

TOWARD TiO₂ — MnO₂ NANOCOMPOSITE PHOTOELECTRODES FOR ORGANIC DYES DEGRADATION

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As a green approach, photoelectrocatalytic (PEC) technologies are promising and effective to degrade various kinds of pollutants by utilizing abundant solar energy [1]. Historical retrospective of the issue dates back to the 19th century when A. Becquerel discovered the photovoltaic (PV) phenomena in electrochemical systems (photoelectric effect) [2]. A. Fujishima and K. Honda [3] reported the first indication of a photoelectrochemical (PEC) application in 1972. Electrocatalysis as a phenomenon suggests the electrode process efficiency improvement depending on the nature of indifferent electrode material. In turn, the further growth of activity takes place in PEC when quantum of light is absorbed by photoelectrocatalyst.

Unlike electrocatalysis, semiconductor electrodes based on transition metal (TM) oxides are the best photoelectrocatalysts. Their advantages are also low price and abundance in nature. Among disadvantages, their low conductivity and brittleness can be mentioned. There is another unique opportunity in TM oxides to involve the inner space for electrochemical transformations. Molecular sieves (MS) structures as microporous solids were involved since decades in industrial processes of purification, separation, and petroleum refining, among others⁴. Such materials were coined as octahedral MS (OMS) of manganese (IV) oxide family of tunneled

polymorphs formed by MnO_6 octahedrons. The crystals of tunnelled polymorphs consists of $n \times m$ edge-shared MnO_6 octahedral chains, which are corner-connected to form one-dimensional channels. Among these compounds, tunnel structures with regular lattice such as pyrolusite (1×1 , $\beta\text{-MnO}_2$), ramsdellite (1×2 ; $\gamma\text{-MnO}_2$), hollandite (2×2 , $\alpha\text{-MnO}_2$), 2×3 romanechite and 3×3 todorokite can be distinguished [5].

Titanium dioxide has many advantages that are the reason of strong research interest and the widest practical application. This compound is naturally abundant, commercially available, economically viable, chemically stable, non-toxic, and environmental eco-friendly [6]. That's why the titanium dioxide annual production is significant and made up more than 5 million tons in 2011 [7]. Its consumption includes production of pigments, textile, plastics, and even in cosmetics and food industry (food additive E171) [7, 8]. Nanoparticles of titanium dioxide assessed and allowed by European authorities as UV-filters in sunscreen product formulations and belong to the limited number of nanomaterials having cosmetical application [9].

Doping of the semiconductor is a very important instrument to tune its functional properties especially in the search for more photoactive materials using nanostructured semiconductors capable of being more active under visible light irradiation. The positive effect of so-called *self-doping* is also mentioned in the literature as Ti^{3+} into TiO_2 [10, 11], resulting in increased electrical conductivity and visible light absorption. The red shift of the absorption edge is linked to the formation of color centers, which include Ti^{3+} centers and oxygen vacancies [12].

Photoelectrocatalysis belongs to the advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals ($\bullet\text{OH}$), which are highly active oxidizing species able to mineralize organics. The hole (h^+) in the valence band produces $\bullet\text{OH}$ radicals through the oxidation of H_2O molecules or OH^- ions adsorbed on the semiconductor surface and is also able to oxidize organic molecules directly. The band gap in TiO_2 (3.0 – 3.2 eV) is too large to be overcome with the visible light energy and it corresponds to more energetic UV-spectrum region. The *coupling* of

two semiconductors reduces e^-/h^+ pair recombination due to opportunity to use both regions UV/Vis of spectrum and also of carriers transfer from one semiconductor to the other [Ошибка! Закладка не определена.]. It can greatly promote the photo-carrier separation and enhance the photocatalytic quantum yields [13, 14]. Modified TiO₂ nanotube arrays with CuInS₂ presented a band gap of 1.5 eV, and the compound obtained showed enhanced UV and visible absorption with higher PEC oxidation rate of 2-chlorophenol. Similar effects are expected when coupling MnO₂ as a semiconductor with lower band gap (1.3 eV [15]) and TiO₂. Both have isostructural polymorphs of rutile type that opens opportunities for cationic doping also.

