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SOL-GEL SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS TiO₂ MODIFIED WITH TRANSITION METAL IONS (Co, Ni, Mn, Cu)

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Mesoporous nanosized titania films and powders modified with Co²⁺, Ni²⁺, Mn³⁺ and Cu²⁺ ions have been produced by templated sol-gel method and characterized by optical spectroscopy, XRD, and BET surface area measurement. After calcinations at 400 °C, XRD patterns showed the anatase nanocrystalline phase formation (8–20 nm). The characteristic bands of Co²⁺ and Co³⁺ in octahedral and tetrahedral oxygen environment registered in diffusion reflectance spectra indicated the formation of Co₃O₄ spinel phase; crystallization of M/TiO₂ powders after heat treatment at 650 °C led to an appearance of absorption bands belonging to Ni²⁺ or Mn³⁺ ions in an octahedral environment. Band gap energy and the position of flat band potentials were estimated by photoelectrochemical measurements. The films doped with transition metals possessed higher photocurrent quantum yield than that for undoped samples.

INTRODUCTION

Among the semiconductor materials, titanium dioxide attracts a great attention of the researchers because of its chemical stability, biological inertness, low toxicity, and relatively low cost. TiO₂ is a promising material for application in environmental photocatalysis, for the generation of electricity in the solar and fuel cells, gas sensors, optical and protective coatings, electrochemical devices etc. [1, 2]. The sol-gel synthesis is a simple, relatively inexpensive, and reliable method for receiving of mesoporous materials [3, 4] that achieves high chemical homogeneity of formed products with significantly decrease of the heating temperature and duration of heat treatment. It provides a probability to control the particle size and pore structure of materials at different stages of the synthesis (by changing the reaction time, temperature, concentration and chemical composition of reagents) and to modify the rheological properties of disperse systems in a wide range. This is a promising approach to the synthesis of powders and films of individual oxides [5] and mixed oxide materials [6, 7], production of nanostructured TiO₂ doped with nanoparticles of noble metals [8] or transition metal oxides, due to a number of its advantages:

the possibility of controlling the size of the crystals and the phase composition, the production of unstable transition crystal structures, the formation of high surface area.

In this paper, template sol-gel synthesis of mesoporous films and powders of titanium dioxide modified with transition metal ions (cobalt, nickel, manganese and copper) is reported. Phase composition, optical properties and energy parameters (band gap E_g and flat band potential E_{fb}) of the resulting materials are investigated.

EXPERIMENTAL

Mesoporous TiO₂, Coⁿ⁺/TiO₂, Niⁿ⁺/TiO₂, Mnⁿ⁺/TiO₂ and Cuⁿ⁺/TiO₂ films and powders were synthesized via templated sol-gel method according to [8] using Ti(OiPr)₄, CuSO₄·5H₂O, Co(CH₃COO)₂·4H₂O, Ni(HCOO)₂·2H₂O, MnCl₂·4H₂O as titania and 3d-metal sources, Pluronic F68 or Pluronic P123 as template and acetylacetone as complexing agent. The molar ratios of the components were as follows: Pluronic F68 (or P123) : acetylacetone : HNO₃ : Ti(OiPr)₄ = 0.1 : 1 : 2 : 2. For film deposition onto glass or titanium substrates, dip-coating technique was utilized. After deposition of the film, gelation, and gel ripening, it was dried in

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air at room temperature for 2 h. Then the dried films were sintered to 400 °C. F68 and P123 burns out at these temperatures and so this process should be carefully carried out for keeping the ordered porous structure of the oxide film. To facilitate structural investigations by XRD, powders with the same chemical composition were prepared via gelation of the films' precursors, their drying in air with following heat treatment to 450 or 650 °C. XRD analysis of crystalline phases was performed using a DRON-4-07 (Burevestnik, St. Petersburg) diffractometer (CuK α radiation with Ni filter) with Bragg-Brentano registration geometry ($2\theta = 10\text{--}60^\circ$). The average size of crystallites was determined using Sherrer equation applied to the most intensive peak. The degree of the powders crystallinity was estimated as the ratio of integrated intensities, such as for the (101) line of the studied and reference standard samples (reference standard: TiO $_2$, anatase 100 %). Optical spectra of the films and powders were recorded using a Perkin-Elmer Lambda Bio 35 UV-Vis with integrating sphere Labsphere RSA-PR-20 in spectral diapason 200–1000 nm. The film thickness and refractive index were measured using a LEF-3M multi-angle ellipsometer ($\lambda = 632.8$ nm).

