activity of synthesized TiO_2, deposited the Ag into the TiO_2 matrix. Amorphous structure of nanoparticles of TiO_2 was changed to anataze structure and also silver ion changed to silver oxide by calcinated the Ag / TiO_2 sheet in furnace at 550 ^{0}C. With immobilizing the nanoparticles of TiO_2 on the Ti surface, recovery process is very restful and filtration of the solution is not necessary. Photocatalytic properties of the surface modified and Ag ion doped TiO_2 catalyst was investigated by degradation of methyl orange in UV light as a model. The results show that Ag / TiO_2 nanoparticles have suitable activity for degradation of methyl orange. The effect of film layers, embeding Ag^+, anneling and time on the degradation ratio was studied. The concentration of methyl orange, distance from ligth, O_2 and pH would be the optional parameters for the Ag / TiO_2 photocatalytic degradation. The $AgNO_3$ embedded, treated at 550 ^{0}C for 1 h, exhibites good performance. The establishment of nanoparticles on the surface was determinated by SEM.

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Keywords: Titanium dioxide nanoparticle, Photodegradation, Methyl orange,
Water pollution, Ag dopped

1. Introduction

Photocatalysis process based on the utilized the semiconductors from purification and disinfection of air and water has been reported [1] . This is a vital subject that is very studied and more attention was paid to such material in the past few years. [2]

Metal oxide semiconductors have been much recent attention for a variety of practical applications. [3] Among various semiconductors titanium dioxide have become a highly promising technology for remove of the pollutant from water and environmental. [4-7]

Titanic is a very useful photo catalyst because this has considerable properties such as: high activity [8], chemical and biological internees [9], commercial availability [10] and etc. From this important properties, TiO_2 is very applicable in many area, for example benefited from TiO_2 in the structure of solar cell [11], biosensors, semiconductors electrode, UV radiation inhibitor [12], etc. Photaocatalytic activity is a remarkable function of titania [13]. Brookite, anatase and rutile are different structures of titanium dioxide. [14]

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*Corresponding author:mbehpour @kashanu.ac.ir

The photocatalytic activity of TiO_2 started with UV light irradiation. The first step of this reaction to begin by the establishing the electron – hole pairs under appropriate illumination. [15] Generation of electron hole pairs leading to generated the hydroxyl (OH) and super oxide radicals on the surface of TiO_2. [16,17] Among the different structure of titanium dioxide, anatase, appears to be the most active from another structure in photocatalytic process. The band gap of anatas is 3.2 ev and for rutile is 3.1 ev. The efficiency from photocatalytic activity of TiO_2 depend on the crystalline structure that this are originated from synthesize process of TiO_2. [18]

To heighten the efficiency of photocatalytic process ought to depletion recombination of electron–hole. Recently doping TiO_2 with metal or non–metal elements decreases this recombination. Resulting deposition element into titanic matrix increase hole concentration, down bond gap energy to visible light and cause the suitable photoactive system. [19]

Titanium dioxide is commonly benefited in two forms: powder (suspension) and immobilize (film). Using of suspension has several problems. Filtration and retrieval stage are a time consuming and costliness process for the suspension forms. While fixing and immobilizing the TiO_2 on various substrate solving these problems and optimized their catalytic operation. [20-22]

Various techniques found from the synthesized of immobilizing titanic. The some of these are chemical vapor deposition (CVD)[23], sputtering, sol – gel [24] and electrochemical process .[25]

Electrochemical process is the best method from them because these have special advantageous. Some of the beneficial character of this method coming below:

Low cost, suitable process temperature of process, using low energy, use of inexpensive solution, control the condition of reaction is very easy, using the compound without pollutant of environment. [26]

Recently immobilizing TiO_2 nanoparticles on metal Ti substrates to done by electrochemical technique. Immobilizing reaction carried out in percents of DC current, electrolyte solution and excursuses voltage. With changing the voltage can form different size of nanoparticles and resulting various color on the substrates.

In our previous work, we synthesized TiO_2 and TiO_2- doped with low concentration of Ag using $AgNO_3$ as a procedure and found that it was of higher activity under UV irradiation. We will present the details of the TiO_2 loading procedure. The use of SEM will give detailed information on the surface of catalyst layer, there after its activating were evaluated by the photodegradation of Methyl orange (MO) as a model for water pollution. For the reason that the nanoparticles are completely fixed onto Ti substrate, it is unnecessary the filtration and recovery stag. The dependence of photocatalytic reaction on the following parameters were examined: concentration of MO, distance of irradiation source, concentration of Ag etc.