Anatase and rutile are the most thermodynamically stable and photocatalytically active TiO₂ polymorphs. The commercially available TiO₂ photocatalyst with P25 name has anatase: rutile 80:20 phase ratio. Synergetic effect of *coupling* between TiO₂ polymorphs exists here. Li and coworkers [10] demonstrated that the formation of exposed surface anatase–rutile phase coupling is critical to achieve enhanced photocatalytic activity of TiO₂ nanoparticles owing to the efficient synergic effects of the two phases.

As mentioned above, coupling with other narrower band gap semiconductors is also one of the most efficient strategies to develop highly-active TiO₂. Superfine manganese dioxide (MnO₂) particles can increase the utilization rate of visible light irradiation due to its narrow band gap, large surface area and negatively charged surface [16,[17]. Therefore, MnO₂ deposition to the surface of TiO₂ photoelectrode combines the advantages of wider visible-light absorption and higher efficiency of electron-hole separation. Therefore, MnO₂ with TiO₂ coupling is expected to be prospective from the point of view of electrocatalytic applications.

The strong dependence of the functional properties of non-stoichiometric oxides on the origin, dispersion, particle shape of the material stimulated our interest to the new preparation methods of active titanium dioxide PEC. The aim of this work was to study the activity of composite electrodes based on titanium dioxide in photoelectrocatalytic degradation of methyl orange (MO) under UV-irradiation and conditions of its further improvement by coupling effect with more conducting

manganese dioxides. The physicochemical properties of the corresponding materials were studied using chemical, X-ray diffraction phase analysis, electron microscopy, and UV spectroscopy.

1. Experimental

Titanium dioxide (sample No. 1) was obtained at Frantsevich Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine. $\text{TiO}(\text{OH})_2$ raw material is a product of intermediate stage of the titanium concentrates and slags processing at PJSC “Sumykhimprom”. Manganese(IV) oxide sample was electrodeposited galvanostatically ($i = 10 \text{ [A/dm}^2\text{]}$) at the platinum anode and platinum plate as an auxiliary electrode [18]. The pristine fluorine-containing electrolyte consisted of 0.1 M HF + 0.7 M MnSO_4 . Dopant additives were sulfates of the following concentration in the electrolyte: 1.5 M $(\text{NH}_4)_2\text{SO}_4$ [5, 19]. The precipitates were filtered, rinsed with distilled water till the negative reaction on BaSO_4 , dried 3 hours at 120 °C. Samples were studied further by XRD, FTIR, AAS, TGA, SEM, TEM EPR and other methods.

Linear voltammetry method with a sweep potential scan (potentiodynamic method) was the main method for studying the photoelectrocatalytic anode oxidation of organic compounds. A potentiostat-galvanostat IPC-PRO (Russia), consisting of a measuring unit of a potentiostat, and a PC with the IPC2000 software. Electrode potential was measured versus standard silver chloride reference electrode. Polarization measurements were performed starting with the stationary potential. The potential scan rate was in the range of 0.001 — 0.5 $\text{V}\cdot\text{s}^{-1}$. The paste carbon electrode material fabrication for PEC degradation included several steps. The oxide sample or $\text{TiO}_2 + \text{MnO}_2$ mixture were individually ground in a mortar, then with gradually added graphite of spectral purity in the ratio of graphite : TiO_2 ($\text{TiO}_2 + \text{MnO}_2$) 50 : 50 or 70 : 30, respectively, to improve the electrical conductivity. PTFE fluoroplastic emulsion (Merck, 60% (wt.)) was added to plastify the obtained electrode material. The resulting electrode material was pressed with a constant push onto the copper current collector with diameter of $\varnothing = 0.3 \text{ cm}$. The weight of the electrode active mass was to within 10 mg. Luggin's capillary was situated as close as possible to the

working electrode edge in the three-electrode cell. A glassy carbon plate with 10 times larger area than of the working electrode served as an auxiliary electrode. The measurements were carried out in 10^{-4} M MO solution with 0.1 M KCl electrolyte at the dark conditions and with the UV radiation. Cell was placed in a closed container with a UV lamp (OSRAM, PURITEC HNS 6WT5 G5, 212 mm) at a distance of 5 cm.

