Photoelectrochemical and Electrocatalytic Behaviors of TiO₂ Nanostructures and TiO₂-Au Nanocomposites: Effect of Synthesis Conditions

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Abstract—Mesoporous TiO₂ nanostructures and TiO₂—Au nanocomposites with stabilized Au nanoparticles are synthesized by the template sol-gel process. The effects of synthesis conditions on the particle size, electronic structure, morphology, composition, and texture of prepared materials are determined. TiO₂- and TiO₂—Au-based electrodes are shown to be photoactive in the wavelength range of 250–412 nm and in the methylene blue (MB) photodecomposition and feature high catalytic activity in an oxygen electroreduction reaction. The presence of hydroxyl and carboxylate groups in the amorphous phase is the key factor affecting the photosensitivity of our TiO₂ nanostructures and contributing to enhancement of their photoactivity in the MB photodecomposition reaction. Due to their catalytic activity and consistent performance in the oxygen electroreduction reaction, the TiO₂ nanostructures and TiO₂—Au nanocomposites can be considered as promising materials for use in electrochemical oxygen sensors with application to aqueous solutions.

Keywords: mesoporous TiO_2 nanostructures, nanocomposites, gold nanoparticles, photoelectrochemical, photocatalytic, electrocatalytic behavior

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INTRODUCTION

The semiconducting nature of TiO_2 and its ability to separate photogenerated charges produced upon exposure to light, as well as its good chemical inertness, water insolubility, hydrophilicity, nontoxicity, among other properties [1-8], along with its relatively low cost, constitute the basis of many of its applications. It is used, e.g., in photocatalysts, electrode materials for modern power sources, sensor materials, and to address environmental problems. Typically, TiO_2 is obtained by the sol-gel process [1–9], where the oxide is the product of hydrolysis reactions and inorganic polymerization of a titanium-containing precursor, with the synthesis often carried out in an organic solvent at low temperature. Subsequent solvothermal treatment (STT) noticeably improves the catalytic and photocatalytic behaviors of TiO₂ [10]. The applications listed above are limited by the large band gap of TiO₂ ($E_g = 3.2$ eV for anatase and bruxite and $E_g = 3.0$ eV for rutile), which limits its photoactivity to wavelengths $\lambda < 400$ nm [2, 3]. Since sunlight consists of ultraviolet (UV; 5%), visible (43%), and near-infrared (IR; 52%) radiation, the efficiency of TiO₂-based materials in photocatalytic and photoelectrochemical processes can be enhanced by improving their photoactivity in the visible range [1-9, 11-14] or even in the near-IR region [2]. In this respect, a few strategies to modify TiO₂ were proposed and implemented. Relevant examples include coupling it with a narrow-band semiconductor, surface sensibilization with organic dyes or metal complexes, surface fluorination, metal and nonmetal ion doping, and deposition of noble metals [2, 5]. These approaches contribute to enhancing its quantum efficiency and improve the rate of organic pollutant degradation reactions that occur upon exposure to UV radiation and visible light from the solar spectrum [1-9, 11-14].

Doping of TiO₂ with nonmetals (e.g., B, C, and N) was shown to produce doped materials with photoactivity in the visible range due to emergence of additional states between its valence and conduction bands [2, 6, 15], which expands possibilities for their use in photocatalytic and photoelectrochemical processes.

A variety of synthetic approaches (e.g., sol-gel process, hydrothermal method, wet impregnation, and photodeposition) were proposed to produce TiO_2 modified with noble metals, e.g., Au [16–18], with Ptand Au-modified samples identified as the most effective and less sensitive to synthesis methods used. The photocatalytic activity of the Au- and Pt-modified TiO₂ samples was shown to be related to the synthesis method used [2]. It was found, in particular, that, when the metal was added in excess, i.e., above an optimal level, the photocatalytic performance of TiO₂-M diminished due to reduction in the photon absorption by TiO₂ and recombination of electrons and holes at excessive metal sites [19].

TiO₂-M composites with noble metal nanoparticles (NPs) featuring surface plasmon resonance displayed excellent photocatalytic performance upon irradiation with visible light [2, 20, 21]. Plasmonic NPs incorporated into the TiO₂-M composites improve the efficiencies in water-splitting and decomposition of organic compounds, such as methanol and ethanol [2, 21–23].

Amongst noble metals, gold is a highly effective additive to TiO_2 materials that brings them to photoactivity in the visible range, thereby improving the effectiveness of TiO_2 -based photocatalysts [18]. The Fermi level of Au NPs is lower than in TiO_2 , which makes the transfer of photogenerated electrons from the conduction band of TiO_2 to the metal particles more efficient [24], and, consequently, improves its photocatalytic activity, e.g., in photocatalytic splitting of water—ethanol mixtures [25], by lowering the electron—hole recombination rate [24, 26]. It was concluded that the TiO_2 photoactivity was due in this case in part to surface plasmon resonance mediated by local electromagnetic field of Au NPs [2, 22, 23, 27].