2. Materials and methods

Materials

Sulfuric acid (98%), hydroflouric acid, silver nitrate and MO were used for this research. All the reagent were analytical grade quality and all the rest of reagents were obtained from Merck. Millipore water was used in all experiment. Ti sheet prepared from local industrial, used as substrate. The 400 W mercury lamp were used as light source. The absorption and diffuse reflection spectra were measured using a UV- Visible Lambda 2S Perkin Elmer spectrophotometer of double beam. The pH of solution was measured using a pH meter METROHM 609. DC source made of LEYBOLD _ HERAEUS Dms 1/65 were used in electrochemical process.

Preparation of TiO_2 Nanoparticles by Anodization Technique

Titanium sheet in 25mm×50mm×1 mm shape were scraped with sand paper (mesh 1000) and then immersion into concentrate HF solution for 10 seconds and then washed with distilled water. On the other hand, immersion of Ti sheets in HF solution less than 10 s is not enough to remove the oxide layer on the surface.

This stage to be repeat for two or three times until the surface of the plate lacking from any oxide, then completletely washed with distilled water and filnally dried.

The titanium dioxide nano particles were prepared by the electrochemical process. Electrochemical cell include: DC source, cathode and anode electrodes (Ti sheet) and sulfuric acid (2M) as electrolyte solution. TiO_2 was synthesized by a regulated DC power supply in sulfuric acid solution for a few second in different voltage and Ti sheet annealed at 500 ^{0}C in muffle. Thermal step used for changing of the crystal structure of TiO_2 nanoparticles and improve its photocatalytic activity. Anodizing voltage, holding time and annealing temperature were changed to evaluate the influence of experiment condition on nano particles characterizes.

The doped Ag was performed directly on the TiO_2 nanoparticles by immersing the TiO_2 / Ti sheet in 0.12 M $AgNO_3$ for about 10-60 times and dry surface by hotair in any stage. Then prepared sheets transferred to the muffle at 500 ^{0}C for 1 hour. The thermal process furthermore is changed the crystalline structure of TiO_2 nanoparticles therefore the Ag ion also convert to the Ag oxide on the surface.

Standard Procedure for Photocatalytic Activity

The catalytic activity of synthesized TiO_2 nano particles was evaluated in the photodegradation of MO dye in water as a model. The test was carried out by using a 400 W mercury lamp as UV radiation source. The lamp was kept in irradiation house. The decomposition of MO in variouse concentration was conducted in a 200 ml cylindrical quartz photo reactor.

The pH of the solution was adjusted to 2 using H_2SO_4 (6 M). The TiO_2 nanoparticles were immersed into 75 ml of dye solution by stirring and continuously air bubbled. A blank solution was prepared by the same method without TiO_2/Ag sheet. At regular intervals (30 minute), 5 ml of MO solution was sampled and its concentration measured by its absorbance at 510 nm by a UV – Visible spectrophotometer. The photodegradation efficiency (X) can be calculated as following formula:

$$X = (A_0 - A) / A \tag{1}$$

$$A = A_0 - (A_b - A_s) \tag{2}$$

where A_0 is the initial absorbance of reference MO solution and A is the revised absorption considering MO after photo irradiation. Equation 2 has used for elimination of blank effect and correction the consequence of photodecomposition. A_b is absorbance of blank and A_s is the absorbance of sample.

3. Results and discussion

Effect of Ag Embedded on Photocatalytic Reaction

Fig. 1 presents the photocatalytic decomposition of Ag – doped TiO_2 and also undoped TiO_2 nanoparticles. The results shown that phtodegradation of MO with TiO_2 nanoparticles is about 20%, but doping the TiO_2 nanoparticles with Ag ion, increase the rate and efficiency of decomposition of MO. Therefore the improvement of the phtocatalytic activity of TiO_2 nanoparticles with deposition by Ag ion is very noticeable.