2. Results and Discussions

Sample No. 1 obtained from hydrated titanium dioxide $\text{TiO}(\text{OH})_2$ suspension had pure anatase phase composition. The porous structure study results showed much more developed mesoporous surface for sample No. 1, as well as the specific surface area. Another important feature of the TiO_2 sample studied was the presence of Ti^{3+} . The intense paramagnetic Ti^{3+} ion signal in the solid oxide lattice was detected by EPR only in this sample in comparison with commercial samples. The defective Ti^{3+} positions influence on surface states since small size of this sample particles (about 10 nm). Multivalent states in the lattice of oxide catalysts are known to be active centers of catalysis. The stoichiometric TiO_2 differs significantly in photocatalytic properties, and the presence of surface Ti^{3+} defects reduces the band gap of titanium dioxide and contributes to the fact that the photocatalytic process can be initiated by photons closer to the edge of the visible range [20].

CVA method allows one to study the ability of chemical compounds to oxidative degradation, in particular, MO to anodic photoelectrocatalytic oxidation. The current-voltage dependences were recorded first in the dark mode and sequentially with the UV source turned on.

Despite the low-power UV irradiation source (6 W), the photoelectrocatalytic effect was manifested clearly at high potential scan rates (more than $0.05 \text{ V}\cdot\text{s}^{-1}$ at electrode potential range -1.0 — $+0.5 \text{ V}$) in comparison with dark conditions for sample No. 1 (Fig. 1). The oxidation current increase was by 100% and higher at the absence of significant changes at the same conditions for commercial TiO_2 samples studied at the same conditions after subtraction of background KCl current on the same electrode. The observed photoelectrocatalytic oxidation process is comparable

to $0.1 \text{ V}\cdot\text{s}^{-1}$ scan rate (since it manifests itself maximally at this potential scan rates) and it is relatively fast. The comparison of TiO_2 electrode activity in 0.1 M KOH versus 0.1M KCl demonstrated advantages of the latter (Fig. 2-3). There is also a significant anode oxidation effect at low electrode potentials in 0.1M KCl (Fig. 1). It was observed only for Ti^{3+} self-doped electrode unlike commercial anatase and rutile electrodes. We suggest that its appearance is attributed with the band gap decrease by Ti^{3+} surface states in the sample. The preliminary investigations of $\text{TiO}_2\text{:MnO}_2$ composite electrodes in different ratios were started in alkaline electrolyte and are consistent with results obtained previously on TiO_2 electrode.

The composite electrode material interface study is an important constituent part of its characterisation. We analysed electrode based on sample No.1 material containing TiO_2 , graphite conductive additive and PTFE binder (60%-emulsion) by SEM method with gold vacuum deposition to improve contrast of SEM images (Fig. 4-5). TiO_2 particles have a plate-like morphology with the dimension of crystallites less than 50-100 nm and except for coupling effect they need graphite as a conductive additive due to their low conductivity. PTFE binder makes electrode material more stable and durable against TiO_2 powder brittleness.

The lower ratio of graphite additive to TiO_2 decreases currents significantly. White colour on such images is typical for low conductive material that reflect electrons and vice versa for black colour material. Conductive additive predominates onto the interface and from this point of view TiO_2 application efficiency can be improved by increase of its conductivity. Grey colour brittle flakes in Fig. 4, 5 are consistent with graphite behaviour. Fig. 5 shows the white colour aggregate of nanoparticles with size that is close to evaluated previously for TiO_2 sample No.1 It lies on nanoflakes of graphite and such a position could be ideal one for PEC process.