TiO₂-based electrode materials also displayed good catalytic activity in the oxygen-reduction reaction (ORR) [28, 29], which underlies the working of electrochemical oxygen sensors. Noble metals or inert carbon are typically used as active layers of working electrodes in oxygen sensors for liquid applications; however, they have a number of limitations, in particular, low stability, narrow potential range where oxygen detection is possible, bulky structure due to the presence of oxygen diffusion membrane, and high overvoltage of oxygen reduction (0.80–1.20 V for carbonbased electrode materials), which results in side electrochemical reactions and added complexity in oxygen concentration measurements. Membrane-free sensor designs employing different titania-based electrode materials, including those doped with different metals, were also proposed to overcome these limitations, with the TiO₂-ZnO-Au structure offering the best set of electrochemical characteristics [30].

The aim of this work was to (1) identify the effects that the conditions of sol-gel process and STT have on the chemical and physical composition, morphology, texture, and crystallite size of titania samples, (2) study the influence of these factors on the photosensitivity and photocatalytic activity of the titania samples and gold NP-stabilized TiO_2 -Au nanocomposites based on them using a model reaction of methylene blue (MB) photodegradation in the presence of visible and UV light, and (3) investigate the electrocatalytic activity of prepared materials toward ORR.

EXPERIMENTAL: METHODS AND MATERIALS

Reagents

Titanium tetrabutoxide, 1-butanol, lanthanum chloride $LaCl_3 \cdot 7H_2O$, and lithium hydroxide were acquired commercially from Aldrich; dibezno-18-corona-6 and dodecylethyldimethylammonium bro-mide were from Fluka; and sodium tetrahydroborate, hydrochloric acid, sodium chloride, propanol, and ethanol were from Ukrorgsynthes and used as received.

Catalyst Synthesis

 TiO_2 was synthesized by a modified templatebased sol-gel process proposed in our previous study [31] for synthesis of hierarchical TiO_2 microspheres.

Samples prepared under different synthesis conditions were denoted as TiO₂ (T_1/T_2), where T_1 is the STT temperature and T_2 is the annealing temperature (Table 1). All of the samples were annealed at 500°C. Our data showed that TiO₂ samples prepared at temperatures of 430–500°C consisted of a single crystalline phase, which was anatase, and displayed better electrocatalytic performance in ORR compared to samples consisting of the mixed anatase and rutile polymorphs, with the latter normally formed at higher annealing temperature (>500°C).

Sample 1 (Table 1) was synthesized using the Na[DB18-C-6]Cl complex that formed during preparation of the reaction mixture. NaCl (0.2134 g) and DB18-C-6 (1.315 g) (molar ratio of 1:1) were dissolved in 130 mL of *n*-butanol. LaCl₃·7H₂O (0.235 g) and dodecylethyldimethylammonium bromide (0.246 g) were sequentially dissolved in the resulting Na[DB18-C-6]Cl solution. Titanium tetrabutoxide (12.5 mL) and *n*-butanol (7 mL) were added dropwise to the indicated reaction mixture, while stirring vigorously. The reaction mixture was then held in a desiccator at constant humidity for 2 weeks, i.e., until the formation of precipitate ceased. The resulting precipitate, along with the mother liquor, was transferred into a Teflon autoclave and subjected to STT at 100°C for 24 h followed by drying in air at room temperature for 7-8 h. The dried precipitate was initially heated at 100°C for 2 h and then annealed at 500°C for 4 h.

Sample 2 (Table 1) was synthesized by the same procedure as sample 1, except that STT temperature was raised to 175° C.

No.	Sample	Crystalline phase content, %	Crystallite diameter d, nm		Particle diameter <i>d</i> , nm	d _{meso} , nm	$S_{\rm BET},$ cm ² g ⁻¹	$V_{\text{pore}},$ cm ³ g ⁻¹
		А	XRD	TEM	SEM			
1	TiO ₂ (100/500)	58	8	11	65	4.8	135	0.44
2	TiO ₂ (175/500)	70	10	11	160	4.8	110	0.37
					(2500-aglomerate)			
3	TiO ₂ (100/500)	72	10	12	70	15.0	145	0.50
	$(no. 1 + 2 mL H_2O)$							
4	TiO_2 (175/500) (no. 2 + 2 mL H ₂ O)	60	9	10	60	4.8	125	0.44
5	TiO_2 (175/500) (no. 2 + 2 mL HCl)	_	31(R)	75	105	4.9	100	0.31
			40 (B)					

Table 1. Phase composition and average particle and crystallite sizes obtained from XRD, SEM, and TEM data

A, anatase; R, rutile (46%), B, brookite (54%); S_{BET} , specific surface area; V_{pore} , pore volume, and d_{meso} , mesopore diameter.

Samples 3 and 4 (Table 1) were synthesized by the same procedure as samples 1 and 2, respectively, except that 2 mL of distilled water were added to the reaction mixture before adding the butanol solution of titanium tetrabutoxide.