Photoelectrochemical investigations were carried out in the wavelength range 250–600 nm in a quartz electrochemical cell under irradiation of a high-pressure xenon lamp, which gave light with a frequency of 20 Hz passing through a monochromator and focused on the semiconductor electrode.

RESULTS AND DISCUSSION

The diffraction reflex at low $2\theta = 2$ values in the diffraction patterns of the initial films and powders corresponds to the ordered mesostructures formed by the template Pluronic. The absence of this reflex in the diffraction patterns of calcined powders indicates the disordering of organized structure in the process of titanium dioxide crystallization. Investigation of the nitrogen adsorption-desorption isotherms at -196 °C and the pore size distribution for the powders calcined at 450 °C showed that a mesoporous structure was formed with the average pore size of 2.5–6 nm and the specific surface (S_{BET}) of 147 (pure TiO $_2$) to 224 m 2 /g for manganese samples. Increasing the concentration

of dopant ions of 1 to 5 % insignificantly influenced on the S_{BET} .

Similarity in the Ti $^{4+}$, Ni $^{2+}$, Co $^{2+}$, Mn $^{3+}$, and Cu $^{2+}$ ionic radii (68, 69, 72, 80 and 72 pm, respectively) allows the interstitial incorporation of the dopant into the anatase lattice [9, 10]. The diffraction peaks in the XRD patterns of films calcined at 400 °C can be attributed to anatase. Transition metal oxide phases were not detected in the XRD pattern suggesting that metal oxide could exist as the amorphous phase without incorporating to the TiO $_2$ lattice or goes to the substitutional sites in the TiO $_2$ lattice or octahedral interstitial sites. We previously [11] investigated the structure of powders obtained from precursors of films that were calcined to 450 °C and 650 °C. CoTiO $_3$, NiTiO $_3$, Mn $_2$ O $_3$ were detected in the XRD patterns of 5 % Co/TiO $_2$, Ni/TiO $_2$ and Mn/TiO $_2$ powders, respectively, when annealing temperature increased up to 650 °C. There were no displacements of the peaks of anatase or rutile in the XRD patterns of these powders, as it was observed for Cu/TiO $_2$ powders (≤ 5 % Cu). Low-intensity phase reflexes of CuO, Cu $_2$ TiO $_3$ and Cu $_3$ TiO $_4$ for copper-containing systems were registered only at Cu $^{2+}$ concentrations of ≥ 15 %. The presence of rutile phase was observed only in the samples of 5 % Cu/TiO $_2$ and 5% Mn/TiO $_2$. The authors [12] previously showed that the doping with manganese ions reduced the temperature of anatase – rutile phase transition. Concentration of rutile in powder 5 % Cu/TiO $_2$ was negligible while in the manganese sample it was 41 %.

Optical properties of films and powders

M/TiO $_2$. Obtained films were transparent, robust, and homogeneous. The refractive index and thickness of the films were measured by ellipsometry method. TiO $_2$ film refractive index was 1.87 (2.55 – for the bulk material) and the thickness was 64 nm. The smaller value of refractive index of the films is due to the contribution of air ($n = 1$) to the developed pore structure in the effective refractive index of TiO $_2$ - air [13]. The refractive indices of the films with Cu content of 5 and 20 % are 1.94 and 1.66, and the thicknesses are 60 and 50 nm, respectively. The refractive indices of the films containing 5 % Co, 5 % Mn, 5 % Ni were 1.92, 1.87, 1.88, and the thicknesses were 95, 100, 108 nm, respectively. Change in the thickness of the films can be attributed to a slight change in viscosity

of the solution due to adding an aqueous solution of salts of transition metals as well as particularity of structure formation during annealing of the films. The size of templating agent molecules has significant influence on the optical properties of the films. The use of the template Pluronic F68 (molecular weight 8400 g/mol) led to the defects shaped as rings with size of 0.2–0.8 μm on the film surfaces due to the peculiarities of relatively large molecules template. These defects caused to a greater light dispersion so reducing their optical properties. Transparent films of high quality were obtained using Pluronic P123 with molecular weight 5800 g/mol. Dispersion of these films does not exceed 1 % in the visible region.

