

Modern Photoactive Nanocomposites Based on TiO₂ and CeO₂

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The unique surface, optical and photocatalytic properties of nanomaterials based on various oxide nanoparticles have found wide application in wastewater treatment. In a number of modern scientific studies, bioactive catalysts based on TiO₂, which exhibit redox activity in water purification, were considered. The presented structures based on titanium dioxide, formed in binary and ternary systems in the presence of silver and cerium with a different degree of crystallinity were obtained by the chemical precipitation method using titanium tetraisopropoxide (TTIP) as a precursor species. XRD data confirmed a homogeneous composition of powders formed in binary systems (anatase with clusters of Ag and CeO₂) with CSR in the range of 9-20 nm. It was stated that in ternary systems, with an increase in the content of doping components, *d* spacing (101) of anatase's lattice shifted to the right, and the degree of tetragonality increased to 2.53. Raman results showed that the most intense band of *E_g* mode for doped samples TiO₂ was shifted from 144 to 152 cm⁻¹ compared to anatase dependence on the noble metal concentration. The features of the silver-ceria and silver – titania interactions are connected with the size effects of both Ag and CeO₂ particles, concentrations of oxygen vacancies in the ceria structure, and possible redox properties due to the interplay between Ag⁺/Ag⁰ and Ce³⁺/Ce⁴⁺ pair (PL) and a Schottky barrier between the metal and TiO₂ and photoexcited electrons in the semiconductor are trapped by Ag nanoparticles. It was shown that the ternary composite TiO₂ & CeO₂ & Ag (2 wt. %) has improved photocatalytic activity due to the inclusion of CeO₂ in the crystal lattice of anatase, which is confirmed by an increase in the degree of tetragonality of the lattice and prevention of oxidation of silver clusters on the surface of anatase under the influence of UV irradiation. These photocatalysts will be a perspective to the hydrogen synthesis technology.

Keywords: Photocatalysis, UV irradiation, Optical activity, Ag, Malachite Green, Discoloration.

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1. INTRODUCTION

Nowadays, TiO₂ nanoparticles have long-term chemical stability, photo-corrosion resistance, strong oxidative properties at ambient temperature and pressure, convenient physical, optical properties, and availability [1]. Additionally, nanosized TiO₂ and its composites are the most promising photocatalytic active materials; some semiconducting and bioactive catalysts based on TiO₂, which have a redox function in water purification, are introduced [2]. Photocatalysis of metal-oxide nanomaterials is a fast and effective strategy for environmental remediation. The study of the morphological architecture of photocatalyst and its properties has significance for the design of stable optical active materials. As such, numerous TiO₂ and Fe₃O₄ photocatalysts have been studied and the results are presented in publications [3] for the treatment of the different contaminants of emerging concern, such as azo-dyes, pharmaceutical pollutants, etc. Over the last few years, the varied synthesis methods (hydrothermal, sol-gel, ultrasonic treatment and etc.), including shape, size, facet control, and element doping have been developed to enhance the photocatalytic activity of metal oxide nanocomposites due to the stability, increasing their capacity for broad absorption of sunlight, and prolongation the lifetime of photoinduced carriers [4-6]. The authors demonstrated that noble metal NPs (Ag, Au, and Pt) do not only absorb visible light but can also serve as electron sinks and as a source of active reaction sites. The photo-generated electron-hole pairs can be separated and the

carriers can be transported efficiently at the interfaces of the metal-TiO₂ system under irradiation [7-8]. The comparative study of the optical properties of nanocomposite thin films TiO₂ & Au and TiO₂ & Ag showed the higher activity of aurum-containing structures because of the differences in instinct properties of noble metals. Gold forms very small dispersed atomic aggregates (clusters) on the TiO₂ surface, while silver forms visible clusters with an average diameter of about 13 nm. Ag-doped TiO₂ nanoparticles showed characteristic photoluminescence (PL) corresponding to the visible spectral range with excitation at 325 nm. The intensity of luminescence emission decreased with doping of silver ions due to decreasing bandgap TiO₂ from 3.2 to 2.7 eV [9]. We have focused on TiO₂ and its nanocomposites due to the following reasons, such as TiO₂ stability in a wide pH range of 0÷14, quantum-dimensional effects because of Mott-Wannier exciton radius depending on the TiO₂ surface area, crystallites size, and the short time migration of photogenerated charges from the bulk of the particles the surface under UV light. However, pure TiO₂ (anatase) has intensive photoluminescence due to autolocalized excitons recombination. Some surface, optical properties of TiO₂ and CeO₂ nanocomposites with metal nanoparticles were presented in [10].

