JOURNAL of the TURKISH CHEMICAL SOCIETY SECTION: B CHEMICAL ENGINEERING
TURKISH CHEMICAL SOCIETY

Preparation and Characterization of TiO_2@SiO_2-Ag Nanospheres Photocatalyst, and Investigation of Its Photocatalytic Activity on Methylene Blue

This article was produced from a poster or oral contribution to the ICAIE Congress, 2017.

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Abstract: Titanium dioxide shows a tremendous potential for the decomposition of organic pollutants under UV and visible light irradiation. In this study TiO_2 nanospheres @ mesoporous silica nanospheres (TiO_2@SiO_2) photocatalyst was synthesized by the sol-gel method. The synthesized TiO_2/SiO_2 photocatalyst was decorated by Ag nanoparticle. The decorated TiO_2@SiO_2–Ag photocatalyst by a hydrothermal method was characterized by scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The SEM results show that TiO_2@SiO_2–Ag nanospheres photocatalyst was uniformly formed. The EDS analysis proves that the nanospheres photocatalyst consists of Ti, Si, O and Ag. The TiO_2@SiO_2–Ag nanospheres photocatalyst exhibited better photocatalytic performance for degradation of methylene blue under direct UV illumination.

Keywords: Titanium dioxide; Core-Shell; Silver nanoparticles; Silica spheres

Submitted: October 05, 2017. **Accepted:** October 20, 2017.

Cite this: Tekin T, Tekin D, Kızıltaş H. Preparation and Characterization of TiO2@SiO2-Ag Nanospheres Photocatalyst, and Investigation of Its Photocatalytic Activity on Methylene Blue. Journal of the Turkish Chemical Society, Section B: Chemical Engineering. 1(sp. is. 1):89–96.

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INTRODUCTION

During the recent years, technological developments affect adversely the environment [1]. The degradation of pollutants with photocatalyst gained more interest because of its efficiency and cheapness [2]. One and most used of semiconductor photocatalysts is TiO_2 with an energy band gap because of high surface area, low toxicity and chemical stability [3].

In the last decade, researchers have studied the very different forms of TiO_2 such as nanotube [4,5], nanorods, nanowires, nanospheres. In addition, the noble metal doping is much used way to increase photocatalytic performance of TiO_2 under UV light. The photocatalytic result of hollow microspheres of TiO2 shows advance photocatalytic activity than another forms of TiO_2 [6-8].

In this study, TiO_2 nanoparticles and TiO_2/SiO_2-Ag nanocomposites were synthesized as a photocatalyst. The photocatalysts were characterized by SEM, EDS and XRD. The photocatalytic performance of the photocatalysts was investigated by decomposition of MB solution under UV light.

MATERIALS AND METHODS

Chemicals

Titanium isopropoxide (TIP; Sigma-Aldrich), hydrochloric acid (HCl; Sigma-Aldrich), ethanol (C_2H_6O; Sigma-Aldrich), Cetyltrimethyl ammoniumbromide (CTAB: Sigma-Aldrich), tetraethyl orthosilicate (TEOS; Sigma-Aldrich), ammonium hydroxide (NH_4OH; Sigma-Aldrich), Silver nitrate ($AgNO_3$; Sigma-Aldrich), sodium borohydride ($NaBH_4$; Sigma-Aldrich) and methylene blue (MB; Sigma-Aldrich) were purchased.

Experimental procedure

- Synthesis of TiO_2 nanoparticles

Titanium isopropoxide as a precursor dissolved in ethanol, HCl and deionized water mixture, and stirred for one hour. After adding10ml of deionized water in the mixture, the mixture was stirred for 2 hours. The formed TiO_2 nanoparticles were separated by centrifuging proses, dried with deionize water 2 times and dried at 80ºC for 2 hours.

- Synthesis of $TiO_2@SiO_2$ nanoparticles

0,1 g of TiO_2 and 0.25 g of CTAB was ultrasonically dissolved in the mixture of 80 ml of ethanol, 60 ml of water and 5 ml of NH_4OH for 20 minutes. 0.25 ml of TEOS was rapidly added in the mixture under the magnetic stirring. After stirring for 2 hours, the formed $TiO_2@SiO_2$

nanoparticles was separated by centrifuged process. The solid product was washed 2 times with ethanol and dried in the oven at 110°C for 18 hours. For removing the CTAB templates, the dried product was refluxed in acetone solution for 8 hours. Then, the product was filtered and dried in the oven.