Fig. 6 showed with 597000 times magnification the needle-like crystallites of obtained from F-containing electrolyte manganese dioxide simultaneously doped with ammonium ions. Fig. 7 demonstrates with 361000 times magnification the random distribution of small white TiO_2 particles in grey-black colour medium of conductive additive that is consistent with 70% by mass content of graphite powder.

Analysing view of TiO₂ 10 nm nanoparticles aggregates of approximately the same size (of about 1 μm in Fig. 5), it is interesting to discuss the issue of optimal for PEC size of these aggregates. On the one hand, their low conductivity contradicts to PEC application, on the other hand, the lower size of aggregates and more uniform distribution in conductive medium could be the direction of further improvement. The next issue here is how to control the size of TiO₂ aggregates. Generally, Ti³⁺-self-doping and other doping strategies could improve PEC characteristics significantly.

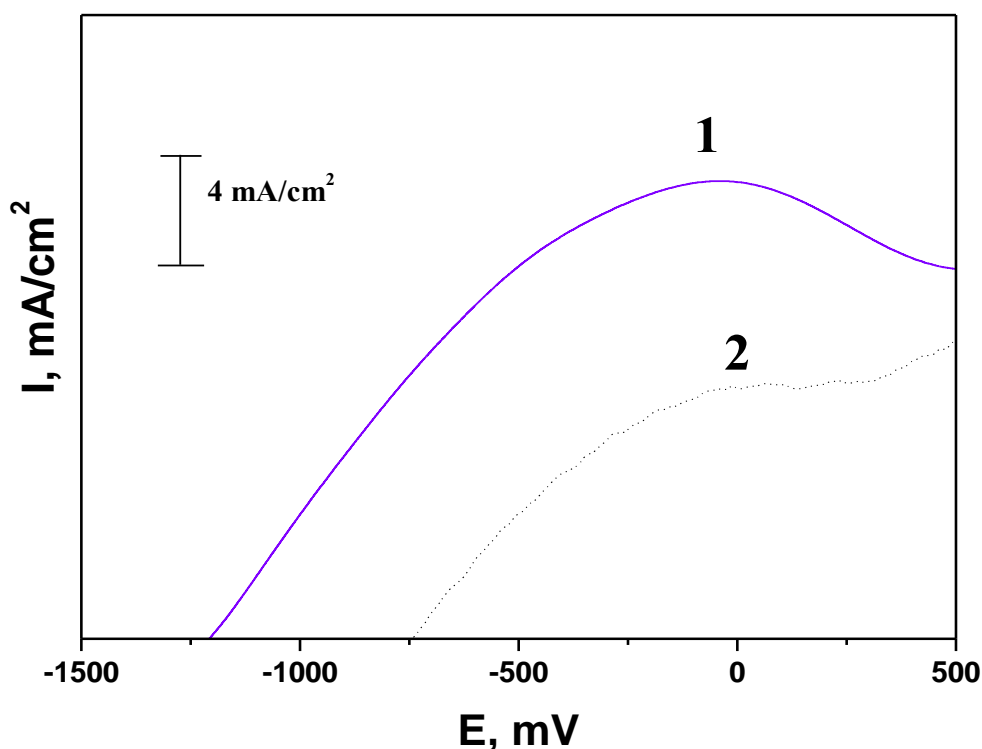


Fig. 1. Polarisation potentiodynamic curves 1-2 registered on working electrode containing TiO₂ sample in 30/70 ratio with graphite, under UV-irradiation at potential scan rates 0.1 V / s (----- — dash line designates polarization curve without UV) in 0.1M KCl with subtracted background current of 0.1 M KCl on the same electrode