In the present study, hybrid optically active metal-oxide nanocomposites were prepared and the concentration of noble metal was optimized for the photocatalytic removal of malachite green as a model pollutant.

2. EXPERIMENTAL

Synthesis of the nanocomposite powders were performed via the co-precipitation method of cerium nitrate (Sigma-Aldrich, Shanghai, China) and TTIP (titanium tetraisopropoxide) (Acros Organics, NJ, USA) solutions with a low concentrated argentum nitrate (Sigma-Aldrich, Shanghai, China) solution in an alkaline (Sigma-Aldrich, Shanghai, China) medium by the presence of nucleating and reducing agents. The weight ratio of argentum was set in the range from 0 to 4.0 wt. %. Synthesis of TiO_2 and TiO_2 & Ag powders were performed [10]. Additionally, gold particles were deposited on the anatase surface using the slow hydrolysis of TTIP with HAuCl_4 (Sigma-Aldrich, Shanghai, China) in water. The composition, CSR and lattice parameters for nanocomposites were performed by X-ray diffraction analysis (XRD) using the DRON-3 with $\text{CuK}\alpha$ anode. The optical properties of silver-doped cerium and titanium oxide nanopowders were shown by Raman spectroscopy using a Horiba Jobin-Yvon T64000 (Horiba, Shanghai, China) a device equipped with Ar-Cr laser at 488 nm. He-Cd laser was used at 325 nm for the PL study.

The photocatalytic activity of metal-oxide nanocomposite powders was tested using solutions of a synthetic diaminotriphenylmethane dye – Malachite Green (MG) $\text{C}_{23}\text{H}_{25}\text{ClN}_2$. The prepared sample of nanopowder (50 mg) was placed in a glass filled with 50 ml of an aqueous solution of MG (20 mg/dm^3). The mixture was stirred in the dark for 30 min until adsorption-desorption equilibrium was reached. After that, it was continuously stirred under UV light (254 nm, Bactosfera lamp) conditions. To prevent the negative impact of nano-sized particles that form colloidal stable sols in the MG solution the suspensions were centrifuged at 8 g for 30 min and the optical density of the colored solutions was measured at a wavelength of 540 nm. The degree discoloration of MG was calculated as in [6].

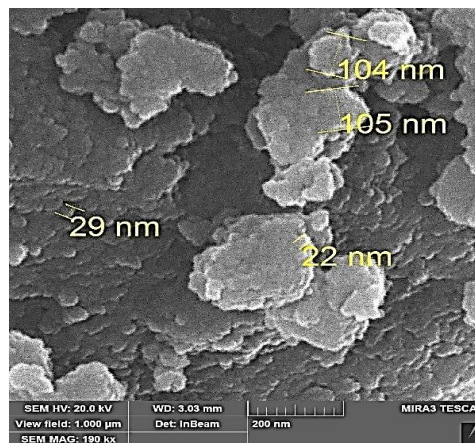
3. RESULTS AND DISCUSSION

The calculations of the elementary cell's parameters and the primary particle's size (CSR) indicate insignificant variations in the structure of the samples (Table 1). Besides, a parameter c , respectively, from 0.9468 nm for the TiO_2 & Au system (2.0 wt. %) to 0.9645 nm for the TiO_2 & CeO_2 system (4 wt. %).