Sample 5 (Table 1) was prepared following the same procedure as sample 1, except that 2 mL of 4 N HCl was added to the reaction mixture before adding the butanol solution of titanium tetrabutoxide and STT was performed at 175°C.

Synthesizing Au NPs

We placed 0.080 mL of a 5.8×10^{-3} M H[AuCl₄] solution into a vial, where 0.8 mL of a 0.01 M histidine solution and 1.12 mL of distilled water were then added while vigorously stirring with a magnetic stirrer. pH was adjusted to 11 by using a saturated LiOH solution. A 2.53×10^{-2} M NaBH₄ solution was added to the resulting solution, and the latter was agitated for 15 min.

Synthesizing TiO₂-0.01% Au Composites

We placed 0.05 g of TiO₂ in a 10-mL flask followed by addition of 0.125 mL of a freshly prepared solution of Au NPs. The resulting suspension was sonicated for 5 min and then dried in a rotary evaporator at 70°C. The dried light-yellow precipitate obtained was washed with dry isopropanol, transferred onto a fritted-glass filter, and washed with ethanol until the washing water was pH neutral as judged using universal pH paper. The resulting precipitate was dried in oven at 80°C for 1 h.

Applying the Samples on Titanium Electrodes

Titanium substrates were pretreated by washing in an alkaline solution, sodium carbonate solution, and isopropanol, followed by drying in an oven at 100° C. The prepared suspension was applied on the titanium electrodes and dried in oven at 70° C for 60 min.

Methods

The phase composition of synthesized samples was analyzed on a Bruker D8 Advance diffractometer using CuK_{α} radiation ($\lambda = 0.1541$ nm). The relative amount of the crystalline phase anatase was estimated from the intensity ratio of anatase's (101) reflex for a sample under analysis to that for a sample with known content of this crystalline phase [32]. The average size of crystallite in prepared samples was calculated from the width of anatase (101) diffraction peak at $2\theta =$ 25.4° using the Scherrer equation $d = n\lambda/\beta \cos\theta$, where d is the crystallite size, λ is the wavelength of incident X-ray radiation, θ is the Bragg angle, β is the line broadening at half the maximum intensity, and n is the shape factor (0.96 for spherical particles) [32].

The band gap was determined from reflection spectra suing the Tauc equation [33] $(\alpha h\nu)^r = h\nu$, where α is the absorption coefficient calculated using the Kubelka–Munk equation and *r* is a factor determined by the nature of electron transitions (0.5 for indirect transitions in TiO₂).

Morphology and size of nanostructures were determined by scanning (SEM) and transmission (TEM) electron microscopies. SEM imaging was performed on a JSM-6060 LA (JEOL) microscope operated at an acceleration voltage of 30 kV, and TEM imaging was performed on a JEOL JEM 1230 instrument at an accelerating voltage of 100 kV.

Fourier transform IR (FTIR) spectroscopy was carried out on a PerkinElmer Spectrum One FTIR spectrometer using KBr pellets (sample-to-KBr ratio, 1 : 100). Diffuse reflectance spectra were recorded on an UV-Vis Evolution 600 spectrophotometer (Thermo Scientific) using $BaSO_4$ as a standard, and absorption



Fig. 1. (a) XRD patterns and (b) adsorption isotherms for TiO_2 samples 1-5 (sample numbers as in Table 1).

spectra of solutions were recorded on a Specord 210 spectrophotometer (Analytik Jena).

The porous structure was determined from N_2 adsorption/desorption isotherms at a temperature of -196° C on a Sorptomatic 1990 adsorption porosimeter. Before measurements, samples were degassed at 150°C for 12 h. Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method and mesopore distribution was found using the Barret–Joyner–Halenda method.

Elemental analysis was carried out on a Carlo Erba 1106 CHN analyzer. The photocatalytic behavior of prepared samples was studied in a model system where they were used in photodecomposition of aqueous methylene blue (MB) solutions (10 mg/L) upon irradiation with UV and visible light. The variation of MB concentration was followed by UV–Vis spectroscopy on the Specord 210 instrument (Analytik Jena). The suspension under study was irradiated with UV and visible light using Delux (26 W) and Maxus lamps (8 W), respectively, with the radiation flux incident on the surface of suspension being 0.05 and 2 mW/cm², respectively.

The electrocatalytic activity of fabricated electrodes was studied from current–voltage profiles recorded under potentiodynamic conditions using a computer-controlled electrochemical installation with the following characteristics: the current range is 2×10^{-9} to 0.1 A, the range of potential scan rates is 0.01– 50 mV/s, and the range of working electrode potentials is -4 to +4 V. Photoelectrochemical studies were performed in the wavelength range of 250–600 nm in a three-electrode quartz electrochemical cell with separate cathodic and anodic compartments using 1 N KCI as the electrolyte. For irradiation, light from a highpressure xenon lamp was passed through a monochromator with a spectral resolution of 1 nm and focused on the semiconducting working electrode. A platinum auxiliary electrode was used, and an Ag/AgCl electrode was used as the reference electrode [30].