Effect Of Number Of Immersion Of TiO_2 Sheet In Ag Dopand Solution

The photodegradation efficiency increases with increasing the number of Ag component of immersion and then decreases. The most effective decomposition of MO was observed with (30 times) immersion. The effect of number of immersion on the photocatalytic activity was studied as shown in Fig 2. For explain of this results, silver and TiO_2 have different work functions, (Φ_{TiO2} = 4.2 ev, Φ_{Ag} = 4.6 ev). So when silver contacts with TiO_2, electrons will transfer from TiO_2 to silver. Those electrons transferred to silver and loaded on the surface of silver will be scavenged by the electron acceptor, thus decreases the recombination between electron and hole and silver atoms act as electron traps it is well known that the geminate recombination is the main reason for low efficiency of TiO_2 photocatalysis. Therefore, the existence of silver atom in Ag / TiO_2 sheet can help more holes to transport to the surface and enhance the photocatalytic efficiency. However, too much silver loading will result in a negative effect and photocatalytic degradation of MO decreases. The main reason for the low efficiency from covered catalyst surface area by silver, which acts as a barrier is preventing light absorption by TiO_2. On the other hand, excess Ag prevents the organic substrate from contacting the TiO_2 surface.

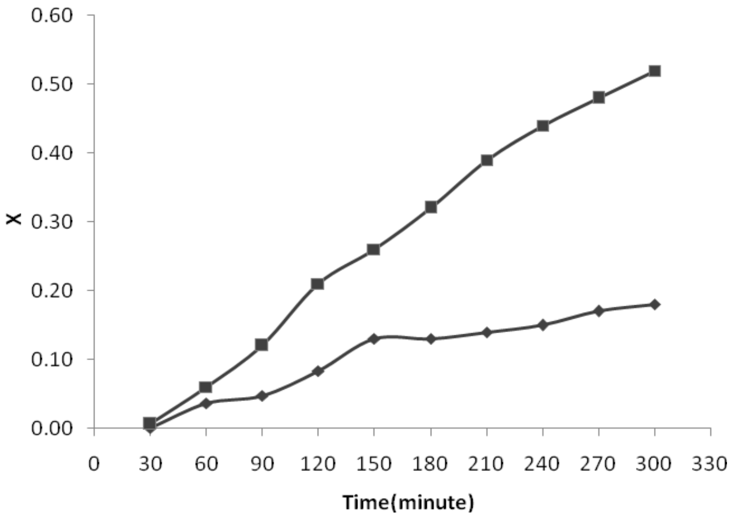

Fig. 1 Comparision of the photocatalytic degradation of MO under UV light with (◆) TiO_2 and (■) Ag / TiO_2 nano particles. Experimental condition: MO concentration 6.3×10^{-3} M, pH = 2, λ=510 nm, presence O_2 and 5h irradiation.

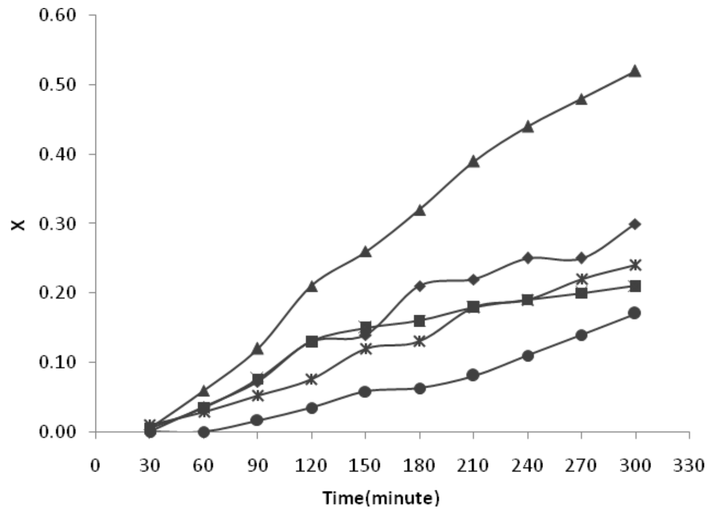

Fig. 2 Effect of Ag concentration on the photo degradation of MO withe Ag / TiO_2 nano particles, number of immersion (◆) 10 times, (■) 30 times, (▲) 40 times, (✹) 50 times, (★) 60 times. Experimental condition: MO concentration 6.1×10^{-5} M, pH = 2, λ=510 nm, presence O_2 and 5h irradiation.