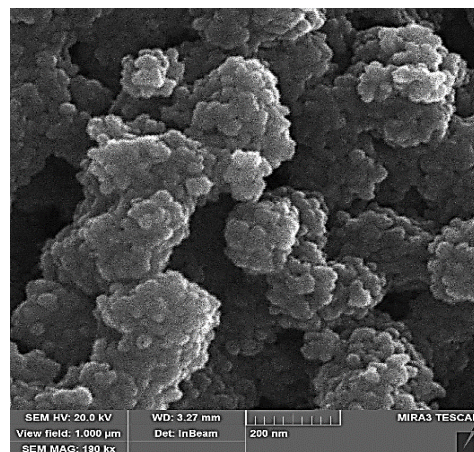
As such, for all other samples, there is a tendency to decrease the CSR with an increase in the content of the doping admixture. TiO_2 particles obtained without the introduction of dopants have a larger size (12.7 nm) compared to the size of the composite particles (8.3-10.3 nm). The obtained data are in good agreement with the results presented in the paper [11] where the size of pure TiO_2 particles obtained by co-precipitation method is larger (10-15 nm) compared to anatase particles doped with cerium (6-10 nm).

The tetragonality degree of the anatase's crystal lattice ($ca > 1$), obtained in the presence of Au or Ag aqua forms, ranges from 2.51 to 2.52, which corresponds to the ratio of the parameters of the standard sample of anatase (JSPDS No. 21-1272) and equals 2.51. For TiO_2 & CeO_2 composites with a dopant content of 2 and 4 wt.%, the

degree of tetragonality increases to 2.56 and 2.57, respectively, which indicates the inclusion of cerium into the anatase structure. The morphology of nanocomposite particles obtained in binary systems based on TiO_2 is presented in Fig. 1. SEM images indicate that nanoscale structures form loose aggregates; the introduction of Ag into the system contributes to an increase in the degree of crystallization of TiO_2 & Ag particles and the development of nanocrystal faces as in [10, 12-14].



(a)



(b)

Fig.1 – SEM images of TiO_2 -based nanocomposite: 2 wt. % CeO_2 (a), 4 wt.% CeO_2 (b)

Table 1 – XRD characteristics of nanocomposites TiO_2

No	System	c , nm	ca	CSR, nm	d_{101} spacing, nm
1	TiO_2	0.9479	2.51	12.7	0.35129
2	TiO_2 & Au (2 wt. %)	0.9468	2.51	20.0	0.35040
3	TiO_2 & Au (4 wt. %)	0.9512	2.52	18.2	0.35110
4	TiO_2 & A (2 wt. %)	0.9473	2.51	8.6	0,35060
5	TiO_2 & Ag (4 wt. %)	0.9451	2.51	8.3	0.34968
7	TiO_2 & CeO_2 (4 wt. %)	0.9645	2.57	8.5	0.34916
8	TiO_2 & CeO_2 & Ag (2 wt. %)	0.9486	2.52	10.3	0.35025

The composition and concentration of the doping additive affect the size of the unit cell and CSR, as well as the degree of crystallinity of the sample. The calculation of the degree of tetragonality shows that Au and Ag form small clusters on the surface of anatase particles, and CeO₂ clusters are included in the structure (matrix) of titanium dioxide. Nanosized particles of anatase-based composites form loose aggregates. The composition of samples in addition to the main elements includes small amounts of auxiliary substances.

Raman spectra of TiO₂ & Ag and TiO₂ & Au powders (Fig. 2) exhibit no other peaks for the brookite/rutile phase, which confirms that all powders are in a single anatase phase (correlation with XRD). The peak intensities at 142-147 cm⁻¹ were found decreasing whereas the width of the peak increased because of the lattice distortion and presence of defect levels. As such, the incorporation of Au with anatase helps to reduce the intensity and broaden the peaks at 510-520, 630-640 cm⁻¹, and 750-800 cm⁻¹. Since in the Raman spectra all oscillations move mainly oxygen atoms, the introduction of silver atoms changes the local coordination of oxygen around Ti⁴⁺. The doping by the silver to maintain charge neutrality creates oxygen vacancies in the TiO₂ lattice. If the silver ion replaces the Ti⁴⁺ ion during doping, the bonds of the Ti-O-Ti complex will be distorted and new bonds of the Ag-O-Ti or Ag-O-Ag complexes will be formed. It is well known, the doping with metal ions in the optimal concentration prevents the growth of TiO₂ nanocrystallites.