RESULTS AND DISCUSSION

Phase Composition and Crystallite Size

Figure 1a shows X-ray diffraction (XRD) patterns of TiO₂ samples 1-5 synthesized under different conditions (Table 1). XRD patterns of all of the samples (Fig. 1a), except for sample 5, feature prominent peaks related to the crystalline anatase phase, while no traits of the crystalline rutile and brookite phases are observed at all. Main peaks were identified as reflexes of the crystalline anatase phase (JCPDS-Joint Committee on Powder Diffraction Standards). The XRD pattern of sample 5 features prominent reflexes typical of the crystalline rutile and brookite phases. The intensity of characteristic (101) anatase peak varied depending on the synthesis conditions, indicating that the anatase content varied from 58 to 72% (Table 1). The anatase content was calculated as in [34] by comparing the integral intensity of a characteristic reflex of an analyzed sample to that of (101) characteristic reflex of R-25 for which the content of crystalline anatase phase was known. The crystallite size in samples 1-4, as calculated using the Debye–Scherrer equation [35], showed little variation with synthesis conditions and postsynthesis processing and varied in the range of 8-10 nm.

As a result, except for sample 5, which contains the crystalline rutile (46%) and brookite (54%) phases, all the other samples (Table 1) contained only the crystalline anatase phase (58, 70, 72, and 60%, respectively). In an XRD pattern of sample 4, narrow reflexes at $2\theta = 32^{\circ}$ and 46° can be attributed to (200) and (220) reflexes of the crystalline halite phase (JCPDS no. 5-0628) [36]. An important feature of samples 1–4 (Table 1) is that they contain amorphous titania (42, 30, 28, and 40%, respectively) along with anatase.

Textural Characteristics of Synthesized Samples

All of the samples 1-5 (Table 1), in particular nos. 1, 3, and 5, are characterized by type IV adsorption isotherms (Fig. 1b), which are typical of mesoporous materials. The textural characteristics of our TiO₂ samples in relation to the synthesis conditions are provided in Table 1.

Data in Table 1 show that, with increase in the STT temperature from 100 to 175° C, the specific surface area S_{BET} of pores decreased from $135 \text{ m}^2/\text{g}$ for sample 1 to $110 \text{ m}^2/\text{g}$ for sample 2 and so did the total pore volume V_{pore} (from 0.44 to 0.37 cm³/g), while the mesopore volume changed only a little (Table 1). In recognition of the increase in anatase content from 58 to 70% and the crystallite size from 8 to 10 nm, as well as the decrease in the content of amorphous phase with its microporous structure, these changes can be explained by the progression of hydrolysis and polycondensation processes at higher STT temperatures used for sample 2 (175°C).

In synthesizing sample 3, 2 mL of water was added to the sol-gel system used in synthesis of sample 1, when all other factors were held constant, which, in comparison to sample 1, resulted in noticeable increases in pore diameter d_{meso} (from 4.8 to 15.0 nm), specific surface area S_{BET} (from 135 to 145 m²/g), and the total pore volume V_{pore} (from 0.44 to 0.50 cm³/g) (Table 1). Considering the increase in the anatase content from 58 to 72%, these changes can be explained by more advanced hydrolysis and polycondensation processes that occurred in synthesis of sample 3 in the presence of a larger amount of water that was involved in these processes and was the source of oxygen in the TiO₂ formation.

In synthesizing sample 4, we used the sol-gel system with the addition of 2 mL of water and raising the STT temperature to 175°C. Many textural properties of the prepared sample were little different to sample 1, except the decrease in specific surface area S_{BET} from 135 to 125 m²/g. In synthesizing sample 5, we used the sol-gel system for sample 1 with the addition of 2 mL of 4 N HCl and the STT temperature was raised to 175°C. In comparison to sample 1, sample 5 had smaller specific surface area S_{BET} (cf. 135 and 100 m²/g) and pore volume V_{pore} (cf. 0.44 and $0.31 \text{ cm}^3/\text{g}$), whereas the mesopore diameter showed little change (Table 1). Unlike samples 1, 2, 3, and 4, the porous structure revealed in sample 5 is due to its mixed phase composition, i.e., the presence of both rutile and brookite (Table 1).

Results of SEM and TEM Studies

Sample 1, as can be seen in Fig. 2a, represents a porous material consisting of homogeneous spherical secondary NPs with a size of ~ 65 nm, which formed



Fig. 2. SEM images of TiO_2 samples (a) *1*, (c) *2*, and (e) *3*; TEM images of samples (b) *1*, (d) *2*, and (f) *3* (sample numbers as in Table 1).

by aggregation of primary homogeneous spherical anatase NPs with a size of ~ 8 nm (Fig. 2b and Table 1).

Sample 2 (Fig. 2c) consists of spheroid agglomerations with an average size of 2500 nm, which, in turn, consist of secondary homogeneous NPs with a size of ~160 nm formed from aggregates of primary homogeneous spherical anatase NPs with a size of ~10 nm (XRD data) (Fig. 2d and Table 1).

