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PHOTOCATALYTIC ACTIVITY OF ANATASE DOPED WITH GOLD IN THE DESTRUCTION OF ORGANIC DYES

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One of the urgent problems of environmental protection and water resources is the damage of liquid wastes from the production of paper, textile, pharmaceutical, food, dye, and plastic industries, which use organic dyes characterized by non-biodegradability and high toxicity [1]. Photocatalytic decomposition of dye molecules with the formation of simple chemical substances was found to be a recognized method of disposal of such waste [2]. Among the variety of photocatalysts, oxide semiconductors have become widespread. The advantages of titanium and zinc oxides are low cost, photo corrosion resistance in a dispersion medium, low toxicity, convenient physical and optical properties, and efficiency in the destruction of organic dyes [3]. At the same time, the use of TiO_2 in catalysis requires additional exposure to ultraviolet irradiation of the suspension due to the wide band gap of the semiconductor (~3.2 eV), which prevents the absorption of visible light and the rapid recombination of photogenerated holes (h^+) and electrons (e^-) on crystal lattice defects, and leads to relatively low quantum efficiency [4]. Among the strategies proposed to increase the photocatalytic activity of titanium dioxide, the modification of titanium oxide nanoparticles with noble metals [5] or rare earth elements [6] has become widespread.

Noble metals such as Pd, Pt, Au, or Ag localized on the surface of TiO_2 particles or introduced into the TiO_2 matrix as nanoparticles or nanoclusters exhibit a high Schottky barrier value and thus act as electron traps. Thus, it enhances the photogenerated separation of electron-hole pairs and electron transfer in interphase processes [7]. The application of gold to modify titanium dioxide particles and the formation of metal clusters on the surface of titanium dioxide particles are able to cause the effect of Surface Plasmon Resonance (SPR) [8]. The positive experience of using particles of composites based on gold-modified titanium dioxide in the destruction of organic dyes is highlighted in a number of publications, for example [9]. In general, the doping of titanium dioxide particles with noble metals and Rare Earth Elements (REE) leads to the extension of the photocatalytic activity of TiO_2 to the visible light spectrum, which was shown by us during the destruction of Malachite Green by particles of binary and ternary nanocomposites based on the anatase doped with noble metals and nanoceria [10].

The aim of the work is to study the photocatalytic activity of gold-doped anatase particles during the destruction of anionic and cationic dyes in a neutral medium under the influence of UV irradiation.

Objects and Methods of the Research

The synthesis of anatase particles modified with gold was carried out by a chemical method in a weakly alkaline medium using titanium tetraisopropoxide (TTIP) and a solution of gold hydrochloric acid. The gold content was adjusted to obtain particles with 0.2 and 0.8 wt.% of gold. Hydroxide precipitates were washed with a water-ethanol solution, lyophilized, and calcined at 600 °C for 2 hours. The particles were characterized by the method of X-ray diffraction phase analysis (XRD), on the DRON-3.0 device with copper anode (CuKα) radiation. The scanning step was 0.05-0.1 0, the exposure was 4 s, and the range of 2Θ angles was from 15 to 90°. The morphology and elemental composition of the samples were studied by Scanning Electron Microscopy (SEM) on a Tescan Mira 3 LMU scanning electron microscope equipped with an Energy-Dispersive Module for microanalysis.

The photocatalytic activity of the particles was studied through the photodegradation of Methylene Blue (MB), Rhodamine B (RB), Methyl Orange (MO), and Orange G (OG) with a concentration of 20 mg/dm^3. To this end, a nanocomposite powder (100 mg) was transferred to a dye solution (80 ml) and stirred in the dark until the system reached sorption-desorption equilibrium. To study the photocatalytic activity under the influence of UV irradiation, a portable Xe 15A lamp with a power of 300 W was used. Sampling was carried out after 20, 40, and 60 min of UV irradiation in the suspension mixing mode. The optical density of the solutions was measured on a UV-Vis-NIR Spectrometer (Cary 5000, Agilent) in the range of wavelength from 200 to 800 nm.

