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PHOTOLYSIS OF THE PHENOLIC SOLUTION IN THE PRESENCE OF TiO₂ NANOPARTICLES**E.M.Gadirova, I.R.Hasanova, G.S.Aliyeva, G.M.Eyvazova, M.M.Aghayev,
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TiO₂ nanoparticles have been prepared using sol-gel method from titanium(IV), isopropoxide, isopropyl alcohol, ammonia hydroxide as precursors at mild condition without any post heat treatment for crystallization. The nanocrystalline TiO₂ powders were composed of rutile form TiO₂ by X-ray diffraction. The size of nanoparticles was examined by transmission electron microscopy and is about 10–15 nm, and the Brunauer-Emmett-Teller specific surface area of the rutile nanopowder makes up 159.6 m²/g. Photochemical degradation of phenol solution under ultraviolet irradiation of the synthesized TiO₂ nanoparticles has been carried out.

Keywords: nanoTiO₂, phenol, photocatalytic process, X-ray diffraction, transmission electron microscopy.

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Introduction

TiO₂ is an environmentally friendly optical semiconductor material. It has broad application value in many areas due to its excellent structural, optical and chemical properties. The photocatalytic process nanoTiO₂ converts light energy into electrical or chemical energy under mild conditions.

To date, photoluminescent titanium dioxide (TiO₂) has been the most effective and useful photocatalyst used for basic practical applications due to its highly efficient, photochemical stability, non-toxic nature and low cost [1, 2]. Many studies have been carried out to study the photocatalytic activity of the photoluminescence of TiO₂ nanoparticles [3–5]. The mechanism of the photocatalytic activity of nano-TiO₂ has been widely studied in the literature [6–8].

When absorbing light energy, the excited electrons of TiO₂ create (e⁻) and (h⁺) pairs. These charge carriers can quickly migrate to the surface of the catalyst particles, where they are eventually captured and subjected to redox reaction by suitable substrates. Thus, a trapped hole can interact with chemisorbed OH⁻ or H₂O to form OH radicals [9, 10]. Oxygen, which is present in the system, acts as an effective electron absorber. In addition, any other oxidizing

agent, such as OH⁻, can capture electrons [11].

Photoluminescence of nano TiO₂ has many applications in many areas, including photocatalysis, agriculture, solar cells that are sensitive to dyes, and biomedical devices [12–14].

Photoluminescence of nano TiO₂ continues to attract the attention of agricultural researchers due to its favourable physico-chemical properties, low cost, availability and high stability [15]. Thus, photoluminescence of nanoTiO₂ has many applications in agriculture, including the degradation of pesticides, plant protection etc. [16].

The photocatalyst TiO₂ attracts attention for use in the water purification from organic pollutants due to its low toxicity and environmentally friendly properties. In recent years, pollution of water basins has become a serious problem. Methods of biological, chemical, and physicochemical water purification are often ineffective or environmentally incompatible. The photocatalytic effects of nanoTiO₂ on water molecules cause the formation of hydroxyl radicals and reactive oxygen species. Such highly reactive particles attack organic pollutant molecules, leading to their degradation.

In this paper, well crystallized nanoTiO₂ powders have been prepared by a mild sol-gel method from titanium(IV) isopropoxide (TTIP),

isopropyl alcohol, ammonia hydroxide as precursors under mild condition without any post heat treatment for crystallization. The photocatalytic performance of the synthesized powders was evaluated by degradation of phenol in aqueous solution under UV light irradiation.

Experimental part

NanoTiO₂ powders have been prepared by a mild sol gel method from titanium(IV) isopropoxide, isopropyl alcohol, ammonia hydroxide as precursors in mild conditions without any post heat treatment for crystallization. Technical grade TTIP, isopropyl alcohol, NH₄OH were used as received and without any further purification. In a typical synthesis process, titanium(IV) isopropoxide at vigorous stirring was previously dissolved in isopropyl alcohol. Then dropwise was added (without stopping stirring) - an aqueous solution of NH₄OH taken in two-fold excess. After that, the resulting suspension was set to stir for three hours. To complete the gel formation process, the samples were kept at room temperature for seven days. The precipitate was separated from the liquid phase on a porous glass filter. To clean the samples from soluble impurities, the gels on the filter were washed twice with alcohol and acetone, then dried at a temperature of 50°C in a drying apparatus.