Sample 3 (Fig. 2e and Table 1) consists of larger secondary spherical NPs with an average size of \sim 70 nm (Fig. 2e) formed by aggregation of larger homogeneous primary spherical NPs, which are anatase crystallites with a size of \sim 10 nm (XRD data) (Fig. 2f and Table 1). The dimensions of particles constituting the other samples (4 and 5) obtained from SEM and TEM data are given in Table 1.

Electronic Absorption and FTIR Studies

Electronic absorption spectra of samples 1 and 3 (Fig. 3a, traces 1 and 3) feature higher absorption in the visible range and a slight redshift in the absorption edge due to lesser extent of hydrolysis and condensation compared to samples 2 and 4, a consequence of lower STT temperature (100° C).

Elemental analysis showed that these samples contained residues of organic compounds (Table 2). Raising the STT temperature to 175° C contributed to an increase in the crystalline anatase phase as a result of further progression of hydrolysis and condensation reactions, which manifested as a blueshift in the absorption edge of samples 2 and 4 (Fig. 3a, curves 2, 4).



Fig. 3. (a) Diffuse reflectance spectra of TiO₂ samples 1-5. (b) Diffuse reflectance spectra of (1) TiO₂ sample 3 and (2) TiO₂-0.01% Au nanocomposite based on sample 3 and (3) electronic absorption spectrum of an Au NP solution (sample numbers as in Table 1).

The shift in the absorption edge of sample 5 into the visible range (Fig. 3a, curve 5) can be explained by the presence of crystalline rutile and brookite phases, which have a band gap of 3.00 and 3.31 eV, respectively [37].

A reflectance spectrum of the TiO₂-0.01% Au nanocomposite fabricated based on sample 3 (Fig. 3b, trace 2) features an increased absorption in the visible region related to surface plasmon resonance of gold NPs. A surface plasmon resonance spectrum of the gold NPs in solution is shown in Fig. 3b (trace 3). Our TEM studies showed that the average size of Au NPs used in fabricating the TiO₂-0.01% Au composite was 6 nm and they had a reasonably narrow size distribution.

FTIR spectra of all of our samples (Fig. 4) have absorption bands around 3430, 3240, and 1635 cm⁻¹, which can be assigned to stretching (v_{as} (OH) and v_{s} (OH)) and bending (δ (OH)) vibrations of the O–H bond in water and Ti–OH groups, respectively [38]. We note that FTIR spectra are presented only for samples 1, 4, and 5, because of high similarity between spectra for sample pairs 1–3 and 2–4.

Broadening of the stretching vibration bands is a consequence of strong hydrogen bonding. In the FTIR spectra of samples 1, 2, 3, and 4, there are also groups of bands in the region of $3000-2700 \text{ cm}^{-1}$ and $1800-1240 \text{ cm}^{-1}$, which can be assigned to stretching and bending vibrations in the methyl and methylene groups [39]. Thus, in the spectrum of sample 1 (Fig. 4, trace *I*), groups of bands at 2965 and 2873 cm⁻¹, as

Table 2. Elemental analysis of TiO₂ nanostructures

Sample no.	1	2	3	4	5
C, %	0.58	0.35	0.48	0.21	0.03
Н, %	0.15	0.27	0.21	0.17	0.01

well as at 2926 and 2854 cm^{-1} , can be assigned to the stretching vibrations $v_{as}(CH)$ and $v_{s}(CH)$ in the methyl and methylene groups, respectively; groups of bands at 1467, 1460, and 1385 cm^{-1} can be assigned to scissoring bending vibrations in the methylene group and bending vibrations δ_{as} and δ_{s} in methyl groups of residual organic impurities. The spectrum also features bands at 1050 and 1090 cm⁻¹ as well as shoulder peaks at 1120 and 1165 cm⁻¹, which can be assigned to vibrations of Ti-O-C bonds [40] formed between titanium and alcohol molecules, which may contribute to additional absorption of radiation near the long-wavelength absorption edge. Bands at 1530 and 1415 cm^{-1} , which can be assigned to stretching vibrations in the carbonyl group, $v_{as}(C-O)$ and $v_{s}(C-O)$, respectively [40, 41], may indicate that chemicals containing carbonyl groups bonded to titanium atoms occur among other products of thermal decomposition.

The presence of stretching and bending vibrations of methyl and methylene groups in the considered FTIR spectra, along with hydroxyl and carboxyl groups, is indicative of the presence of residual organic compounds in synthesized samples that persisted even through calcination at 500°C. These chemicals can be both products of the thermal decomposition of template and the starting reagents bonded to titanium atoms in the amorphous component of the sample.