The degree of discoloration of the solutions or the efficiency of the dye's destruction (D, %) was estimated according to the standard equation:

$$D, \% = (1-C/C_0)*100,$$

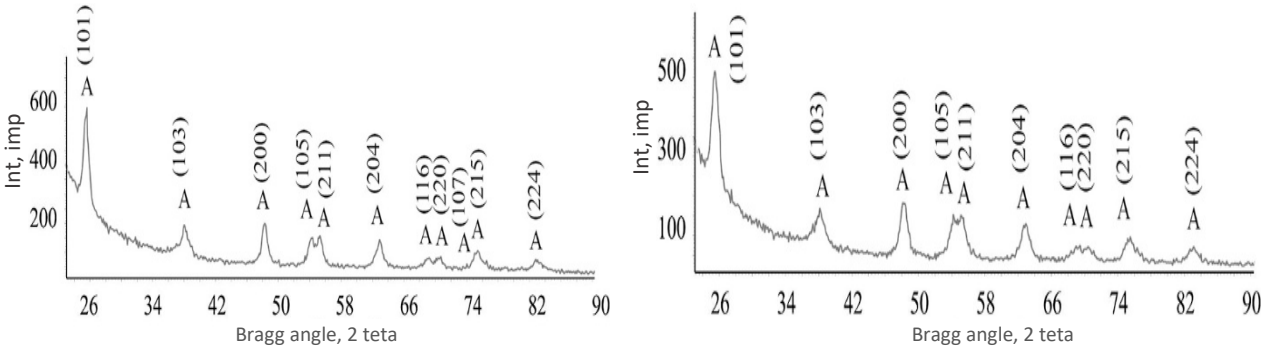
Where C is the residual concentration of the dye, and C_0 is the initial concentration of the dye.

The concentration of the dyes was found by calibration curves.

Results and Discussion

1. The characteristics of the nanocomposite sample

According to X-ray phase analysis, TiO_2&Au nanocomposites, which were subjected to processing at a temperature of 600 °C, crystallize in an anatase structure (JCPDS file No. 21-1272). The diffractogram (Fig. 1a) shows the broadening of anatase reflexes and the absence of peaks of low intensity, which indicates the nanometer size of the particles. The results of the calculation of the parameters of the anatase crystal lattice are presented in Table 1. The parameter *a* of a tetragonal lattice of both composites is almost the same, and the *c* parameter is smaller for the TiO_2&Au composite (0.2 wt.%). The degree of tetragonality (c/a ratio), which characterizes the deformation of the crystal lattice, for the TiO_2&Au sample (0.8 wt.%) does not differ from this parameter for the standard anatase sample (JCPDS file No. 21-1272), or slightly exceeds it in sample TiO_2&Au (0.2 wt.%). At the same time, for both samples, there is a shift of the (101) reflex towards larger angles compared to the standard sample, for which $d_{(101)} = 0.35129$ nm. The coherent scattering region (CSR), or the size of primary particles of polycrystalline composite powders, is 8.6-9.2 nm. The absence of gold reflexes is explained by the sensitivity threshold of the X-ray diffraction method, which does not allow identifying phases with a content of < 5% in the composition of powders. By analogy with the TiO_2&Ag system, gold can either be distributed in the crystal structure of anatase (titanium dioxide matrix) in the form of metal atoms or nanoparticles [11] but they can be localized on the surface of anatase in the form of clusters, preventing the growth of titanium dioxide particles.



а б

Fig. 1. XRD patterns of gold-doped anatase powders:
a – TiO_2&Au (0.2 wt.%); b – TiO_2&Au (0.8 wt.%).