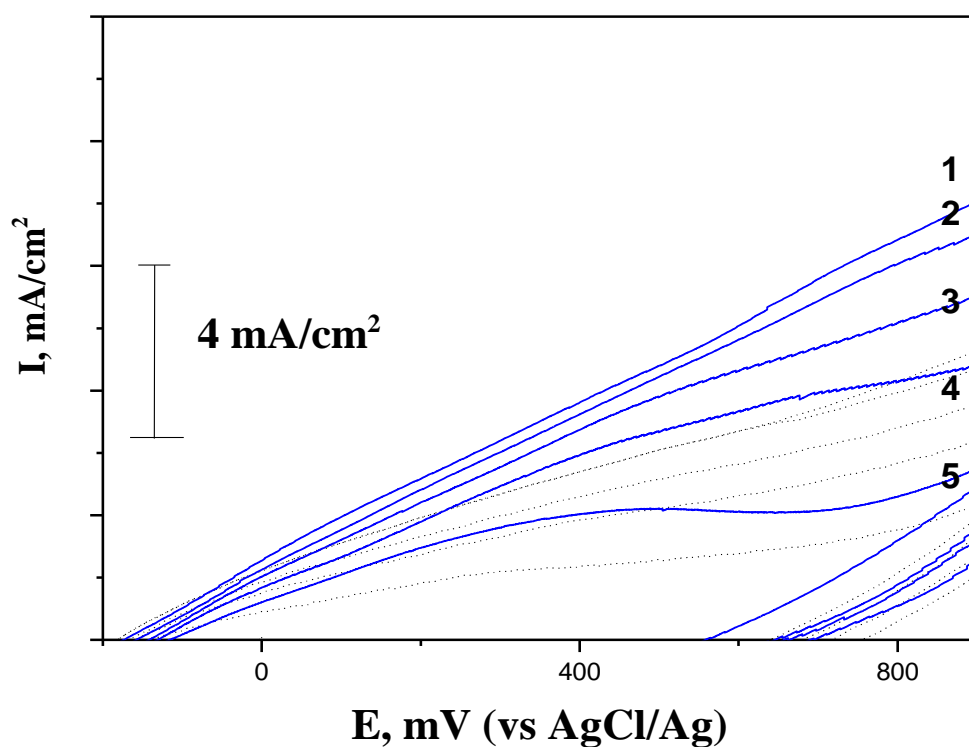


Fig. 2. CVA curves 1-5 registered on working electrode containing TiO₂ sample in 30/70 ratio with graphite, under UV-irradiation at potential scan rates 0.1(1,2), 0.5(3), 0,2(4) 0.1(5) V / s (----- — dash line designates polarization curve without UV) in 0.1M KOH

