SILAR Preparation of CuO Nanoparticles on TiO2 Sol-Gel Layer for Efficient Visible Light Photocatalysis

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***Abstract*—In recent times photocatalysis is attracting extensive attention due to the environmental problems with toxic organic compounds. One of the most actively used materials for photocatalysis is titanium oxide. However, the photocatalytic activity of titanium oxide is insignificant in the visible spectrum. In this case, the creation of composites based on TiO2, which is photocatalytically active in the visible light irradiation is the actual aim.**

In this work, formation features and the photocatalytic properties of the CuO-TiO_2 composite was studied. TiO_2-CuO composite was fabricated by the sol-gel process (TiO_2) and successive ionic layer adsorption and reaction (SILAR) method (CuO) with a different number of deposition cycles. Structure, morphology and composition of samples were investigated by Raman spectroscopy, and SEM methods. The photocatalytic activity was examined under UV and visible irradiation. Photocatalytic activity of CuO-TiO_2 composites was investigated from the number of SILAR deposition cycles.

Keywords— photocatalysis; SILAR; CuO; TiO_2; sol-gel; photocatalytic activity; nanoparticles

I. INTRODUCTION

At the present time, TiO_2 is widely studied and used as a photocatalyst due to its high hydrophilicity, good chemical stability, non-toxicity, low cost and strong oxidizing abilities for the decomposition of organic pollutants [1]. Anatase polymorphic modification of TiO_2, due to its lower recombination rate and a high mobility of charge carriers compared to rutile phase, has great interest for use in photocatalysis [2]. However, the band gap of the TiO_2 is 3.2 eV, which prevents widespread use of this material in photocatalysis. Because of its large band gap, TiO_2 requires ultraviolet radiation for photocatalytic activation. Since UV radiation accounts for a small part (5%) of the solar spectrum compared to visible light (52%) and infrared light (43%), any shift in the optical response of the TiO2 towards the longer wavelength region allows for higher photocatalytic activity.

The increased photoactivity of the TiO_2 in the visible range of radiation, as well as an increase in the efficiency of separation and decrease of recombination of the charge carriers, is associated with a number of approaches for modifying the surface and structure of the photocatalyst material [3]. The approaches mainly consist in introducing cationic and anionic impurities into the crystal lattice of the material, as well as modifying the surface with metal or semiconductor nanoparticles. The formation of semiconductor and metal nanoparticles on the surface of titanium oxide is the simplest method to implement. One of the promising methods for producing nanoparticles is successive ionic layer adsorption and reaction method (SILAR). The main advantages of the SILAR method are low cost and ease of controlling the size of the nanoparticles by changing the number of deposition cycles.

Using the SILAR method to obtain nanoparticles of the transient metal oxides to formation a heterojunction can be a simple and cheap way to increase the photocatalytic activity of TiO_2. Among various transient metal oxides, copper oxides attract considerable attention due to their photochemical and photomagnetic properties. The copper oxides (CuO_x) can exist in different stoichiometries and phases, such as Cu_2O and CuO, which have a band gap in the range from 1.2 to 2 eV. CuO can be used to formation heterojunction between the TiO_2 layer to increase the efficiency of the charge carriers separation and the absorption spectrum of TiO_2 in the visible wavelength range [4]. The charge carrier separation occurs due to conduction band (CB) position of CuO below the CB of titanium dioxide. Figure 1 shows a diagram of the energy levels of the TiO_2 – CuO heterojunction.

In this paper, we investigated the photocatalytic properties of the titanium dioxide layers obtained by the sol-gel method on a glass substrate with CuO nanoparticles obtained by the SILAR method. The copper oxide stoichiometry was determined by the Raman spectroscopy method. The morphology of the obtained samples was investigated using a scanning electron microscope (SEM). The morphology of the obtained samples was investigated using a scanning electron microscope (SEM).