The absorption band in the UV-region ($\lambda = 380$ nm) of diffuse reflectance spectra of the M/TiO₂ powders after heat treatment at 450 °C

(Fig. 1) can be attributed to the band gap excitation of anatase TiO₂ which corresponds to the band to band transition from Ti 3d to O 2p levels [14]. There is a significant bathochromic shift of the absorption edge for all powders doped with transition metal ions. When transition metal ions incorporated into the lattice, the dopant level appeared between the valence band and the conduction band of TiO₂, thus altering the band-gap energy and shifting the absorbance edge to the visible light region [15]. Additional energy levels appear in the band gap of TiO₂ and the E_g value decreases induced by transition metal ions [14, 16, 17]. Such energy changes in a number of cases (at low concentrations of dopants) can increase the photocatalyst sensitivity in the visible region of the spectrum [14].

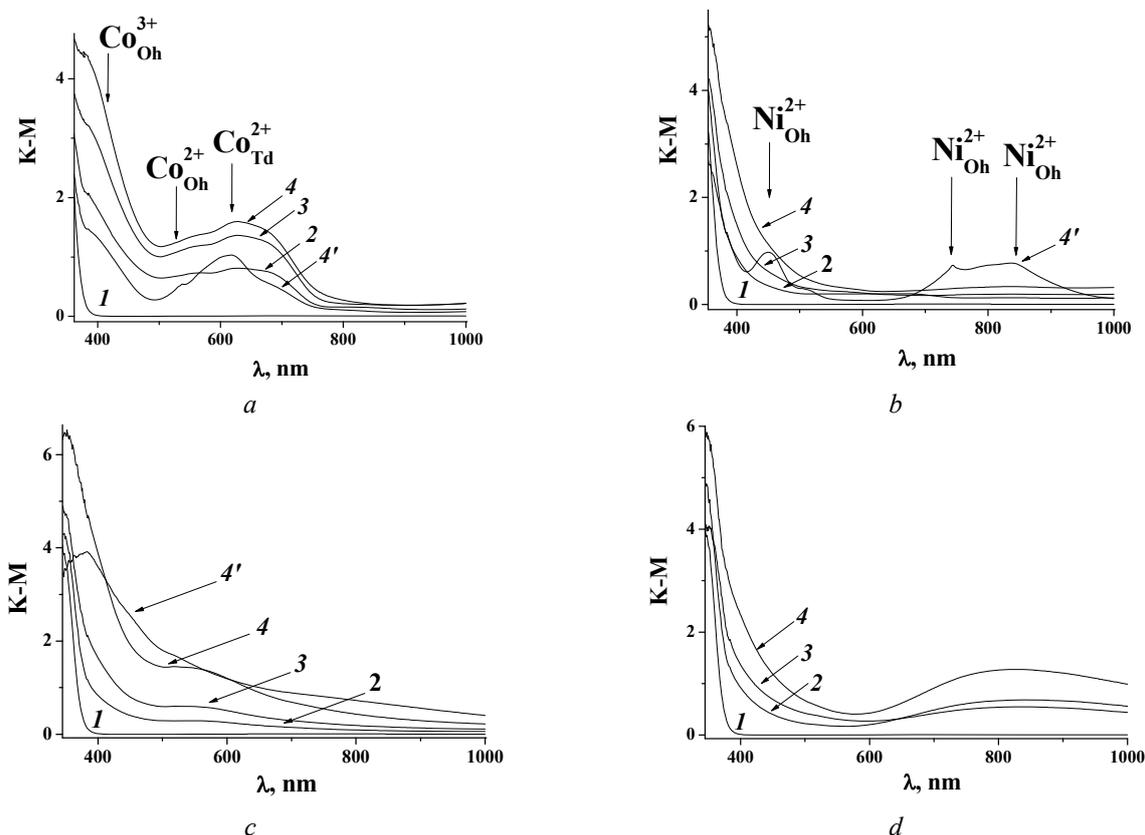


Fig. 1. Diffuse reflectance spectra of the powders converted by the Kubelka-Munk function, Co/TiO₂ (a), Ni/TiO₂ (b), Mn/TiO₂ (c), Cu/TiO₂ (d) with dopant content 0 % (1), 1 % (2), 3 % (3), 5 % (4) calcined to 450 °C, and with 5 % calcined to 650 °C (4')

In the diffuse reflectance spectra of cobalt-containing powders of titanium dioxide absorption bands were observed in the region of 650–800 nm ($\text{Co}^{2+}_{\text{Td}}$), 450–550 nm ($\text{Co}^{2+}_{\text{Oh}}$) and

350–440 nm ($\text{Co}^{3+}_{\text{Oh}}$) corresponding to d-d transitions in ions of cobalt octahedral and tetrahedral coordination [18, 19] (Fig. 1 a). The absorption band at 350–440 nm is overlapped with

the fundamental absorption band of titanium dioxide. According to [20], the presence of a band at 600–670 nm ($\text{Co}^{2+}_{\text{Td}}$), along with the characteristic absorption bands of $\text{Co}^{2+}_{\text{Oh}}$ and $\text{Co}^{3+}_{\text{Oh}}$, indicates the presence of spinel Co_3O_4 in samples. This d-d transition is characterized by a high extinction which allows detecting a state of cobalt among others, even if it is a small amount [20].