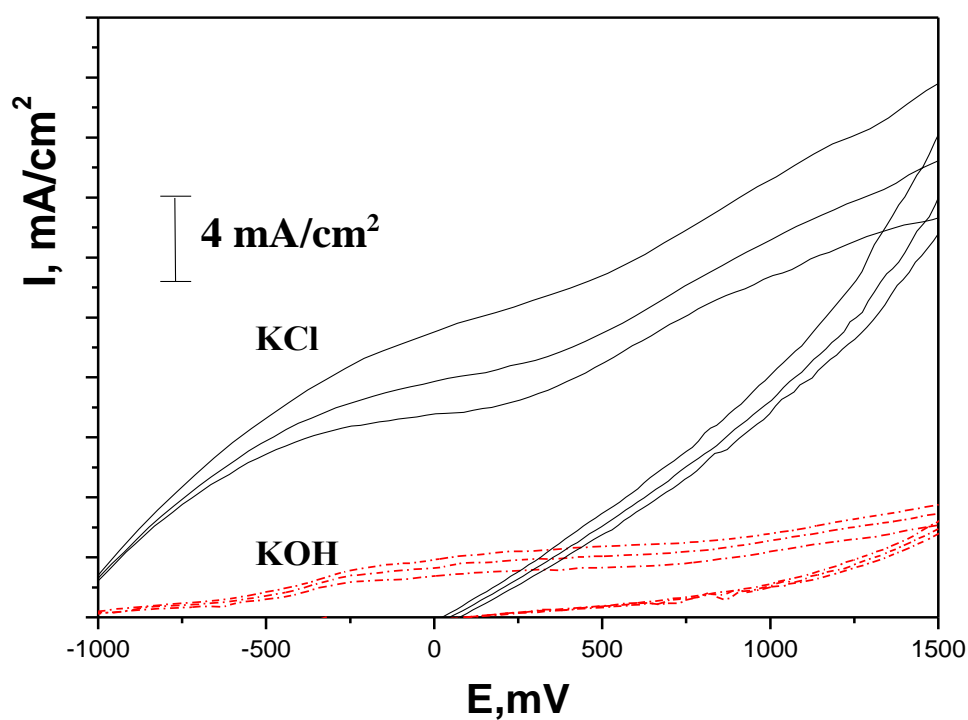


Fig. 3. CVA curves registered on working TiO₂ electrode sample in 30/70 ratio with graphite at potential scan rates 0.1, 0.5, 0,2 V / s in 0.1M KCl and 0.1M KOH

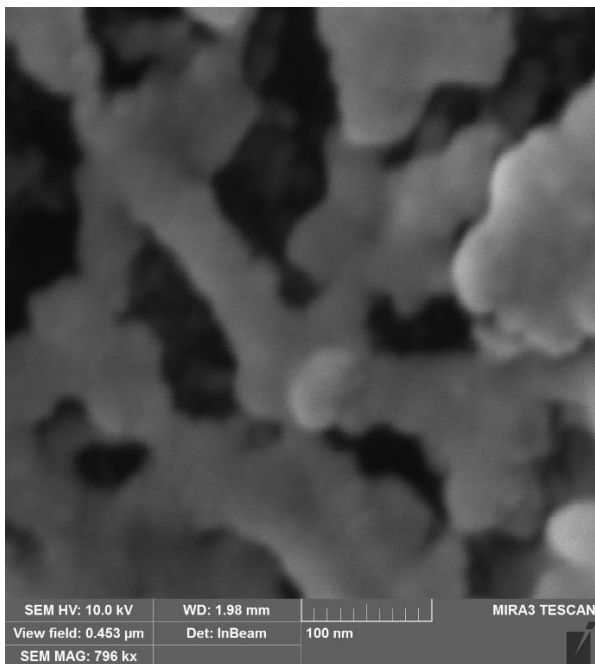


Fig. 4. SEM image of sample No. 1 based electrode material with titanium dioxide produced in IPMS NASU (magnification by 796,000 times)

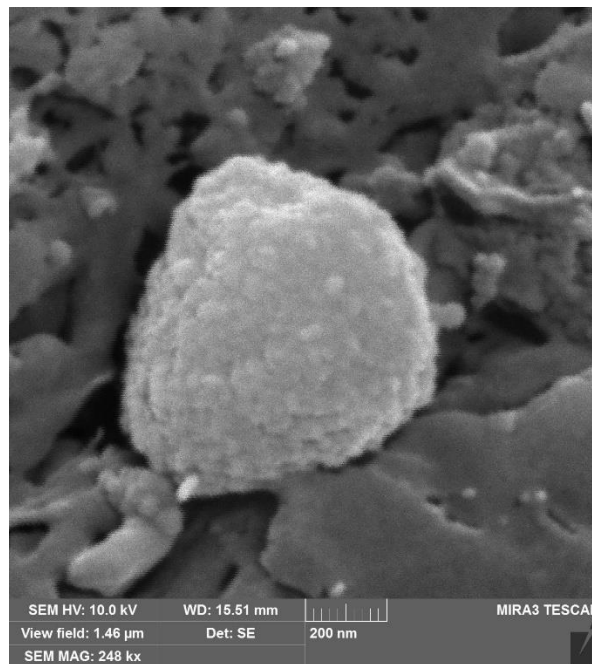


Fig. 5. SEM image of sample No. 1 based electrode material with titanium dioxide produced in IPMS NASU (magnification by 248,000 times)