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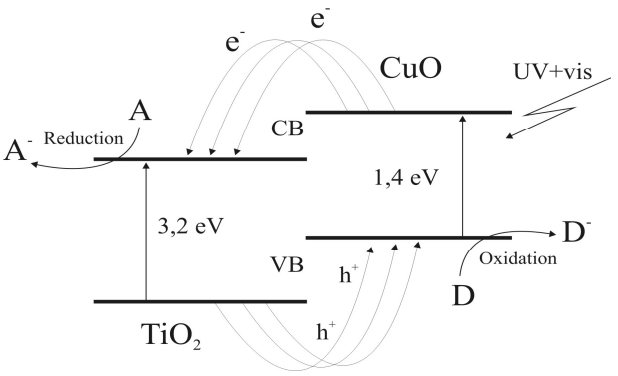

Fig. 1. . Diagram of the energy levels of the TiO_2/CuO heterojunction under UV+vis irradiation

II. EXPERIMENT

A. Prepearing samples

TiO_2 layers were obtained by sol-gel process using dip coating technique with a substrate pulling out rate of 22 mm/min. As the precursor solution, titanium isopropoxide and isopropyl alcohol was used in a ratio of 1:9. The obtained TiO_2 layers on glass were thermally treated on air at a temperature of 450 ºC for 1 hour to obtain anatase phase of the TiO_2.

CuO nanoparticles on the TiO_2 layers surface were prepared using the SILAR method. As the source of the copper ions an aqueous solution of $CuCl_2 \cdot 2H_2O$ with a concentration of 0.01 M was used. The pH of the solution was adjusted to 10 with a 25% NH_4OH aqueous solution. A solution of ethyl alcohol with deionized water in the ratio 1: 3 heated up to 70 ° C was used as a source of the anions.

One cycle of the deposition of CuO nanoparticles by the SILAR method consisted of three steps. The first step immersing the TiO_2 sample in $[Cu(NH_3)_4]^{+2}$ solution for 30 seconds; the second step - immersing the sample in ethyl alcohol with deionized water for 7 seconds; the third step - washing the sample in deionized water for 30 seconds. After completion of the deposition process, the obtained samples were annealed in a furnace at 300 ºC for 2 hours in air to crystallize the deposited layer CuO. The samples with different number of deposition cycles of the CuO nanoparticles 7, 14, and 21 were obtained.

Also, the CuO sample on a glass substrate without a TiO_2 layer was prepared to determine the structural modification and stoichiometry of precipitated copper oxide by the Raman spectroscopy method. Measurements were performed on a Horiba LABRAM HR EVOLUtion unit using 4 mW 514 nm Ar laser with x100 optic magnification.

B. Photocatalytic mesurments

The study of the photocatalytic properties of the samples was carried out using a light source simulator of the Newport 67005 Sun with an Xe 150W lamp. The lighting was carried out as close as possible to the natural, that is, AM1.5. For the calibration measurements, the Coherent FieldMaxII light power meter and the Coherent PowerMax PM10 sensor were used. Solution of the methylene blue with a concentration of 0.78 μM and a volume of 20 ml was used in photocatalytic measurements.

Before carrying out the process of photocatalysis, the sample was placed in 20 ml of the prepared solution of the methylene blue for 1 hour to pre-adsorb the dye to the sample surface. Then the photocatalysis process was started and the transmission of the decomposable solution was measured on the spectrophotometer for 1 hour for every 15 minutes. To avoid severe degradation of the methylene blue due to the heating of the lamp radiation in a thermocup, an optimum temperature of about 20 ºC was maintained by using water circulating thermostat. The transmission of the methylene blue aqueous solution was carried out using an SF-102 spectrophotometer at the wavelength 662 nm as it corresponds to the absorption peak of the studied solution [6].

The morphology of the samples was investigated using a MIET Quanta 3D FEG scanning electron microscope with an accelerating voltage of 5 kV.

III. DISCUSSION

Figure 1 shows digital photos of the samples after carrying out the process of deposition of CuO nanoparticles and thermal annealing on air for 2 hours at 300 °C and the sample without the deposited layer of CuO.

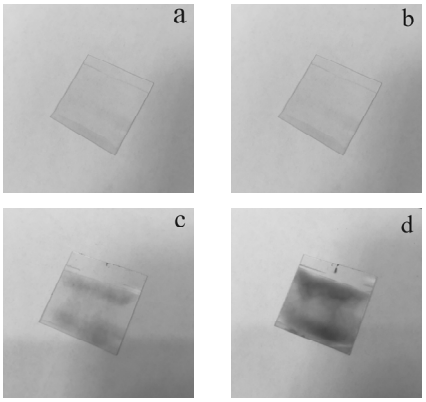

Fig. 2. Digital photos of the samples with different number of deposition cycles of CuO: a - sample with TiO2; b - 7 cycles of CuO with TiO2; c - 14 cycles of CuO with TiO2; d - 21 cycles CuO with TiO2

As can be seen from the presented digital photos, samples of the TiO_2-CuO darken with an increase in the number of deposition cycles. However, it can be seen that the deposited CuO layer is not uniform. Therefore, it is necessary to work off the methodology for the SILAR process.