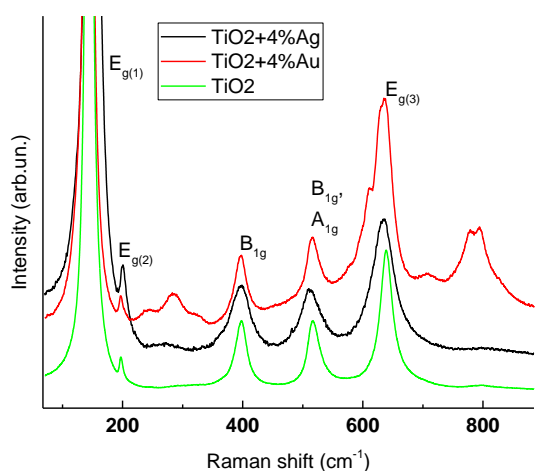


Fig. 2 – Raman spectra of nanocomposites TiO₂ & Ag and TiO₂ & Au

The spectrum of TiO₂ & Au (curve red color) is characterized by the appearance of peaks at 220-300 cm⁻¹ (multiphonon scattering); we suppose that metal Au is located on the surface of anatase but it does not exclude that Au can be partially incorporated into TiO₂ too. Doping of TiO₂ nanopowder with 2-4 wt. % of CeO₂ leads to some reduction in the intensity of all vibrational bands, with some broadening of the peaks with a small shift. The most intense band E_g is shifted in the high-frequency side from 144 to 146 cm⁻¹ compared to TiO₂ sample, while its half-width (FWHM) increases from 10 to 16 cm⁻¹. The reason for this is the oxides surface defects existence. Probably, the injection of oxide series contributes to the

dimensional effect.

A decrease in the peak's intensity of PL in the range of 390-400 nm and 550-600 nm (Fig. 3) is observed with the injection of a low concentration of silver (2 wt. %) in nanocomposite system of TiO₂ & CeO₂ & Ag compared to pure TiO₂ [10]. The silver injection helps to reduce the TiO₂ particles' size. Silver causes some changes in the molecular structure of TiO₂ sample, thereby reducing the band gap [4]. Therefore, we assume that the cations of argentum can be partially included in the crystal lattice of titanium dioxide and cause its deformation through the ionic radii of the cations Ti⁴⁺ (0.068 nm) and Ag⁺ (0.126 nm) in the synthesis process too. Such quenching help to increase lifetime of charges in the anatase electron structure during irradiation and improving the optical activity of nanocomposite system TiO₂ & CeO₂ & Ag. Besides, the features of the silver-ceria interaction are connected with the morphology and size effects of both Ag and CeO₂ particles, concentrations of oxygen vacancies in the ceria structure, and possible redox properties that are caused by the interplay between Ag⁺/Ag⁰ and Ce³⁺/Ce⁴⁺ pair.