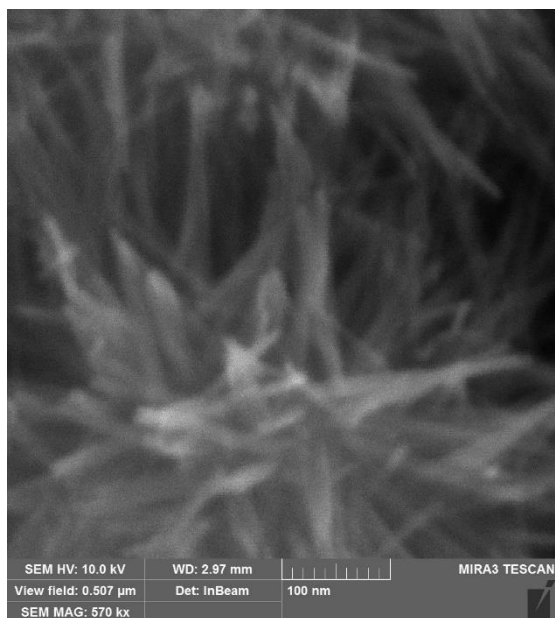


Fig. 6. SEM image of manganese dioxide nanoparticles obtained from IPMS NASU (magnification 570,000 times)

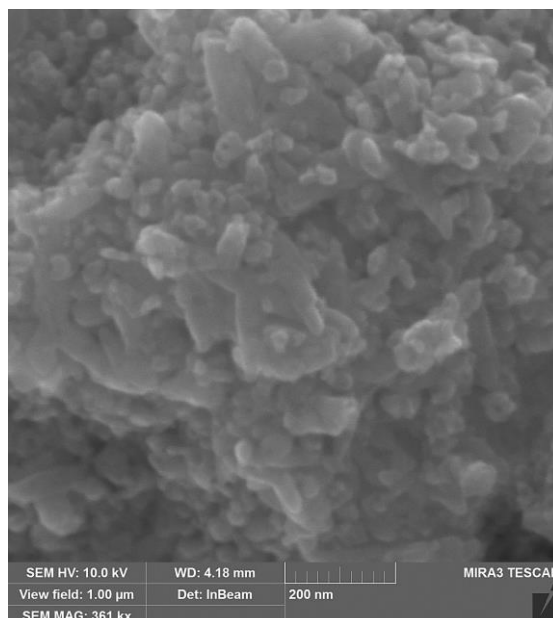


Fig. 7. SEM image of sample No. 1 based electrode material with titanium dioxide produced in IPMS NASU (magnification 361,000 times)

by 361,000 times)

3. Conclusions

Although the electrode area was very small ($\varnothing = 3$ mm) comparing with the cell volume (about 50 ml) and low power of UV source, the solution acquired brown colour at the end of a short experiment as a confirmation of active degradation processes of MO amino dye in the electrolyte.

Thus, the process of photoelectrocatalytic aminoazodye methyl orange (MO) degradation was studied in a neutral salt and alkaline electrolyte under UV irradiation with the titanium dioxide photoelectrocatalyst of nanodispersed morphology and anatase structure synthesized by developed by authors technology from metatitanic acid $\text{TiO}(\text{OH})_2$ suspension. The presence of Ti^{3+} defects is shown by EPR that could be the reason of the semiconductor band gap decrease in the synthesized sample. The coupling with manganese dioxide nanoparticles obtained from F-containing electrolytes will be studied further and prospective taking into account results obtained. The photoelectrocatalytic activity of samples is defined by nanodispersity, crystallite morphology, pore size distribution, varies symbatically with the concentration of Ti^{3+} , surface hydroxide groups.

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