The presence of organic component in synthesized samples was substantiated by the results of elemental analysis provided in Table 2, which show that the carbon content of analyzed samples is 0.6-0.2%. We note that vibration bands associated with CH, carboxyl groups, and Ti-O-C (see, e.g., Fig. 4, trace 2) are barely noticeable in FTIR spectra of samples subjected to STT at 175°C demonstrating that the amount of these groups in the considered samples is lower than in the samples subjected to STT at 100°C. Further, the carbon content of these samples decreased as well



Fig. 4. FTIR spectroscopy of (1-3) TiO₂ nanostructures, (4, 5) TiO₂-0.01% Au composites, and (6) histidine-stabilized Au NPs: (1) TiO₂ sample 1; (2) TiO₂ sample 4; (3) TiO₂ sample 5; (4) TiO₂-0.01% Au nanocomposite based on sample 1; and (5) TiO₂-0.01% Au based on sample 3 (sample numbers as in Table 1).

(Table 2). A broad band in the region of 950–400 cm⁻¹ (Fig. 3, traces 1, 2) can be attributed to Ti–O–Ti vibrations of the framework of both the crystalline anatase phase and the amorphous component, which have different Ti–O–Ti angles and Ti–O bond lengths [42]. In the FTIR spectrum of sample 5 (Fig. 3, trace 3), a broad band at 620 cm⁻¹, a band at 532 cm⁻¹, and a narrow band at 420 cm⁻¹ can be assigned to Ti–O–Ti vibrations in the crystalline rutile and bruxite phases [43].

Photoactivity of TiO_2 Nanostructures and TiO_2 -0.01% Au Composites

Spectral dependences of quantum yield η of photoelectrochemical current (Fig. 5) were measured for electrodes fabricated using our TiO₂ and TiO₂-Au films (Table 3, samples 1–5) and used to determine photoelectrochemical parameters, such as flat band potential $E_{\rm fb}$ and band gap $E_{\rm g}$ for indirect optical transitions within the TiO₂ band gap. Flat band potential $E_{\rm fb}$ was determined from of photocurrent-potential



Fig. 5. Spectral dependences of photocurrent quantum efficiency for TiO₂ and TiO₂-0.01% Au films (sample numbers as in Table 3).

dependences $I_{\rm ph}-E$. $E_{\rm fb}$ can be used to estimate the position of the bottom of the conduction band and the energy of electrons involved in reduction processes, including ORR [44]. To estimate band gap $E_{\rm g}$, the spectral dependences of photoelectrochemical current were plotted in $(h\nu\eta)^{0.5}-h\nu$ coordinates for allowed indirect transitions in TiO₂, where η is the quantum yield and $h\nu$ is the photon energy.

The considered electrodes based on TiO₂ nanostructures and TiO₂–0.01% Au nanocomposites (Table 3) were photoactive in the wavelength range of 250–400 nm (Fig. 5), with the quantum yield $\eta =$ 0.08–0.20 (Table 3). We note that the TiO₂–Au nanocomposites (samples 1a and 3a, Table 3) displayed increased photoactivity in the long-wavelength range (Fig. 5), compared to the initial TiO₂ nanostructures (samples 1 and 3, Table 3), likely due to peculiarities of their chemical makeup, electronic structure, and texture, which depend on both the synthesis procedures used and the presence of Au NPs. The higher photoactivity of sample 3 (Table 3) in comparison to sample 1 (Table 3) may be related to its higher anatase content and larger specific surface area.

The photoactivity of TiO_2 films improved as a result of their modification with Au NPs (0.01%), which manifested as an increase in quantum efficiency

No.	Sample	$E_{1/2}, V$	$\Delta E, V$	η	$E_{\rm fb}, V$	$E_{\rm g},{\rm eV}$
1	TiO ₂ (100/500)	-0.45	0.16	0.08	-0.24	3.04
1a	TiO ₂ (100/500)-0.01% Au	-0.41	0.20	0.20	-0.25	3.05
2	TiO ₂ (175/500)	-0.65	0.16	0.09	-0.32	3.05
3	$TiO_2(100/500)$ (no. 1 + 2 mL H ₂ O)	-0.35	0.15	0.10	-0.30	3.00
3a	TiO ₂ (100/500)–0.01% Au (no. 1 + 2 mL HCl)	-0.32	0.20	0.17	-0.27	3.04

Table 3. Characteristics of TiO₂- and TiO₂-0.01% Au-based electrodes: η , $E_{\rm fb}$, $E_{\rm g}$, $E_{1/2}$, and ΔE

 η , quantum efficiency of electrochemical current; E_{fb} , flat-band potential; E_g , band gap; $E_{1/2}$, ORR half-wave potential; ΔE , range of ORR working potentials.

 η of photoelectrochemical current (Fig. 5 and Table 3). In doing so, band gap E_{g} of considered electrodes did not appreciably change (Table 3), except for sample 3a for which $E_{\rm g} = 3.0$ eV, a value similar to the band gap in rutile ($E_g = 3.00 \text{ eV}$) [37], which is known to display low photoactivity. Significantly, for the composites that displayed some increase in photoactivity in the long-wavelength region (Fig. 5), marked changes were also observed in the visible range of their diffuse reflectance spectra (Fig. 3). As can be observed from Fig. 3b, further absorption of radiation in the visible range observed for the TiO₂-Au nanocomposites is related to a plasmon resonance band of Au NPs $(\lambda_{max} = 514 \text{ nm})$ used in the synthesis of these nanocomposites, which, when incorporated into the composites, retained their individual size (6 nm) and did not aggregate.