According to [19], there are three allowed spin transitions from ${}^3\text{A}_{2g}$ to ${}^3\text{T}_{2g}$, ${}^3\text{T}_{1g}$, ${}^3\text{T}_{1g}(\text{P})$ located in the range of 770–1430, 500–910 and 370–525 nm for the systems of octahedral nickel (II). The state corresponding to forbidden spin transition to ${}^1\text{E}_g$ lies close to the ${}^3\text{T}_{1g}$, so their considerable mixing occurs. Therefore, a doublet band is observed in the spectrum. The optical spectra of Ni^{2+} is characterized by absorption at 410 and 730 nm related to nickel ions in octahedral environment ($\text{Ni}^{2+}_{\text{Oh}}$) and that at 525 and 650 nm corresponding to Ni^{2+} ions in tetrahedral environment ($\text{Ni}^{2+}_{\text{Td}}$) [21]. The absorption band of $\text{Ni}^{2+}_{\text{Oh}}$ at 400–450 nm is hard to distinguish from the fundamental absorption band of titanium dioxide (Fig. 1 b). However, for the samples annealed at 650 °C there is a distinct band with the maximum at 450 nm and doublet at 750–850 nm. Three main characteristic absorption bands for nickel oxide NiO are observed at 407, 671, and 741 nm [19]. In the diffuse reflectance spectra of sample 5% Ni/TiO₂ (650 °C) these bands are shifted to longer wavelengths (450, 743, and 837 nm, respectively), probably due to the distortion of the octahedral environment due to the formation of nickel titanate.

The increase of Mn concentration in manganese-containing samples up to 5% (Fig. 1 c) led to appearance of the shoulder at 550 nm in the diffuse reflectance spectra that corresponds to the transition in Mn^{3+} -ions in an octahedral environment ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ [19, 22]. Characteristic absorption bands of $\text{Mn}^{2+}_{\text{Oh}}$ and $\text{Mn}^{4+}_{\text{Oh}}$ [19, 22] in the short-wavelength region (450 nm) are overlapped with the fundamental absorption bands of titanium dioxide.