- Synthesis of $TiO_2@SiO_2$-Ag nanoparticles

0.1 gr of synthesized $TiO_2@SiO_2$ nanoparticles was added in 100 ml of deionized water under magnetic stirring. The $AgNO_3$ solution was added and stirred towards the reduction of Ag ions upon the dropwise addition of $NaBH_4$ until the color changed to greenish yellow. The solution was stirred for 1 hour. Then formed $TiO_2@SiO_2$–Ag nanostructures were centrifuged, washed with deionized water 5 times, dried at 70°C for 2 hours, and calcined at 500°C for 2 hours.

- Characterization

The produced nanospheres photocatalysts were characterized by SEM, EDS and XRD. The surface morphology was investigated by SEM with coated a thin layer Au to prevent the charge problem. The composition of nanospheres was determined by EDS analysis. The structural and phase identification of the nanospheres were investigated by XRD in the 2 theta range from 20 to 80 degree.

- Evaluation of Photocatalytic Activity

The photocatalytic activity performance of the prepared nanospeheres photocatalysts was investigated on the decomposition of MB solution. Degradation of MB solution was performed in the jacketed reactor at room temperature. The photocatalytic experiment was carry out by 25 mg of the prepared nanospheres photocatalysts with 200 ml of a solution consisting of 20 mg. L^{-1} of MB. The MB aqueous was irritated by UV-light at 254 nm ($44 W/m^2$). The saturated O_2 concentration in the reaction medium was provided by air-pump. The quantitative analysis of MB concentration was determined by withdrawing 2 ml of samples from the reactor solution and measuring in UV-vis spectrophotometer.

RESULTS AND DISCUSSION

As shown in Figure 1, the surface morphology of the prepared nanospheres was investigated by SEM. The TiO_2, $TiO_2@SiO_2$-Ag nanoparticles show spherical shape with uniform structure, as shown Figure 1a-c. The TiO_2 disorderly form and agglomeration in Figure 1a. The surface of $TiO_2@SiO_2$ nanospheres shows smoothness because of coating with thin SiO_2 layer in Figure 1b. The SEM image of the $TiO_2@SiO_2$-Ag photocatalyst demonstrates porous and rough structure, which is increasing the photocatalytic activity with more active areas.

The EDS results present the presence of Ag, O, Si and Ti in the composition of TiO_2@SiO_2-Ag, as shown Figure 1d.