We found that interstitial Ti–O–C groups, which are known to be able to give rise to additional energy levels above and below the valence band in titania [2, 6], were present in all of our samples. Due to their contact to interstitial Ti-O-C groups inside pores and their surface plasmon absorption at 514 nm, Au NPs can absorb photons, effectively functioning as antennas, and excite the indicated additional states, thereby enhancing photoactivity and slightly decreasing the band gap. At the same time, the fact that the influence of recombination processes diminished can be another factor contributing to enhancement of photoactivity. As a result, it is reasonable to assume that the enhancement of photoactivity of our TiO₂-0.01% Au nanocomposites (samples 1a and 3a, Table 3) in comparison to other studied samples (Table 3 and Fig. 5) is due to synergistic interaction between the Au NPs and interstitial Ti-O-C groups, and the developed texture of samples, which improves diffusion and adsorption on the substrate, aids in this interaction. In the case of sample 3a, this effect arises due to more intimate contact between the Ti-O-C groups and Au NPs since the latter penetrate inside mesopores.

The presumption made above is consistent with a number of other results obtained in this study. Thus, nanocomposite 1a, which contains the same number of Au NPs as sample 3a, while having a less developed texture (it is physically impossible for 6-nm NPs to penetrate pores with a diameter of 4.8 nm) and larger amount of Ti-O-C groups (Table 2), was characterized by lower photoactivity than sample 3a.

As a result, the improved photoactivity of our titania–gold nanocomposites (samples 3a and 1a), compared to their respective unmodified counterparts (samples 3 and 1), may stem from synergistic interaction between Au NPs and interstitial Ti–O–C groups. This presumption is consistent with earlier findings where direct contact between TiO₂ NPs and plasmonic Au NPs ensured a direct transfer of electrons from the metal into the semiconductor's conduction band [45–47], with the position of Fermi level in Au NPs relative to the semiconductor's bands being critical for the feasibility of this transfer [2].

Similarly, it was shown that the improved photocatalytic activity of TiO₂-Au did not change even after an intermediate layer between the TiO₂ and plasmonic Au NPs was created [45]. Therefore, if the energies of electronic levels coincide, electron transfer from Au NPs into TiO_2 can occur even at energies lower than the band gap [2]. Study [48] corroborated plasmonmediated electron injection from Au into the conduction band of TiO₂, and a study of charge separation/recombination dynamics in TiO2-Au demonstrated that the electron injection into TiO₂ was induced specifically by plasmon resonance [49]. As stated in [2], "LSPR [localized surface plasmon resonance] improves the photocatalytic activity in three different ways: by (1) extending light absorption of semiconductor to longer wavelengths, (2) increasing the scattering of visible-light, and (3) creating electron-hole pairs by transferring the electrons from the metal nanoparticles to the conduction band of semiconductors." It can be observed from our results for samples 1a and 3a that, at least for the latter, all of the three possibilities listed above are realized. The fact that the effects observed were weak can be explained by the fact that the samples were prepared using small amounts of Au NPs (0.01%). Our intention was to keep the Au NP content at a minimum, because it is known [19] that, when added in excess. Au NPs act as electron-hole recombination centers and hinder absorption of light by the semiconductor [44].

The achieved improvement in photoactivity of our TiO_2 -Au samples may also be related to the presence of a large number of molecules of stabilizing ligand (histidine) on the surface of Au NPs, which may reduce the charge carrier recombination rate in a fashion similar to that demonstrated in [50] for Au NPs coated with a thin SiO₂ layer. Since, in contrast to noticeable changes in the quantum efficiency of photocurrent (Table 3), the flat-band potential of our samples did not change appreciably, we can conclude that the Au NPs mainly affected recombination processes.

Photocatalytic Activity

As can be observed in Fig. 6, noticeably different photocatalytic activity was observed for our samples upon exposure to UV and visible light. For irradiation with UV light, the degree of conversion R60 for 60-min exposure was 47% for sample 1 ($T_{\text{STT}} = 100^{\circ}$ C), which is much larger than a value of 14% obtained for sample 2 ($T_{\text{STT}} = 175^{\circ}$ C), which had a much lower carbon content, as the results of elemental analysis (Table 2) and IR spectroscopy (Fig. 4) suggest. The same tendency was observed for TiO₂-Au nanocomposites prepared based on these samples. With increasing the gold content, initially, the photocatalytic activity of



Fig. 6. Photocatalytic activity of our titania samples and TiO_2 -Au composites in methylene blue photodecomposition reaction upon irradiation with UV and visible light.