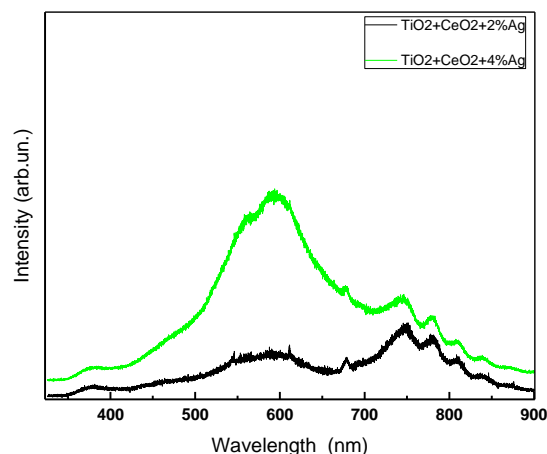


Fig. 3 – PL spectra of ternary system TiO₂ & CeO₂ & Ag

The results of the photocatalytic activity's study of titanium dioxide and TiO₂-based composites are presented in Fig. 4. In general, the positive effect of silver on the photocatalytic activity of nanocomposites based on TiO₂ is indicative. According to the degree of discoloration of the MG solution during 5 minutes of contact under the influence of UV irradiation, we obtain a row: TiO₂ & Au (2 wt.%) < Pure TiO₂ < TiO₂ & CeO₂ (2 wt.%) < TiO₂ & Ag (2 wt. %) < TiO₂ & CeO₂ & Ag (2 wt. %). From the obtained data, it can be assumed that the clusters of silver on the surface of the binary composite particles TiO₂ & Ag (2 wt. %) are oxidized under the influence of UV in contact with the MG solution and loses their activity; the presence of cerium in the TiO₂ & CeO₂ & Ag (2 wt. %) ternary system prevents oxidation of silver and reduction of catalyst activity.

The obtained results indicated that all investigated nanostructures based on TiO₂ exhibited sorption and photocatalytic activity under UV irradiation with a solution of malachite green (20 mg/dm³) at a pH value of ~ 7. It was stated that the lowest efficiency of the nanocomposite TiO₂ & Au (2 wt. %) and the highest efficiency of the ternary nanocomposite TiO₂ & CeO₂ & Ag (2 wt. %),

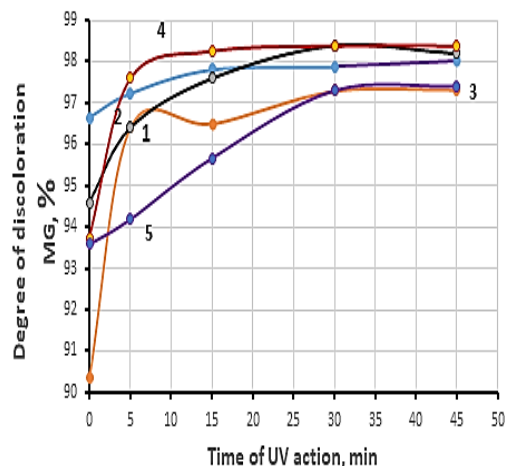


Fig. 4 – The discoloration of the MG water solutions under UV light. Numbers correspond to the systems: 1 – TiO₂; 2 – TiO₂ & Ag (2wt. %), 3 – TiO₂ & CeO₂ (2wt. %), 4 – TiO₂ & CeO₂ & Ag (2wt. %), 5 – CeO₂

but in all cases, the degree of discoloration of the solution was more than 95 % even after 5 min of contact. As such, these structures are promising materials for creating photoactive catalysts to neutralize malachite green solutions.

4. CONCLUSIONS

In summary, optical active nanocomposite systems based on TiO₂ were prepared by the chemical coprecipitation process. The calculation of the degree of tetragonality showed that Au and Ag formed small

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Сучасні фотоактивні наноконползити на основі TiO₂ та CeO₂

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Нині унікальні поверхневі, оптичні та фотокаталітичні властивості наноматеріалів на основі різних оксидних наночастинок знайшли широке застосування в очищенні стічних вод. У ряді сучасних наукових досліджень розглядалися біоактивні каталізатори на основі TiO₂, які виявляють окисно-

clusters on the surface of anatase particles; CeO₂ clusters were included in the structure (matrix) of TiO₂. Moreover, in both ternary systems, with an increase in the content of doping components, d spacing (101) of anatase's lattice shifted to the right, and the degree of tetragonality increased. Due to less negative CB (conductive band) energy in TiO₂, photogenerated electrons in CB of CeO₂ were easily transferred to the CB of TiO₂ (electrons of Ag will transfer to CB of TiO₂) and formed superoxide anion radicals (O₂⁻), which reacted with pollutant molecules such as MG. As such, photogenerated holes in the VB (valence band) of TiO₂ moved to the VB of CeO₂ and produced OH⁻ radicals. Thus, noble metals can be used to fill surface traps by donating electrons into 3d states of coordinated Ti ion. The synthesized photocatalytically active nanocomposite systems will be used for designing advanced nanomaterials for hydrogen technology production and biomedical application.