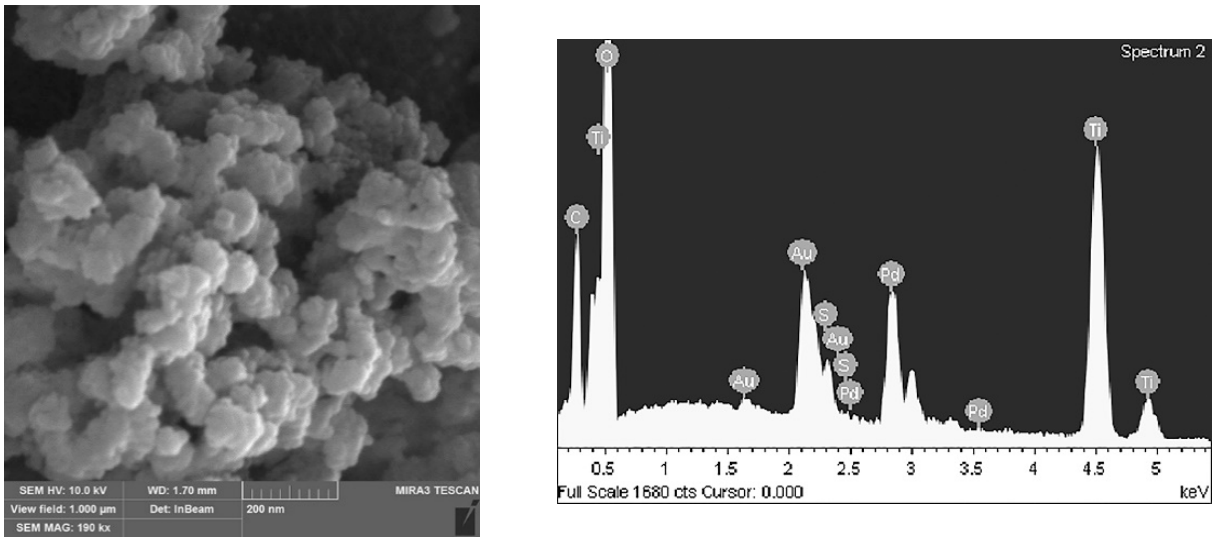
Table 1. Crystal lattice parameters and primary particle size (CSR) of gold-doped anatase

The sample	Crystal lattice parameters of anatase					
	***a*, nm**	***c*, nm**	**c/a**	***V*, nm^3**	**CSR, nm**	***d*$_{(101)}$, nm**
TiO_2&Au (0.2 wt.%)	0.3757	0.9460	2.52	0.133	9.6	0.34919
TiO_2&Au (0.8 wt.%)	0.3758	0.9428	2.51	0.133	8.2	0.34906

Fig. 2a shows the SEM image of nanocomposite TiO_2&Au (0.8 wt.%). Anatase phase was obtained after thermal treatment at T = 600 °C, forms loose aggregates of nanoparticles, which in an aqueous-dispersion medium easily transition into a highly dispersed state and acquire colloidal stability upon contact with molecules of organic dyes, which requires the use of a centrifugal field for their deposition. A typical EDS spectrum of the TiO_2&Au sample (0.8 wt.%) is presented in Fig. 2b. The nanocomposite contains titanium, oxygen, carbon (the main element), sulfur, and gold. In addition, to fix the highly dispersed anatase powder on the base and obtain high-quality SEM images, the surface of the sample was coated by gold-palladium alloys, which explains the presence of corresponding reflections of noble metals in the energy dispersive spectrum.

2. Study of the photocatalytic activity of TiO_2&Au nanocomposites in the dyes discoloration

The analysis of the dye concentration in the solutions carried out after the suspensions reached sorption-desorption equilibrium (40 min in the dark) shows that anatase particles doped with gold show little sorption activity in MB and MO solutions. The maximum degree of discoloration of the MB solution (28.5%) was recorded in the presence of TiO_2&Au particles (0.2 wt.%). At the same time, the sorption activity of gold-doped anatase powders for the extraction of MO and OG is absent, with the exception of the TiO_2&Au sample (0.8 wt.%) in the MO solution. Under the visible light action, a slight desorption of dye molecules is observed in all systems. At the same time, no change in the color of the suspension was observed in any experiment, which indicated the decomposition of the dye.



a b

Fig. 2. The electron microscopic study of the TiO_2&Au nanocomposite (0.8 wt.%): *a – SEM image, b – EDS spectrum***.**

The degree of discoloration of dye solutions under the UV irradiation of the suspension for 60 min (Table 2) indicates that for all dyes, and the TiO_2&Au sample (0.8 wt.%) shows the highest activity, forming the activity series:

Rhodamine B < Methyl Orange < Methylene Blue < Orange G.

At the same time, for the TiO_2&Au sample (0.2 wt.%), the series of dye discoloration efficiency is slightly different:

Rhodamine B < Orange G < Methyl Orange < Methylene Blue.