TiO₂-Au nanocomposites improved, but then diminished, with the highest activity observed at a gold content of 1%. In doing so, the photocatalytic activity upon UV irradiation was noticeably higher for sample 1 and the nanocomposite based on it than for sample 3 and the nanocomposite based on it. Conversely, upon irradiation with visible light, sample 3 and composites based on it displayed higher photocatalytic activity (Fig. 6). At the same time, one cause of diminished photocatalytic activity of TiO₂-2% Au nanocomposites (Fig. 6), in comparison to samples with lower gold content, can be that, as the content of Au NPs is increased to 2%, they act as recombination centers for photogenerated charge carriers [2] and can screen the surface from light, which contributes to reduction in the photocatalytic activity.

Electrocatalytic Behavior of TiO_2 Nanostructures and TiO_2 -0.01% Au Composites

The electrocatalytic behavior of our TiO₂ nanostructures and TiO₂-Au composites was evaluated by studying their performance in ORR, the core reaction in electrochemical oxygen sensors. Electrodes used in the electrochemical oxygen sensors are characterized by the following important parameters: the ORR potential (or half-wave potential $E_{1/2}$ of a current wave observed in cathodic polarization) and the working range ΔE of potentials in which oxygen sensing in solution can be performed. The $E_{1/2}$ value must be as low as possible to eliminate interference from possible side reactions during oxygen concentration measurements, and ΔE must be as large as possible to achieve higher sensitivity for the working electrode and obtain more accurate readings. Polarization curves for electrodes coated with films based on our TiO₂ nanostructures and TiO₂—Au composites were recorded in normal saline (NaCl) in the potential range of -0.35 to -1.2 V and featured a single current wave (Fig. 7) with well-defined limiting current, which is typical of TiO₂based electrodes and corresponds to ORR [51]. The hydrogen evolution reaction became noticeable at potentials E < -1.2 V. The considered electrodes featured stable performance in repeated potential cycling, which was indicated by constancy of their polarization curves established as soon as after the third cycle.

In normal saline (NaCl), ORR on the considered electrodes was observed at cathodic potentials of -0.35 to -0.85 V vs. Ag/AgCl, and the working potential range for ORR was 0.15–0.20 V (Table 3 and Fig. 7).

The electrodes fabricated using our TiO₂ samples for which STT was performed at 100°C, i.e., samples 1 and 3 (Table 3) displayed higher catalytic activity. For these samples, ORR potential $E_{1/2}$ was -0.35 and -0.45 V, respectively. The samples subjected to STT at $T = 175^{\circ}$ C (sample 2 (Tables 1, 3) and TiO₂ sample 4 (Table 1)), for which $E_{1/2}$ are not listed in Table 3, displayed considerably lower electrochemical activity $(E_{1/2} = -0.65$ and -0.71 V, respectively). As a result, the electrocatalytic activity of our samples was strongly dependent on the conditions of sol-gel synthesis of TiO₂ and subsequent STT as well as on the presence of monodisperse Au NPs.

Electrodes fabricated using Au-NP-containing nanocomposites 1a and 3a that were prepared on the



Fig. 7. Polarization curves for oxygen reduction (ORR) on TiO_2 electrodes: (1) no. 3, (2) no. 1, and (3) no. 2. (sample numbers as in Table 3).

basis of samples 1 and 3 (Table 3), respectively, displayed superior electrocatalytic activity toward ORR, compared to their titania-only counterparts. Halfwave potential $E_{1/2}$ of the O₂ reduction process shifted anodically from -0.45 to -0.41 V for sample 1a compared to sample 1 and from -0.35 to -0.31 V for sample 3a compared to sample 3 while working potential range ΔE for these pairs of samples expanded from 0.16 to 0.20 V and from 0.15 to 0.20 V, respectively. Thus, the effect of modification of TiO₂ film-coated electrodes with Au NPs was twofold: the ORR overvoltage decreased and the potential range for determining the concentration of dissolved oxygen expanded.

The considered electrodes featured good stability during multiple potential cycles.

CONCLUSIONS

By varying the conditions of sol-gel process and postsynthesis solvothermal treatment (STT), we prepared carbon-containing TiO₂ nanostructures and also used them to fabricate TiO₂-0.01% Au nanocomposites containing Au NPs. Films formed on titanium electrodes were photoactive in the range of 250-412 nm, and their quantum efficiency was $\eta = 0.08 -$ 0.20, while the band gap was essentially the same: $E_{g} =$ 3.04-3.05 eV, which is lower than a value normally reported for anatase (3.20 eV). The ORR potential $E_{1/2} = -0.32$ to -0.45 V, reasonably large range of working potentials $\Delta E = 0.15 - 0.20$ V, the presence of clear-cut limiting current, and good stability in continuous potential cycling make them promising electrode materials for use in electrochemical oxygen sensors with application to aqueous solutions.

The presence of groups with hydroxyl and carboxylate nature in the amorphous phase, which can function as bridges between this phase and the anatase crystal surface, is the key factor influencing the sensitivity of our TiO₂ nanostructures to visible light and responsible for the band gap narrowing (compared to pure anatase) and photoactivity enhancement in the methylene blue photodecomposition reaction. The superior photoactivity of TiO₂-0.01% Au composites, compared to their parental titania-only counterparts, can be due to synergy between Au NPs and interstitial Ti-O-C groups.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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