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відновну активність при очищенні води. Представлені структури на основі діоксиду титану, що сформовані у присутності срібла та церію з різним ступенем кристалічності, отримані методом хімічного осадження з використанням тетраізопропоксиду титану (ТТІП) як вихідної форми. Результати РФА підтвердили однорідний склад порошоків, утворених у бінарних системах (анатаз з кластерами Ag і CeO₂) з ОКР в діапазоні 9-20 нм. Встановлено, що в потрібних системах зі збільшенням вмісту допуючих компонентів, відстань $d(101)$ решітки анатазу зміщена вправо, а ступінь тетрагональності зростає до 2,52. Результати комбінаційного розсіювання показали, що найбільш інтенсивна смуга моди E_g для легованих зразків TiO₂ була зміщена від 144 до 152 см⁻¹ порівняно з анатазом залежно від концентрації благородного металу. Особливості взаємодії срібла-церію та срібла-титану пов'язані з розмірними ефектами як Ag, так і CeO₂ частинок, концентраціями кисневих вакансій у структурі діоксиду церію та можливими окисно-відновними властивостями через взаємодію між парою Ag⁺/Ag⁰ та Ce³⁺/Ce⁴⁺ (PL) і бар'єром Шотткі між металом й TiO₂, причому фотозбуджені електрони в напівпровіднику захоплюються наночастинками Ag. Показано, що потрібна композитна система TiO₂ & CeO₂ & Ag (2 мас. %) має покращену фотокаталітичну активність внаслідок включення CeO₂ до кристалічної ґратки анатазу, що підтверджується збільшенням ступеня тетрагональності ґратки та запобігання окисленню кластерів срібла на поверхні анатазу під дією УФ-опромінення. Ці фотокаталізатори стануть перспективною для технології синтезу водню.

Ключові слова: Фотокаталіз, УФ опромінення, Оптична активність, Ag, Малахітовий зелений, Знебарвлення.

APPENDIX

Some results to manuscript

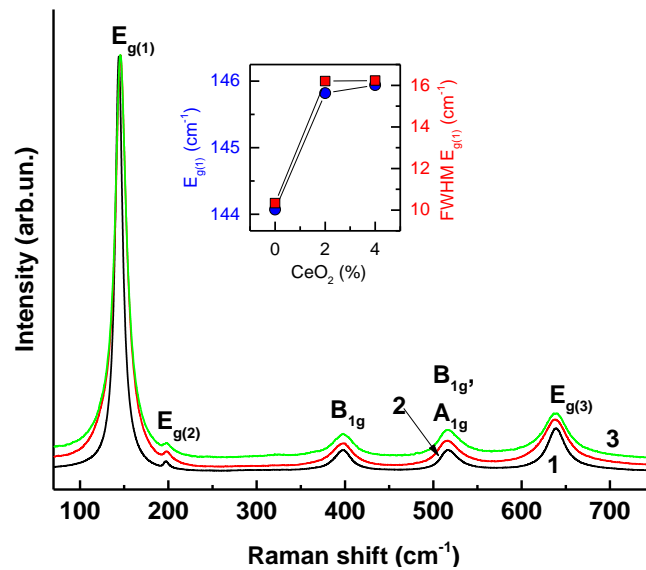


Figure – Raman spectra of nanocomposite with CeO₂: 1 – undoped TiO₂; 2 – TiO₂ & CeO₂ (2 wt. %); 3 – TiO₂ & CeO₂ (4 wt. %)

Doping of TiO₂ nanopowder with 2-4 wt. % of CeO₂ leads to some reduction in the intensity of all vibrational bands, with some broadening of the peaks with a small shift (Figure). The most intense band E_g is shifted in the high-frequency side from 144 to 146 cm⁻¹ compared to TiO₂ sample, while its half-width (FWHM) increases from 10 to 16 cm⁻¹. The reason for this maybe the oxides surface defects existence. Probably, the injection of oxide series contributes to the dimensional effect. We note, that authors [1] show the position of the main vibrational mode E_g with a slight shift (~ 2 cm⁻¹) to TiO₂ & CeO₂ (10 %); E_g anatase mode at 148 cm⁻¹ is associated with the O-Ti-O vibration and the presence of CeO₂ in oxide lattice probably cause a bond distortion resulting in the observed shift of the vibration band.

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