

# Synthesis and Photo-Catalytic Activity of Nanoparticles with Structure "Core/Shell": $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$

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## Abstract

In this work, the nanosized magnetic  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  photocatalyst was prepared by sol-gel methods. First the nuclei of magnetite nanoparticles were prepared by co-precipitation of iron (II&III) salts solutions. Secondly, the magnetite nanoparticles were dispersed in ethanol using sonication, and solutions of both ammonia and tetraethoxysilane were added to the suspension under intense stirring, since it was suggested that the introduction of an intermediate passive  $\text{SiO}_2$  layer between the  $\text{Fe}_3\text{O}_4$  and  $\text{TiO}_2$  phases inhibits the direct electrical contact and hence prevents the photodissolution of the magnetite phase and deterioration of the surface photocatalytic properties. Finally, solution of tetrabutoxytitanium was added dropwise to the mixture of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles under sonication & intense stirring. The resulting particles were separated using a magnet, washed and dried to constant weight, the yield was 70%. The photocatalytic activity of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  nanoparticles was investigated by photodegradation of methyl orange in aqueous solution under UV light irradiation. The photodegradation dynamics revealed that even though the oxidation rate decreases over time, about 90% of methyl orange is oxidized during the first 35 min.

## 1. Introduction

Since the beginning of the titanium dioxide ( $\text{TiO}_2$ ) industrial production in early 20<sup>th</sup> century, it has been widely used as a pigment and filler [1] in sunscreens, paints, ointments, toothpastes, etc [2]. In 1972 Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water under ultraviolet radiation on an electrode coated with titanium dioxide [3]. Further studies have made it possible to determine many promising directions for the use of materials based on  $\text{TiO}_2$  in various fields: from photovoltaics/photocatalysis to photoelectronics/sensors [4]. One of the promising practical applications of  $\text{TiO}_2$  and  $\text{TiO}_2$ -based nanocomposites is purification of water by way of oxidation reaction (photodegradation) of organic pollutants with peroxide anion-radicals formed under ultraviolet radiation in the process of photocatalysis [3].

Titanium dioxide occurs in nature as the well-known minerals rutile, anatase and brookite. The main crystallographic forms of  $\text{TiO}_2$  are rutile, anatase and brookite- the minerals occurred in nature.

Only anatase and rutile forms possess photocatalytic activity, with anatase is reported to be more photocatalytically active compared to rutile [5].

The first magnetic photocatalyst was designed by Hiroshi et al. and was prepared through the deposition of titanium dioxide onto a magnetite core in 1994 [6]. The direct contact between the magnetic particles and photocatalysts leads to the photogenerated electron-hole recombination and the photodissolution of the  $\text{Fe}_3\text{O}_4$  magnetic particles under the UV-irradiation.

The photogenerated holes at the valence band of the  $\text{TiO}_2$  semiconductor are transferred to the valence band of the  $\text{Fe}_3\text{O}_4$ , while the photogenerated electrons move to the conduction band of the magnetic core. The transfers in the direct contact prevent the photogenerated electrons from reaching the  $\text{O}_2$  molecules. As a result, the radicals  $\text{O}_2^-$  cannot be formed. Similarly, the photogenerated holes can oxidize neither the organic molecules nor the water adsorbed to hydroxyl radicals, therefore, the direct contact core/shell catalysts have low activities [7].

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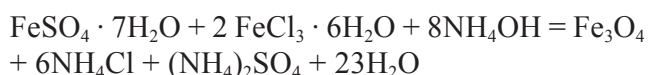
To overcome the drawbacks of the low activities and the photodissolution, Cao and Chen pioneered a three-component magnetic photocatalyst of c-Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> in 1999, in which c-Fe<sub>2</sub>O<sub>3</sub> was used as the magnetic core, SiO<sub>2</sub> interlayer as insulator, and TiO<sub>2</sub> as photocatalytic shell [8].

The resulting magnetic photocatalysts did not only gain the activity comparable to the pure titania but could also be repeatedly reused using the external magnetic force for recovery.

Therefore, it is necessary to develop photocatalysts with separation function for reusable and cyclic application. The concept of magnetic photocatalysts with separation function was raised to benefit from high activity and enable nanosemiconductor photocatalysts to be reused [8]. In addition, the photocatalysts can be immobilized with various metals to obtain a synergistic effect in enhancing their effectiveness [9].