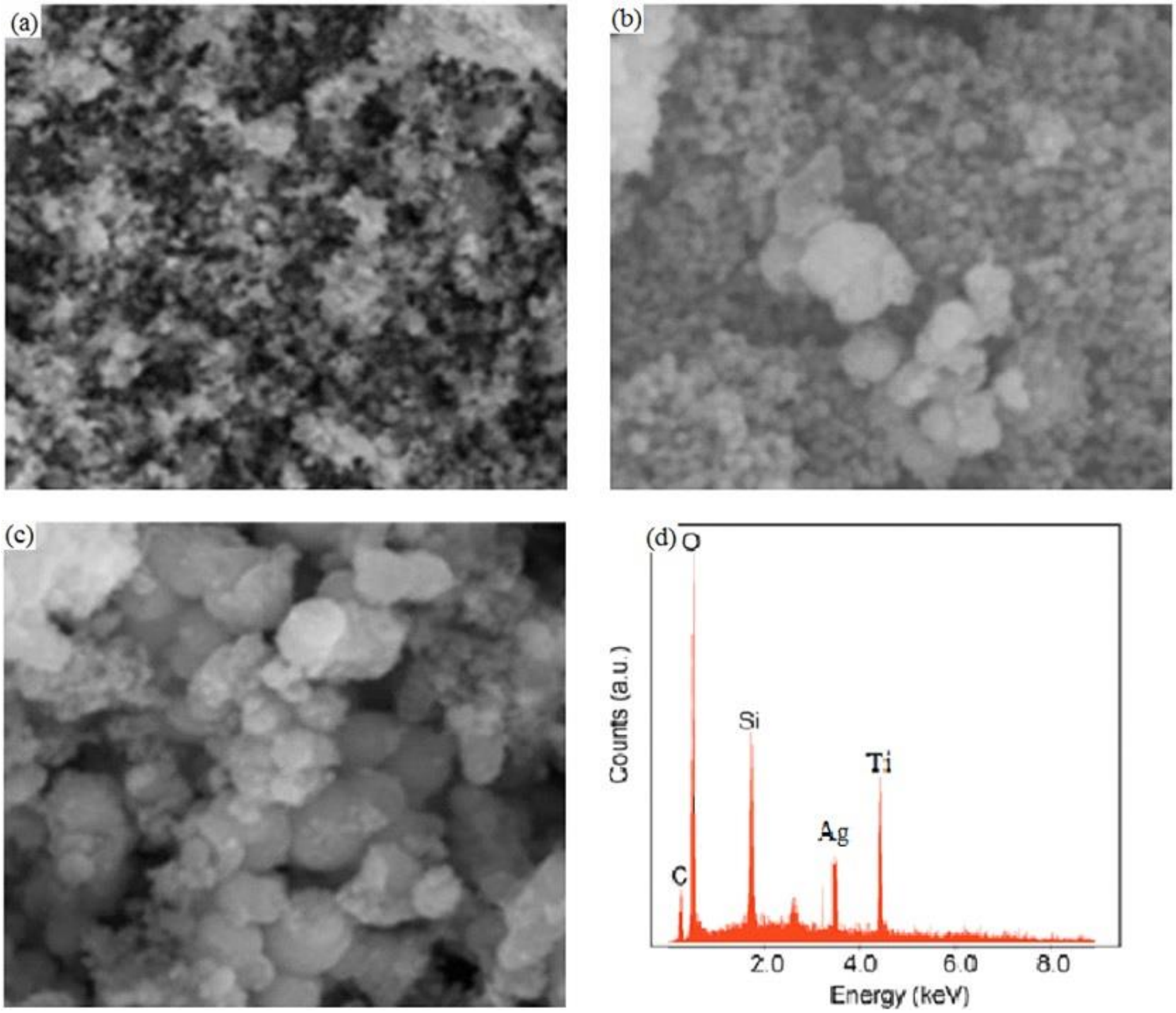

Figure 1. SEM images of TiO_2 (a), TiO_2@SiO_2 (b), and TiO_2@SiO_2-Ag nanocomposites (c), and EDS result of TiO_2@SiO_2-Ag (d).

The TiO_2 and TiO_2@SiO_2 nanoparticles show the similar diffraction peaks with the anatase phase of TiO_2. Ag NPs on the TiO_2@SiO_2 nanocomposite matrix at diffraction peaks values of 38.2 and 44.2 corresponding to the (111) and (200) diffraction plans of the face centered cubic Ag crystals as shown in Figure 2.