Effect of MO Concentration

The initial concentration of MO is one of the influencing factors that affect the photo degradation of MO. To study of this effect, the other reaction variables were adopted as the optimal levels, but concentration of MO changed. The results in Fig.3 show the role of MO concentration on the MO photodegradation by Ag / TiO_2 nanoparticles. Fig 5 shows that with decrease of initial concentration of MO photo degradation of MO by the nano particles decreased. However when the amount of MO is larger than 6.1×10^{-5} M, the photodecomposition process decreases with increasing of the amount of MO concentration. The behavior may be attributed to the reaction between MO and Ag / TiO_2 nanoparticles on surface. When the amount of MO concentration is high, reaction between MO molecules and Ag / TiO_2 nanoparticles is low. In low concentration of MO interaction between MO molecules and UV is higher than the reaction between MO molecules and TiO_2 nanoparticles and therefore the photocatalytic reaction decreases.

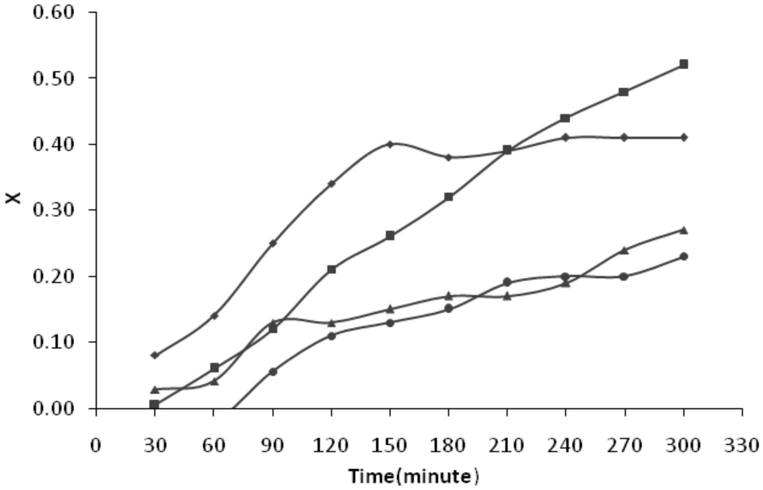

Fig. 3 Photodegradation of MO at variuos concentration of MO with Ag / TiO_2 nano particles in pH=2, λ=510 nm, presence O_2, and 5h irradiation. (■) 6.1×10^{-5}, (▲) 4×10^{-5}, (◆) 2×10^{-5}, (✹) 1×10^{-5}

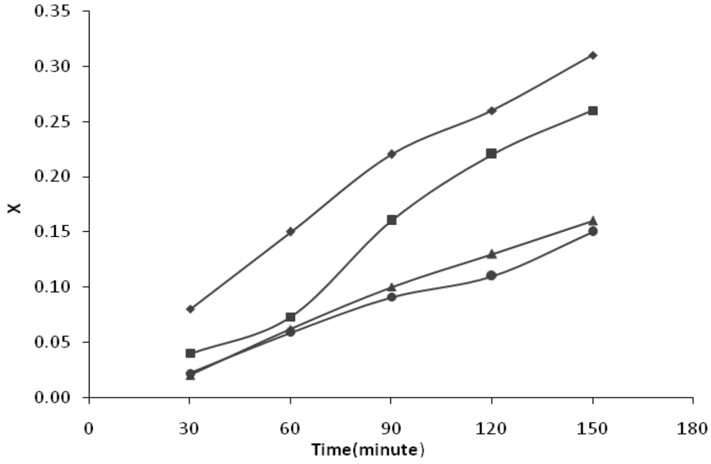

Fig. 4 Effect of distance between light source and Ag / TiO_2 nano particles on the photodegradation of MO withe Ag / TiO_2 nano particles (■) 51cm, (◆) 56cm, (▲) 61cm, (✹) 66cm, Experimental condition: MO concentration 6.3×10^{-3} M, pH = 2, λ=510 nm, presence O_2 and 5h irradiation.

Effect of distance from Radiation Source

In this part we checked the influence of distance between the radiation source and Ag / TiO_2 plate. The consequence of this study shows that, when distance from radiation source is lower than 52 cm, decomposition effect of UV is low for photocatalytic degradation by Ag / TiO_2.