## 2. Experimental part

To obtain magnetite particles, a sol-gel method was used in the work. Formally, the following equation can be used to calculate the mass balance and the ratio of reagents (amounts of iron and ammonia crystal hydrates):



23.35 grams of ferric chloride hexahydrate (FeCl<sub>3</sub> · 6H<sub>2</sub>O) and 12 g of ferrous iron sulfate heptahydrate (FeSO<sub>4</sub> · 7H<sub>2</sub>O) were dissolved in 650 ml of distilled water in an Erlenmeyer flask at 70 °C. 5.5 ml of a 25% ammonia solution were slowly added to the resulting solution with vigorous stirring on a magnetic stirrer for 30 min (Fig. 1a). The obtained magnetite nanoparticles were isolated from the solution using a permanent magnet. For applying a silicon dioxide layer, 1 g of pre-grind dry magnetite was introduced into a round-bottomed flask, a mixture of 50 ml of 96% ethanol and 10 ml of distilled water was added. The flask with the mixture was placed in an ultrasonic bath (ElmaElmasonic S10H), for a better mixing, a mechanical stirrer was also used. The contents of the flask were suspended for 20 min, then 1.5 ml of an aqueous ammonia solution was added to the mixture. After 40 min, a solution of 1.56 g of tetraethoxysilane in 19 ml of 96% ethanol was slowly added to the mixture over a period of 1 h, the suspension was continued for a further 24 h. The suspension was

decanted, the resulting particles were isolated from the solution with a magnet, then again resuspended once in 50 ml of aqueous ethanol, the precipitated particles were dried at 60 °C to constant weight.

To deposit a layer of titanium dioxide (Fig. 1b), 1.01 g of the obtained nanocomposite composition of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> were introduced into a round bottom flask, 150 ml of distilled ethyl alcohol (96.6%) and 200 ml of absolute alcohol (99.5%) were added. The mixture was dispersed by vigorous stirring and simultaneous ultrasonic treatment as described above. After 30 min of stirring, a solution of 17 ml of freshly distilled tetrabutoxytitanium in 300 ml of absolute alcohol was added dropwise to the mixture. The mixture was left for 12 h in an ultrasonic bath with vigorous stirring. The resulting particles were separated from the mother liquor using a magnet, washed with distilled water and dried to a constant weight. The yield of the product was 70%. To transfer the amorphous TiO<sub>2</sub> layer to the anatase phase, the resulting nanocomposite, the composition Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> was calcined at 450 °C for an hour under an argon atmosphere.

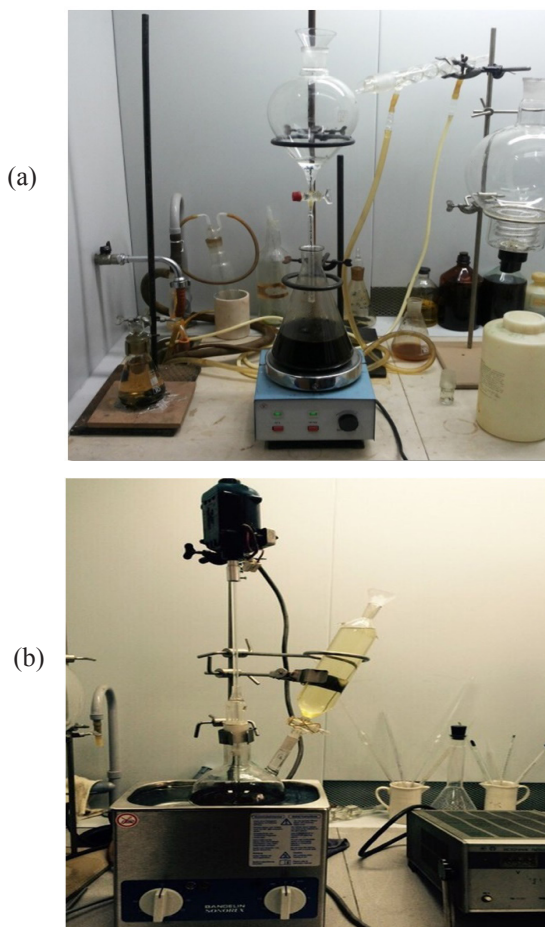


Fig. 1. Installations for the synthesis of nanoparticles: (a) – the production of magnetite; (b) – deposition of a TiO<sub>2</sub> layer on nanoparticles of the composition Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.

The photocatalytic activity of nanoparticles of the composition  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  was studied using oxidation of an aqueous solution of methyloange under the UV radiation. Five mg of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  composite were added in five quartz tubes with a 5 ml solution of methyloange (0.01 mol/l). One tube with a solution of methyloange, without a catalyst, was used as a control. The contents of the tubes were suspended in an ultrasonic bath. A tripod with test tubes was installed at a distance of 10 cm from a standard medical lamp for quartz (YZ25WT) and irradiated with constant mixing of the solutions by bubbling air through the capillaries. The concentrations of methyloange were determined by UV spectroscopy on a Jenway 6705 instrument from measurements of optical density at 650 nm at 10, 20, 35, and 50 min.