The surface morphology of the formed TiO_2-CuO samples were studied using SEM, and the results are presented in Figure 2. On the surface of the sample TiO_2-CuO that has passed 7 depositional cycles the nanoparticles with a size of 30 nm can observe. The increase of the number of cycles leads to the size of CuO nanoparticles increases, and at 21 deposition cycles, the size of nanoparticles can reach 0.5 μm. However, the nanoparticles for the sample that has passed 14 deposition cycles, more densely placed, which can adversely affect the photocatalytic activity.

An SEM cross section image of the TiO_2-CuO sample was also obtained. Using such SEM image titanium oxide layer thickness was estimated (Fig. 3). As can be seen from the obtained image, the thickness of the deposited layer of TiO_2 is about 1 μm.

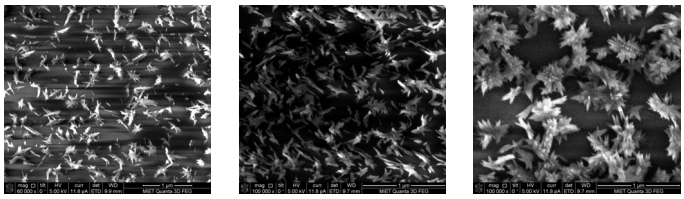

Fig. 3. SEM images of the TiO2-CuO samples with different number of nanoparticle deposition cycles using the SILAR method: 7, 14 and 21, respectively

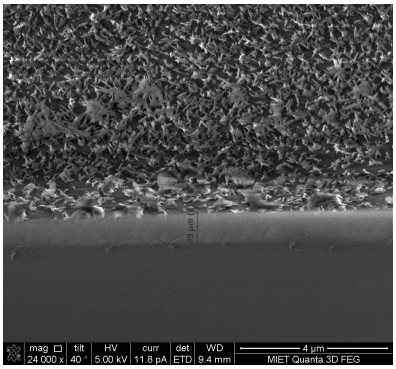

Fig. 4. SEM image of the cross section sample of the TiO2-CuO with 14 cycles of deposition of the CuO nanoparticles using the SILAR method

Figure 5 shows the Raman spectrum of a CuO sample that has passed 60 cycles deposition of the nanoparticles CuO using the SILAR method and is thermal treated on air for two hours at a temperature of 300 ºC. As can be seen on the obtained Raman spectrum, three combination peaks are observed at 282, 330, and 616 cm^{-1}, which correspond to the stoichiometry of copper oxide CuO [6].

To estimate the photocatalytic activity of the TiO_2-CuO samples, the decomposition kinetics of methylene blue in aqueous solution were obtained. The obtained ratios of C_t/C_0 (Fig. 6).

As can be seen from the obtained data, an increase in the number of deposition cycles does not have the straight correlation to photocatalytic activity. However, it can be stated that modification of the TiO_2 surface with CuO nanoparticles leads to an increase in photocatalytic activity. The sample TiO_2-CuO that has passed 21 deposition cycles of CuO has the highest photocatalytic activity. At the same time, it can be observed that the photocatalytic activity of samples that have passed 7 and 14 deposition cycles does not practically differ. However, a sample that has passed 7 cycles of deposition demonstrates a slightly higher efficiency of methylene blue decomposition than a sample with 14 cycles of deposition of CuO nanoparticles.

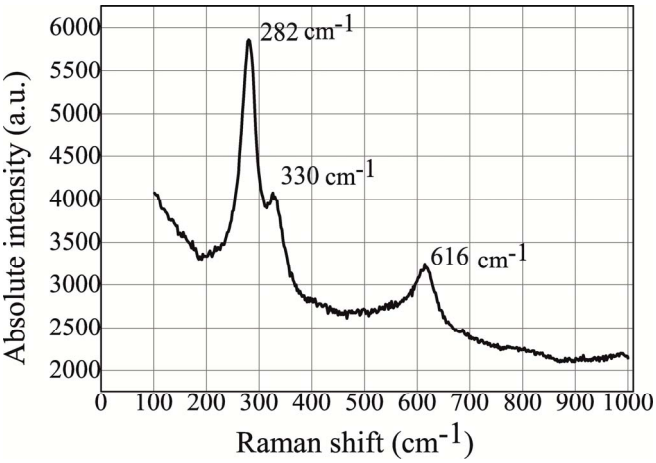

Fig. 5. Raman spectrum of the sample nanoparticles CuO that passed thermal treated at 300 ° C for 2 hours