On the other hand, if distance between the radiation source and Ag/TiO_2 plate was uper than 66 cm, the received light on the surface of Ag / TiO_2 decreased. It is noticeable that from bestring the TiO_2 nanoparticles, they should be placed under illumination, therefore settle TiO_2 nanoparticles away from radiation source reduce the photocatalytic activity of them. Fig 4 shows that, 56 cm is the best distance between the radiation source and Ag / TiO_2 nanoparticles in this study.

Effect of O_2

Fig. 5 shows the decomposition and photodegradation of MO mediated by Ag / TiO_2 nano particles in presence and absence of O_2. It can be seen that the decomposition of MO by Ag / TiO_2 nanoparticles without O_2 is very slow. On the other hand, in the presence of O_2 and UV irradiation the MO photodecomposition is so fast. Fig. 5 shows the increase of the photo degradation of MO in homogenous solution. The electron acceptor role of O_2 decrease the electron and hole combination at the Ag / TiO_2 surface allowing reactions to proceed. O_2 generating the superoxide radical $O_2^{\cdot}$ by the scavenged the e^- on the Ag / TiO_2 nano particles surface.

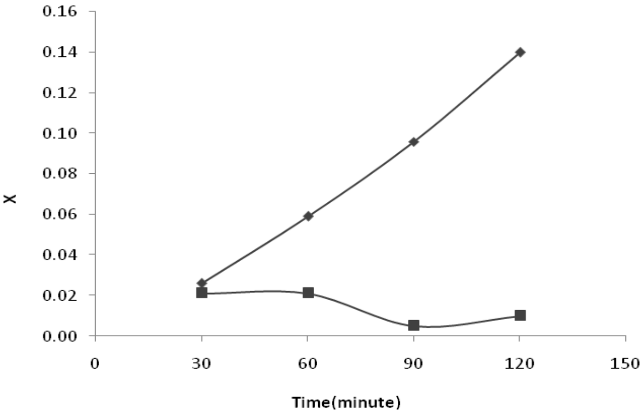

Fig. 5 Effect of O2 in photodegradation of MO with Ag / TiO2 nano particles in pH=2, λ=510 nm, MO concentration 6.3×10-3 M and 150 min irradiation.(■) Absence O2.(◆) present O2.

Following reaction show the emergency of present O_2 in reaction [27]:

$$\begin{aligned}
&TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{\nu b}\\
&h^+_{\nu b} + H_2O \rightarrow OH^{\cdot} + H^+\\
&h^+_{\nu b} + OH^- \rightarrow OH^{\cdot}_{ad}\\
&h^+_{\nu b} + R_{ads} \rightarrow R^+\\
&e^-_{cb} + O_2 \rightarrow O_2^{\cdot -}\\
&e^-_{cb} + h^+_{\nu b} \rightarrow TiO_2 + h\nu
\end{aligned} \qquad (3)$$

Effect of Photodegradation of MO in Different pH

Photodegradation of MO was studied by UV irradiation at various pH values. The results have shown in Fig. 6 pH values were adjusted by adding of H_2SO_4. The highest efficiency of photodecomposition process was obtained at pH = 2, while the photoactivity process was much low at another pH.

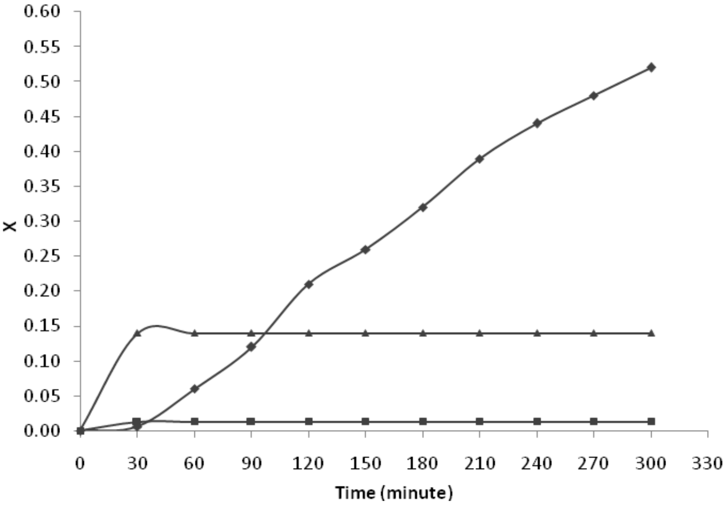

Fig. 6 pH effect on the photodegradation of MO with concentration of MO at 6.3×10-3 M, pH=2, λ=510 nm, presence O2 and 2h irradiation.(◆) pH=2, (■) pH=3, (▲) pH=4