The broad structureless absorption band with the maximum at 800 nm observed in the diffuse reflectance spectra of $\text{Cu}^{2+}/\text{TiO}_2$ powders. The absorption in the spectral region 600–1100 nm may be indicative for the existence of copper (II) with a tetrahedral structure or a similar distorted structure (Fig. 1 d) It is known that divalent

copper ions have the electron configuration of $3d^9$. Such ions as a rule exhibit the stoichiometric mobility. Only one term ${}^2\text{D}$ belongs to this configuration, which splits into two terms ${}^2\text{T}_2$ and ${}^2\text{E}$ in a cubic field. In a tetrahedral field the lower level is the first term, in the octahedral – the second one. The observed peak can be attributed to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition [19, 23].

Photoelectrochemical characterisation of M/TiO_2 ($M - \text{Co}, \text{Ni}, \text{Mn}, \text{Cu}$) films. Spectral dependences of photocurrent were measured for the TiO_2 and M^{n+}/TiO_2 electrodes produced via coating of M^{n+}/TiO_2 films on Ti substrate (Fig. 2) to obtain the value of the band gap energy. Photocurrent quantum yield for all of 1% M/TiO_2 films is higher than that for undoped TiO_2 . The enhancement of photocurrent efficiency indicates that M^{n+} ions addition is beneficial to promote charge separation within nanostructured TiO_2 film and to improve interfacial charge transfer process due to formation of impurity electron levels of 3d-metals in the band gap of titanium dioxide [16, 17, 24], acting as traps of charge which retard the recombination process.

It is well known that quantum yield of photoelectrochemical current η in semiconductors can be expressed as [25]:

$$\eta = \frac{A}{h\nu} (h\nu - E_g)^m,$$

where $h\nu$ is the photon energy, $m = 1/2$ for the direct transition and $m = 2$ for the indirect transition.

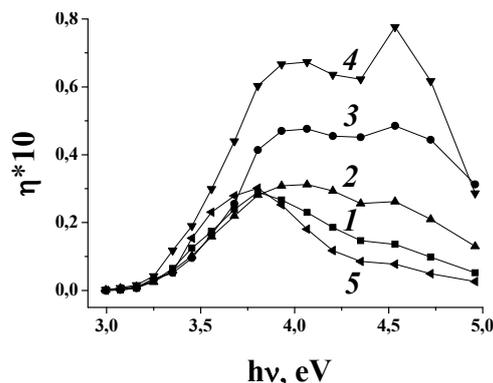


Fig. 2. Quantum yield of photocurrent of 1% M^{n+}/TiO_2 electrodes: TiO_2 (1), Co/TiO_2 (2), Ni/TiO_2 (3), Mn/TiO_2 (4), Cu/TiO_2 (5)

For the tested M^{n+}/TiO_2 compositions, photocurrent spectra were presented as

$(\eta \cdot hv)^{1/2} = f(hv)$ dependence which was linear in the wide range of wavelength. Experimental data fit better to an indirect transition. Band gap (E_g) values were calculated [26,27] by straight line extrapolation of these dependences to the abscissa (Table).

E_g values obtained by this method are located in the range of 2.88–3.09 eV (Table). For M/TiO₂ films, the E_g values decrease with the

increase in dopant content. That is probably associated with the formation of new phases.

To test whether the narrower band gap is caused by a shift of the valence (E_{vb}) or conduction band (E_{cb}) edges, the position of the flat band potential (E_{fb}) of the catalysts was determined by the direct electrochemical measurements of photocurrent in aqueous 0.5 NaCl as a function of applied potential.