### 3. Results and discussion

From the X-ray diffraction patterns shown in Fig. 2, it follows that as a result of the deposition of silicon dioxide, the original magnetite has not changed (Fig. 2a).

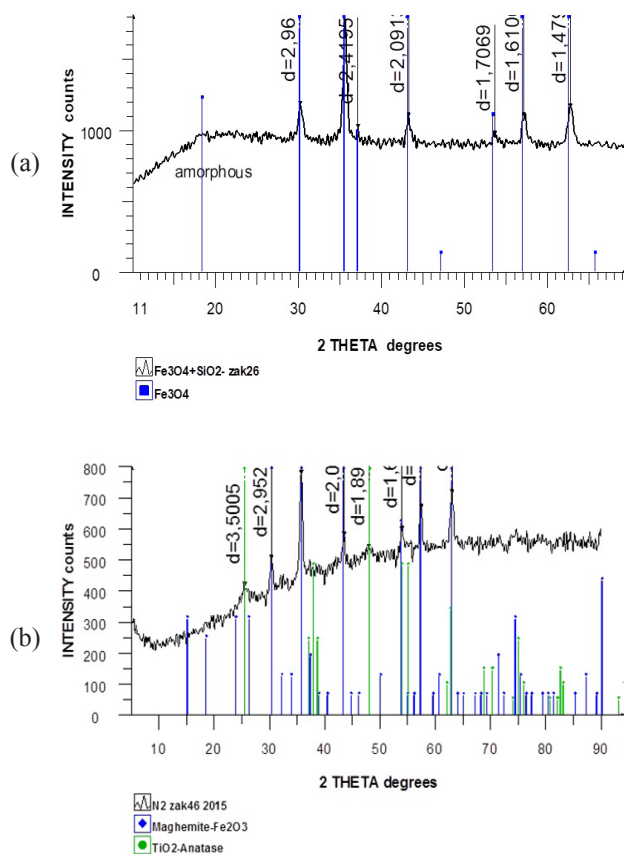
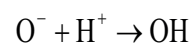
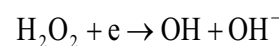
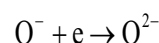
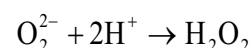
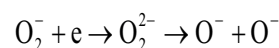
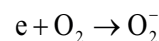


Fig. 2. Diffractograms of the samples: (a) –  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ; (b) –  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  calcined at 450 °C.

When the nanopowder  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  is heated at 450 °C, a system is formed in which titanium dioxide has an anatase modification (Fig. 2b). Electrons and holes trapped by the surface of titanium dioxide are extremely reactive. Thus, when an electron reacts with atmospheric oxygen, the following reactions take place [10, 11]:



In this case, powerful oxidizing agents such as the OH and OH radicals are formed, capable of oxidizing any organic compound. Magnetic particles were coated with silicon dioxide to create a dielectric layer and prevent interaction between a layer of titanium dioxide and a core of magnetite, because otherwise, in the process of photoexcitation, a heterojunction of electrons is observed, which leads to the redistribution of electrons/holes, and there is a transition of photogenerated holes into the phase of iron oxide, as a result of which gradual oxidation of magnetite and destruction of the nucleus, and also deteriorate photocatalytic properties of the surface [12].

Figure 3 shows the images of the obtained samples obtained with the help of TEM.

Statistical processing of images of samples of the sol-gel obtained by the magnetite method shows that the particles have a spherical structure and a size in the range of 10–20 nm. The thickness of the silicon dioxide layer covering magnetite is in the range of 6–10 nm (Fig. 3b).

Figure 4 shows the dynamics of oxidation of a solution of methyloange under the influence of UV radiation in the presence of a synthesized magnetic photocatalyst.

It is seen from the presented graph that the oxidation rate of methyloange is slowing down however the main amount of methyloange (more than 87%) is oxidized within the first 35 min. Thus, it is shown that the resulting composite nanoparticles exhibit photocatalytic activity.