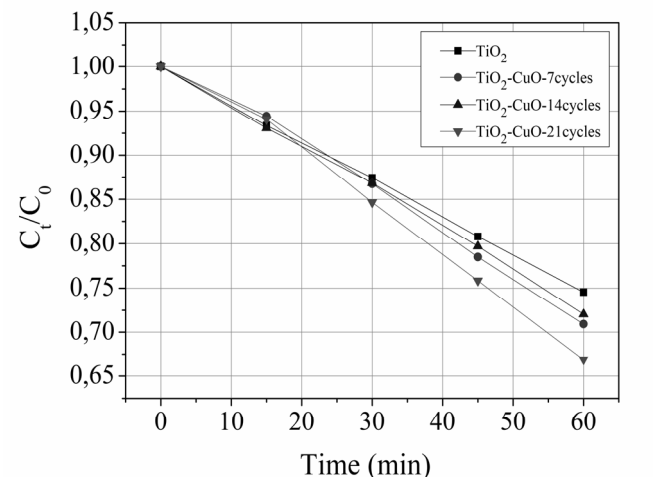

Fig. 6. Kinetic plots for the photocatalytic degradation of methyl blue by samples TiO2-CuO

To estimate the efficiency of the decomposition of methylene blue by the obtained samples of TiO_2-CuO, the reaction rate constants were calculated. Figure 6 shows a histogram of the methylene blue decomposition reaction rate constants for samples with 0, 7, 14, 21 cycles of CuO deposition. As can be seen from the presented histogram (Fig. 7), the highest reaction rate constant value for the methylene blue decomposition reaction (0.0068) corresponds to the sample that has passed 21 cycles of deposition of CuO. The lowest value of reaction rate constant corresponds to a sample with a TiO_2 layer without CuO nanoparticles. For the samples with 7 and 14 deposition cycles of nanoparticles CuO, the value of reaction rate constants is 0.0058 and 0.0054, respectively.

From the obtained data, it can be concluded that the densely placed of the CuO nanoparticles on the surface of TiO_2 can adversely affect the photocatalytic activity of such a structure. At the same time, from the selected deposition parameters of TiO_2 layer, CuO nanoparticles using the SILAR method and their annealing procedures is hard to determine the true optimum for their morphology and structural features to obtain

the highest photocatalytic activity. Thus, the current study should be continued further.

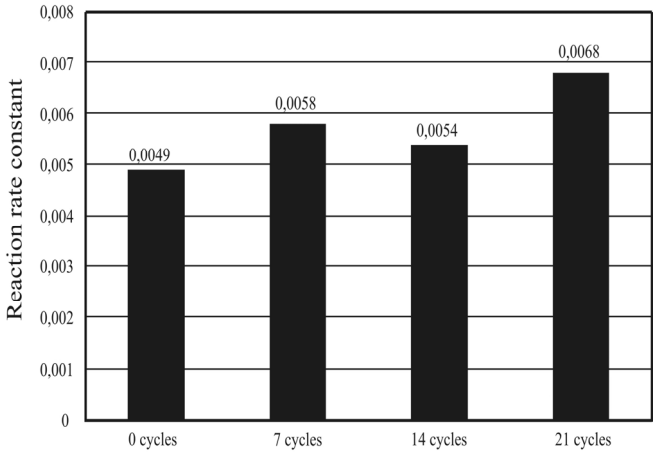

Fig. 7. The values of reaction rate constant for the decomposition of methylene blue for TiO2-CuO samples that have passed 7, 14 and 21 cycles of the deposition of CuO nanoparticles using the SILAR method and the sample with the TiO2 layer on a glass substrate without CuO nanoparticles

IV. CONCLUSIONS

In the present work, a comparative analysis of the TiO_2-CuO samples with different deposition cycles quantity of CuO and the sample the TiO_2 without CuO was performed. It was determined that with an increase in the number of deposition cycles, the size of CuO nanoparticles increases to about 0.5 microns with a 21 deposition cycles. It was revealed that with an increase in the number of deposition cycles of nanoparticles CuO, the photocatalytic activity of TiO_2-CuO samples increases. However, it can be concluded that the optimum ratio between the area of CuO nanoparticles in contact with TiO_2 surface and free TiO_2 surface in contact with the polluted solution. To achieve the optimal size and distribution of the CuO nanoparticles on the TiO_2 surface it is necessary to investigate the dependences of photocatalytic activity from TiO_2-CuO heterostructure parameters further.

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