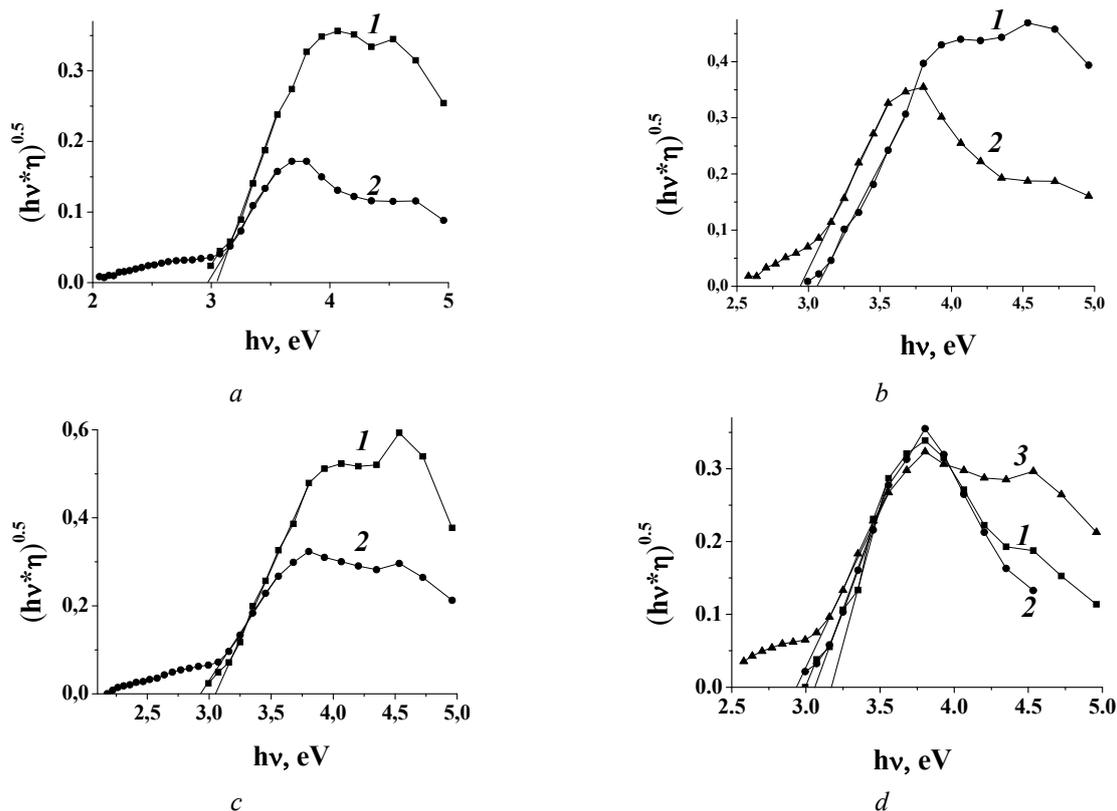


Fig. 3. $(hv \cdot \eta)^{1/2} = f(hv)$ dependence of Co/TiO₂ (a), Ni/TiO₂ (b), Mn/TiO₂ (c), Cu/TiO₂ (d) films with 1 (1), 5 (2) and 30 % (3) dopant content

Table. Photoelectrochemical characterisation of M/TiO₂ films (M – Co, Ni, Mn, Cu)

Sample	E_{fb} , eV vs NHE	Quantum yield of photocurrent η , a.u.	E_g , eV
TiO ₂	-0.42	1	3.09
1 % Ni /TiO ₂	-0.42	1.66	3.07
5 % Ni/TiO ₂	-0.45	1.14	2.95
1 % Co/TiO ₂	-0.36	1.07	3.07
5 % Co/TiO ₂	-0.80	0.28	2.97
1 % Mn /TiO ₂	-0.48	2.80	3.08
5 % Mn/TiO ₂	-0.40	0.93	2.88
1 % Cu/TiO ₂	-0.30	1.03	3.08
5 % Cu/TiO ₂	-0.15	1.14	3.07
30 % Cu/TiO ₂	-0.10	0.94	2.99

Flat band potentials were estimated from i_{ph} changes measured at the photocurrent maximum for TiO_2 and M^{n+}/TiO_2 films coated onto titanium substrate in aqueous 0.5M NaCl plotted against applied potential by straight line extrapolation of these dependences to the abscissa. Flat band potential values (Table) for the TiO_2 differ insignificantly and are comparable with the value from -0.47 to -0.49 V vs NHE, obtained at $pH \approx 7$ for nitrogen-doped titanium dioxide [28] and $E_{fb} = -0.58$ V measured for anatase single crystal [29].