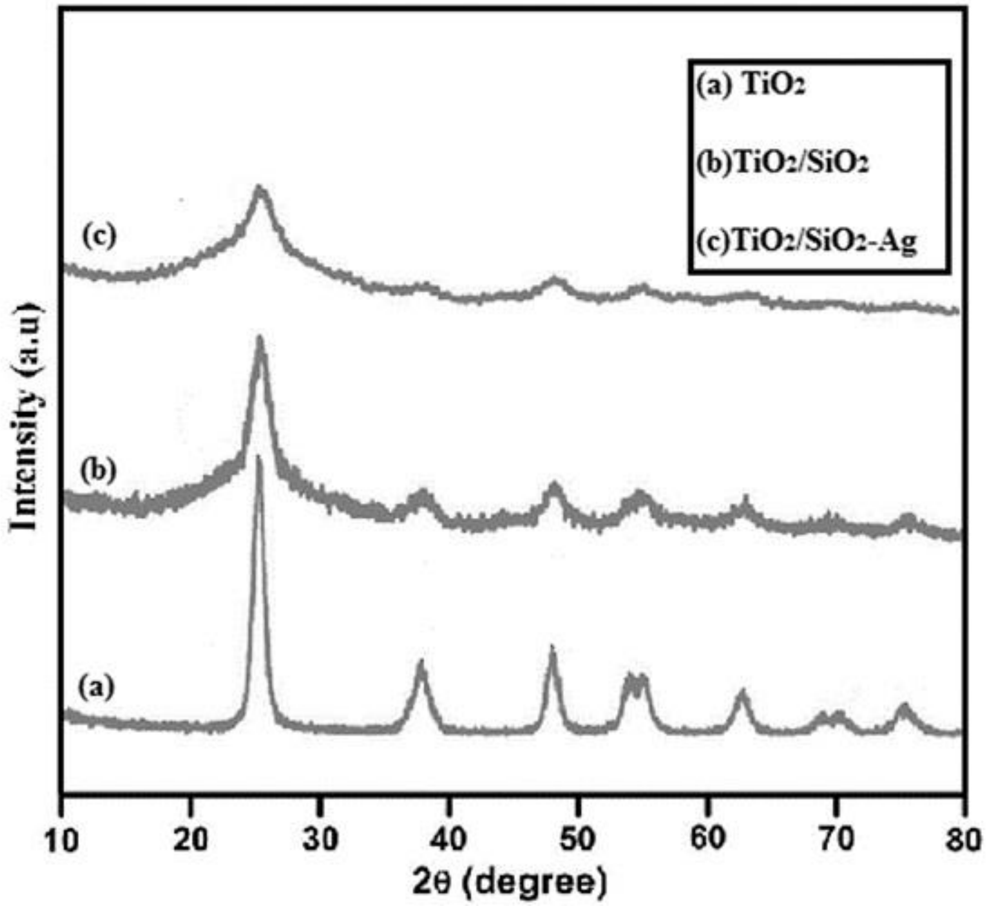

Figure 2. XRD pattern of Photocatalyst

The photocatalytic performance of TiO_2@SiO_2-Ag nanospheres was commentated by measuring the degradation of MB solution. Degradation of MB solution is not determined in the absent of photocatalyst or in the dark environment. The photocatalytic performance of TiO_2@SiO_2-Ag nanospheres is higher than commercial TiO_2 photocatalyst. The results of the degradation of MB solution for different photocatalysts are given in Figure 3.

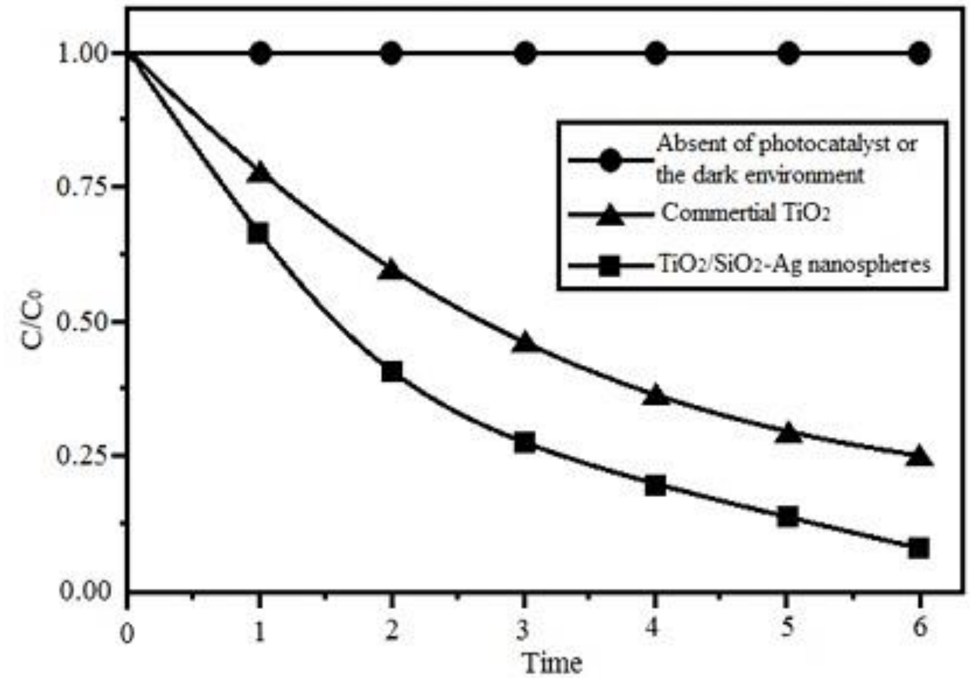

Figure 3. Degradation of MB solution

CONCLUSIONS

The $TiO_2@SiO_2$-Ag nanospheres were synthesized by sol-gel method. The $TiO_2@SiO_2$–Ag nanospheres show excellent structure and high surface area. The photocatalytic performance of the synthesized nanospheres was investigated by decomposition of Methylene Blue solution. The $TiO_2@SiO_2$-Ag photocatalyst showed a better photocatalytic activity then the commercial in solution of Methylene Blue.

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