The likely reason for this difference may be due to the gold content in the anatase structure and the electrokinetic properties of the composite particles, in particular, ZPC (zero point of charge).

Table 2. Degree of discoloration of organic dye solutions after 60 minutes of UV irradiation of gold-doped anatase suspension

The sample	**Discoloration degree, %**			
	Methylene Blue	**Rhodamine B**	**Methyl Orange**	**Orange G**
TiO_2&Au (0.2 wt.%)	77.2	31.5	75.8	58.3
TiO_2&Au (0.8 wt.%)	91.0	50.0	81.5	95.2

Fig. 3 shows the kinetic regularities of discoloration of anionic (Fig. 3a) and cationic (Fig. 3b) dyes under the UV irradiation. The correlation coefficient indicated the pseudo-first order of the reaction neitralization of Orange G by both systems of TiO_2&Au ($R^2 = 1$); the destruction of Rhodamine B by TiO_2&Au particles (0.2 wt.%) and Methylene Blue by TiO_2&Au particles (0.8 wt.%), where $R^2 = 0.99$. In other cases, the coefficient of correlation is significantly lower.

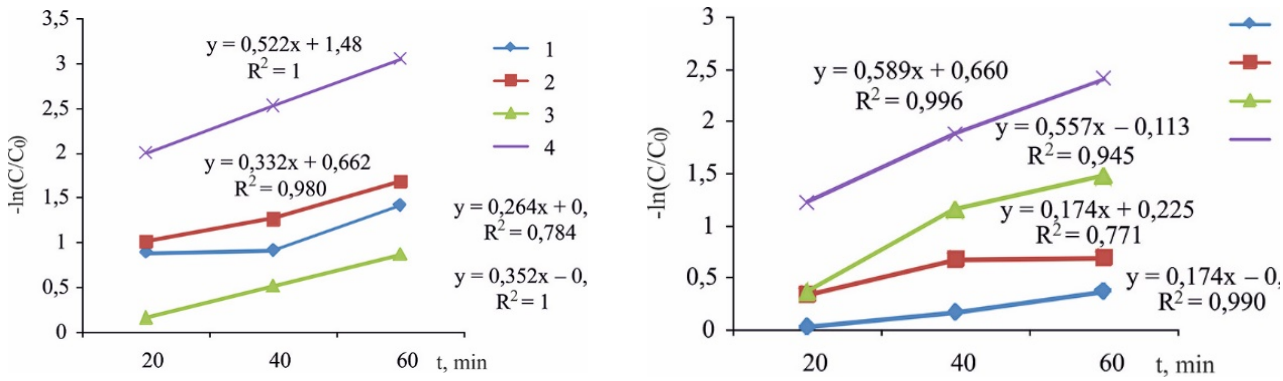


Fig. 3. Kinetic regularities of the dye's discoloration under UV irradiation of the suspension: *a – anionic dyes, where numbers indicate: 1 – TiO_2&Au (0.2 wt.%), MO; 2 – TiO_2&Au (0.8 wt.%), MO; 3 – TiO_2&Au (0.2 wt.%), OG; 4 – TiO_2&Au (0.8 wt.%), OG; b - cationic dyes, where numbers indicate: 1 - TiO_2&Au (0.2 wt.%), RB; 2 – TiO_2&Au (0.8 wt.%), RB; 3 – TiO_2&Au (0.2 wt.%), MB; 4 – TiO_2&Au (0.8 wt.%), MB.*

Conclusion

Nanosized particles of anatase with a gold content of 0.2 and 0.8 wt.% were synthesized using the sol-gel method. Particles of binary composites are characterized by the size of CSR 8.6±9.2 nm and form loose aggregates that spontaneously disperse in solutions of dyes with the formation of colloid-resistant sols. Particles of nanocomposites show low sorption activity in cationic dyes and the absence of sorption for anionic dyes. Such composite particles TiO_2&Au have the heterojunction between TiO_2 and Au and efficient separation of photo-generated carriers for the initiation photo-catalytic processes of organic anionic and cationic dyes neitralization and reduce the degree of discoloration of solutions (20 mg/dm^3) of Rhodamine B to 31-50%, Methyl Orange to 75-81%, Methylene Blue to 77-91% and Orange G up to 58-92% depending on the gold content in the composite.

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