As follows from Table, increase in M^{n+} content leads to the cathodic shift of the bottom of conduction band ΔE_{cb} along with E_g decrease. The most significant changes of flat band potential values were observed for Cu-doped samples and 5 % Co/ TiO_2 that probably related with coexistence of two valence states of dopant ions. As the location of the conduction band is a measure of the reduction power of the photogenerated electrons, we can predict the enhancing of catalytic activity in photoreduction processes. As shown in our previous investigations [30], M/ TiO_2 (M – Co, Ni, Mn, Cu) with low dopant content possess high efficiency in electrocatalytic reduction of dissolved oxygen.

CONCLUSIONS

After calcinations at $400^\circ C$ in the XRD patterns of annealed samples, only anatase nanocrystalline phase (8–20 nm) was observed. The characteristic bands of Co^{2+} and Co^{3+} in octahedral and tetrahedral oxygen environment registered in diffusion reflectance spectra indicated the formation of Co_3O_4 spinel phase; crystallization of nickel titanate after heat treatment at $650^\circ C$ was accompanied by the appearance of absorption bands characteristic of Ni^{2+} in octahedral environment.

The photoelectrochemical characteristics of electrodes based on mesoporous TiO_2 films modified with Co, Ni, Mn, Cu ions depended on the composition and concentration of the doping agent. The films doped with transition metals showed a higher photocurrent quantum yield in comparison with undoped samples. Synthesized films can be used as effective photocatalysts and sensor elements.

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Золь-гель синтез та дослідження мезопористого діоксиду титану, модифікованого перехідними металами (Co, Ni, Mn, Cu)

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Нанорозмірні мезопористі порошки і плівки діоксиду титану, модифікованого іонами Co^{2+} , Ni^{2+} , Mn^{3+} та Cu^{2+} , синтезовані темплатним золь-гель методом та охарактеризовані за допомогою адсорбційних методів, оптичної спектроскопії і РФА. Після термообробки при 400 °С в дифрактограмах є лише рефлекси нанокристалічної фази анатазу (8–20 нм). Характеристичні смуги поглинання іонів Co^{2+} та Co^{3+} в октаедричному та тетраедричному оточенні в спектрах дифузного відбиття свідчать про формування фази шпінелі Co_3O_4 ; кристалізація порошків M/TiO_2 після термообробки при 650 °С приводить до появи смуг поглинання, характерних для іонів Ni^{2+} або Mn^{3+} в октаедричному оточенні. Прямими фотоелектрохімічними вимірами встановлені ширина забороненої зони та положення потенціалів плоских зон. Допування перехідними металами приводить до підвищення квантового виходу фотоструму у порівнянні з немодифікованими плівками діоксиду титану.

Золь-гель синтез и исследование мезопористого диоксида титана, модифицированного переходными металлами (Co, Ni, Mn, Cu)

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Наноразмерные мезопористые порошки и пленки диоксида титана, модифицированного ионами Co^{2+} , Ni^{2+} , Mn^{3+} и Cu^{2+} , синтезированы темплатным золь-гель методом и охарактеризованы с помощью адсорбционных методов, оптической спектроскопии и РФА. После термообработки при 400 °С в дифрактограммах пленок и порошков регистрируются только рефлексы нанокристаллической фазы анатаза (8–20 нм). Характеристические полосы поглощения ионов Co^{2+} и Co^{3+} в октаэдрическом и тетраэдрическом окружении в спектрах диффузного отражения свидетельствуют о формировании фазы шпинели Co_3O_4 ; кристаллизация порошков M/TiO_2 после термообработки при 650 °С приводит к появлению полос поглощения, характерных для ионов Ni^{2+} или Mn^{3+} в октаэдрическом окружении. Прямыми фотоэлектрохимическими измерениями определены ширина запрещенной зоны и положения потенциалов плоских зон. Допирование переходными металлами приводит к повышению квантового выхода фототока по сравнению с немодифицированными пленками диоксида титана.