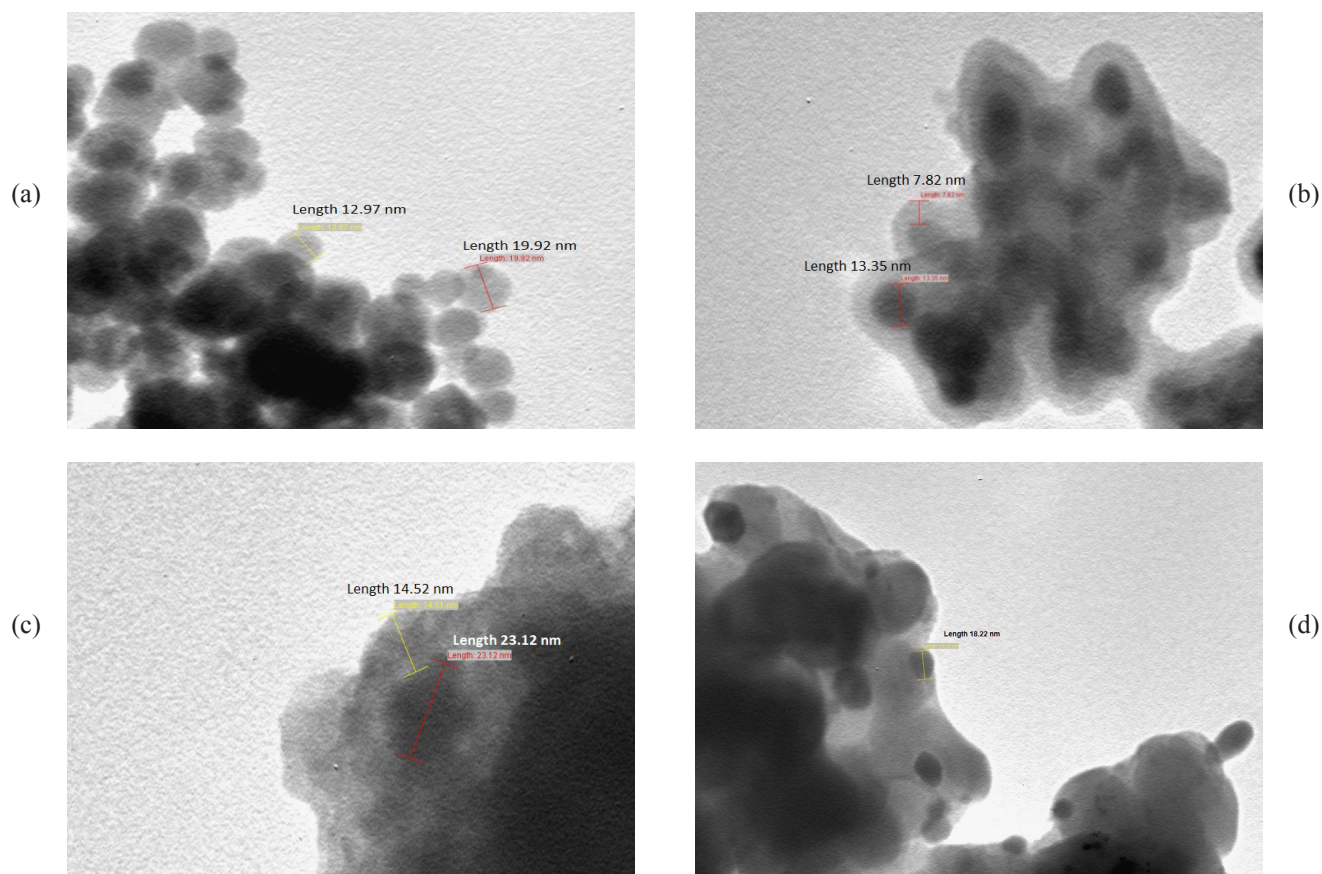


Fig. 3. Photographs of the obtained nanoparticle samples obtained with the help of TEM: (a) – magnetite; (b) –  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ ; (c, d) –  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{TiO}_2$ , calcined at 450 °C.

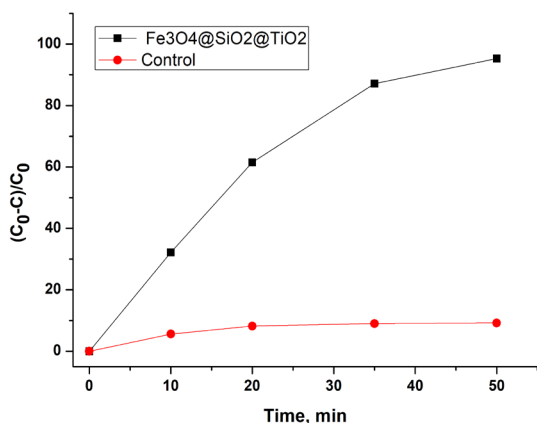


Fig. 4. Kinetics of oxidation of methylorange in the presence of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{TiO}_2$  nanoparticles under the UV radiation.

#### 4. Conclusion

According to the methods presented in the paper, particles of magnetite 10–20 nm in size, coated successively with silica layers, and then with titanium dioxide, were obtained. As a result of

calcination of the obtained nanoparticles  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{TiO}_2$  at 450 °C, titanium dioxide from amorphous passes into the crystalline phase of anatase. The nuclei synthesized after application of the layers and calcination remain superparamagnetic and can easily be recovered from the suspension by means of a magnet, which is convenient for the recuperation of the photocatalyst from solutions. It is established that the obtained nanoparticles exhibit photocatalytic activity and can potentially be used for purification from organic contaminants, in the form of suspensions and coatings.

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