The synthesized white powders were characterized by X-ray diffraction, Brunauer-Em-

mett-Teller (BET) analysis, Transmission electron microscopy (TEM). The photocatalytic activity of prepared TiO₂ nanopowders was examined by photodegradation of phenol in aqueous solution under 200~650 nm visible light irradiation with illuminant intensity of 15.54 mW/cm. Firstly, preliminarily sonicated water solution containing 0.05 g of TiO₂ nanopowders were mixed with 100 mL of phenol aqueous solution with a concentration of 15 mg/L. The suspension was stirred in the dark for 2 h to reach the balance of adsorption/desorption. Then, the light was turned on to start photodegradation. The suspension was sampled at an intervals of 15–20 min and centrifuged to remove the TiO₂ nanoparticles. The concentration of phenol was measured on a UV-Visible spectrophotometer (Varian) at the wavelength of 270 nm to obtain the absorbance of the solution.

Results and discussions

In the sol-gel process forms the colloidal suspension, or sol by the hydrolysis and polymerizing reactions of TTIP precursor substance. Complete polymerisation or solvent removal converts the liquid sol to a solid gel phase. TiO₂ nanostructures are synthesized by the sol-gel method by the hydrolysis of titanium(IV) isopropoxide. This process usually proceeds through hydrolysis of titanium(IV) isopropoxide, followed by condensation of formed Ti(OH)₄:

The development of the chain of Ti–O–Ti bonds is promoted by a low water content (low

level of hydrolysis) and an excess of titanium alkoxide in the reaction mixture. The formation

of chains leads to the formation of a three-dimensional polymer structure with a short degree of order. The high rate of hydrolysis contributes to the formation of $\text{Ti}(\text{OH})_4$, which interrupts the development of the chain $\text{Ti}-\text{O}-\text{Ti}$. The presence of a large number of $\text{Ti}-\text{OH}$ groups and the low development of a three-dimensional polymer structure leads to a low degree packing of particles. The purity and crystalline properties of the TiO_2 nanoparticles were investigated by powder X-ray diffraction (XRD) method. Figure 1 shows the XRD patterns of the synthesized TiO_2 nanopowders. All the XRD peaks were well defined and corresponded to TiO_2 at rutile phase. From the line broadening of the (101) diffraction peak by Scherrer's method, the average crystal size TiO_2 is about 10.3 nm. The specific surface area

as for TiO_2 is $159.6 \text{ m}^2/\text{g}$. In the pattern all lines can be indexed, using the ICDD (PDF-2/ Release 2011 RDB) DB card number 00-001-1292. The pattern of TiO_2 nanopowder has characteristic peaks at 27.90° (110), 36.01° (101), 41.58° (111), 54.71° (211).

The prepared TiO_2 nanopowders were analysed by TEM method, and the results are presented on Figure 2. As it seen from Figure 2 the obtained nanopowder grain sizes are homogeneous and varies in the range from 10 to 20 nm. The data of TEM analysis very well correlates with the results, obtained from XRD analysis. Figure 2 shows the TEM micrograph TiO_2 nanopowders. The particles are spherical in shape and 10–20 nm in size, which is consistent with the results calculated by Scherrer's method.

Fig. 1. XRD patterns of the TiO_2 nanoparticles.

Fig. 2. TEM micrograph of synthesized TiO_2 powders.

The process of photocatalytic degradation of phenol and its derivatives from water resources carried out by TiO_2 nanoparticles is based on the formation of highly active OH radicals, which are capable of converting phenolic derivatives into relatively harmless final products. However, the limitations of the widespread use of TiO_2 semiconductors for photocatalytic degradation of phenolic derivatives include high electron-hole recombination rates, a wide forbidden gap, and ineffective catalysts for collecting visible light. Minimization of electron-hole recombination and the effective excitation of visible light are the main

problems that increase the photocatalytic efficiency of phenol degradation [17, 18].

As it seen from UV absorption spectra shown on the Figure 3 of degradation of 15 mg/L phenol solution containing 0.05 g of TiO_2 nanopowders, the deeper degradation proceeds with increasing of irradiation time.