SEM Observation

The surface structure of TiO_2 and Ag / TiO_2 film was studied by SEM (Fig 7,8). The SEM pictures (Fig. 8) with the equal magnification reveal that the surface structure of the Ag / TiO_2 films is identical with original TiO_2 film. Fig. 7, shows a uniform distribution of TiO_2 nanoparticles. The similar particle size there is on Ag / TiO_2 film and Ag has no influence on the size of TiO2 particles. Only a few Ag clusters are observed on the surface of Ag / TiO_2 film.

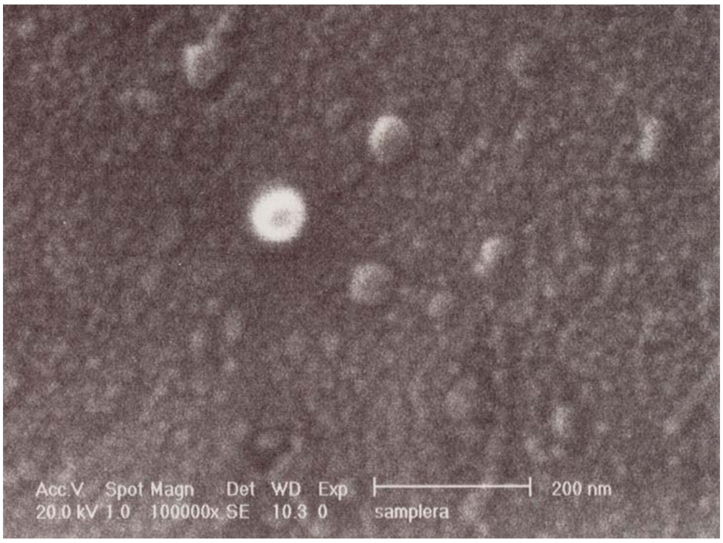

Fig. 7 SEM photographs of TiO2 nano particles on Ti sheet by electrochemical method.

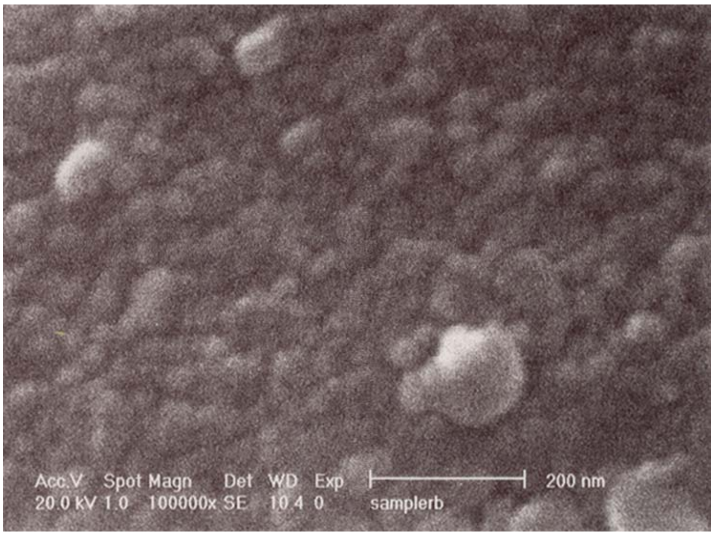

Fig. 8 SEM photographs of Ag / TiO2 nano particles on Ti sheet by electrochemical method.

4. Conclusions

Nano particles of TiO_2 were prepared by electrochemical process. This synthesized photo catalyst is able to decompose MO. The electrochemical process has not required the special and expensive apparatuses and TiO_2 nano particles prepared with this process had high donor density that synthesized with dry oxidation. Ag / TiO_2 nano particles showed higher photocatalytic activity than neat TiO_2 nano particles on the photo decomposition of MO under UV radiation. The efficiency of photodegradation of MO is affected by amount of $OH^{\cdot}$ radicals formed on the nanoparticles surface. At high concentration of MO, higher amounts of MO molecules adsorb on the photocatalytic and inhibited the reaction between the MO molecules and hydroxyl radical or positive holes, because there is not a direct contact of the semiconductor with them. Therefore in this case the photocatalytic activity of TiO_2 nano particles, decreased.

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