A quantitative analysis of treated samples after photolysis was carried out on a 6890N GC-MSD gas chromatograph with an Agilent 5975 high-performance mass-selective detector manufactured by Agilent Technologies (USA). During the analysis of samples used solvents with chromatographic purity [19] (Figure 4).

Fig. 3. UV-Vis absorption spectra of phenol degradation with 0.05 g TiO_2 nanopowders at pH 6 depending on the irradiation time, min: 1 – 0, 2 – 15, 3 – 30, 4 – 90, 5 – 120, 6 – 240.

Fig. 4. GC-MSD – mass spectra of phenol solution after photochemical degradation.

Water samples were extracted in a separatory funnel. Prior to extraction, the pH value of the samples is reduced to $\text{pH} < 4$. As an internal standard, two deuterated polycyclic aromatic compounds naphthalene-d8 and phenanthrene-d10 were added to all samples. Extraction was carried out three times. The obtained extracts were combined in round-bottom flasks and first concentrated on a rotary evaporator at a water bath temperature of $35 \pm 5^\circ\text{C}$ to a volume of 5 ml, then under a thin stream of nitrogen. Concentrated extracts were transferred to 1ml samplers.

The phenol degradation was calculated using quantitative analysis, carried out on a 6890N GC-MSD gas chromatograph with an Agilent 5975 high-performance mass-selective detector. The photodegradation of phenol in the presence of TiO_2 nanopowder made 82%.

Conclusion

TiO_2 nanopowder have been prepared using sol gel method from Titanium(IV) isopropoxide, isopropyl alcohol, ammonia hydroxide as precursors at mild condition without any post heat treatment for crystallization. The nanocrystalline TiO_2 powders were composed of rutile form TiO_2 by XRD. The size of nanoparticles was examined by TEM analysis and is about 10–15 nm, and the BET specific surface area of the rutile nanopowder makes $159.6 \text{ m}^2/\text{g}$. Was carried photochemical degradation of phenol solution under UV irradiation by application of the photocatalytic performance of the synthesized nanopowders. The phenol degradation was calculated using quantitative analysis, carried out on a 6890N GC-MSD gas chromatograph with an Agilent 5975 high-performance mass-selective detector. The photodegradation of phenol in the presence of TiO_2 nanopowder made 82%.

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TiO_2 NANOHISSƏCİKLƏRİ İŞTİRAKINDA FENOL MƏHLULUNUN FOTOLİZİ

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TiO_2 nanohissəciklər zol-gel üsulu ilə mülayim şəraitdə titan(IV) izopropoksid, izopropil spirti və ammonium hidroksiddən heç bir temperatur faktoru olmadan alınmışdır. TiO_2 nanokristallarının quruluşu rentgen quruluş analizi ilə sübut edilmiş, ölçülərinin şəffaf elektron mikroskopu ilə 10–15 nm arasında olması tədqiq edilmiş, nanohissəciklərin ümumi səth sahəsi isə $159.6 \text{ m}^2/\text{g}$ təşkil etmişdir. Alınmış TiO_2 nanohissəciklərinin fenol məhlulunun ultrabənövşəyi şüalanmaya əsasən fotokimyəvi parçalanması aparılmışdır.

Açar sözlər: TiO_2 -nanohissəcikləri, fenol, fotokatalitik proses, rentgen faza analizi, şəffaf elektron mikroskopu.

ФОТОЛИЗ ФЕНОЛЬНОГО РАСТВОРА В ПРИСУТСТВИИ НОНОЧАСТИЦ TiO_2

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Наночастицы TiO_2 получены из изопропоксида титана(IV), изопропилового спирта, гидроксида аммония с использованием золь-гель метода. Реакция продолжалась в мягких условиях без какой-либо термической обработки. Получение наночастиц TiO_2 было доказано методом рентгенофазового анализа. Размер наночастиц был исследован с помощью просвечивающей электронной микроскопии и составил около 10–15 нм, а удельная площадь поверхности нанопорошков – $159.6 \text{ м}^2/\text{г}$. Проведена фотохимическая деградация раствора фенола под действием ультрафиолетовых лучей с применением наночастиц TiO_2 .

Ключевые слова: TiO_2 -наночастицы, фенол, фотокаталитический процесс, рентген фазовый анализ, просвечивающая электронная микроскопия.