

Structure and Photoelectrochemical Properties of the Doped Polycrystalline TiO₂

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Oxidic semiconductors (OS) such as TiO₂, ZrO₂, etc. were widely used as electrodes for photoelectrochemical (PEC) conversion of solar energy, as photocatalysts for decomposition of toxic pollutants and for preparation of the practically important catalysts during the last 25 years. To improve photochemical properties of the OS at $\lambda \geq 400$ nm, doping of the OS matrix with transition metal ions was usually applied. It should be mentioned that influence of various metal dopants on the OS properties is rather well known [1-3], whereas peculiarities of their structure are studied poorly.

The samples of the ceramic polycrystalline TiO₂ doped electrodes have been prepared by elaborate mixing the precise amounts of specially purified TiO₂, V₂O₅, Cr₂O₃ or Nb₂O₅ powders, pressed into bricks and heated in air at 1200° during 2 h in inert atmosphere (He). Then the stuffs were grinded and treated at 1200°C during 2 h in inert atmosphere. Samples of such a set (V-1) contained in their matrix the uncontrolled amount of oxygen vacancies. The samples of the second set V-2 were additionally treated at 900°C in air during 2 h to obviate these vacancies. The X-ray-phase analysis showed that all mixtures had the rutile structure. The bricks of the modified TiO₂ were cut to plates with thickness of 1.0 mm, both faces were polished. The back side was covered by In or Cu using the vacuum-deposition technique, then the ohmic contact was made.

Fig.1 presents the photocurrent spectra of polycrystalline Ti_{1-x}V_xO₂ electrodes at different x values. Similar ones have been obtained for Ti_{1-x}Cr_xO₂ samples. Although there is a strong increase of the visible light absorption at $x > 0.01$, one can observe tenfold drop of the photocurrent with increasing of x (Fig.2). For better understanding the causes of this drop, the spatial organization of the doped OS on a molecular level had been studied [4].

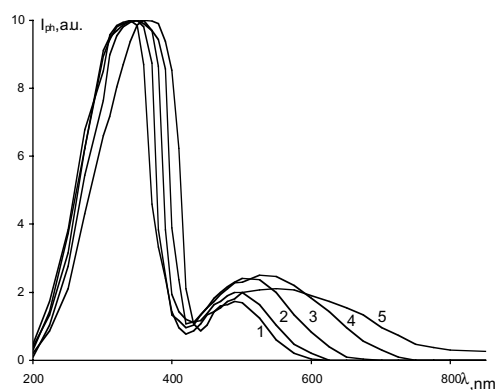


Fig.1. Photocurrent spectra I_{ph} of poly-crystalline Ti_{1-x}V_xO₂ electrodes at $x = 0.005$ (1), 0.01 (2), 0.02 (3), 0.03 (4), 0.05 (5)

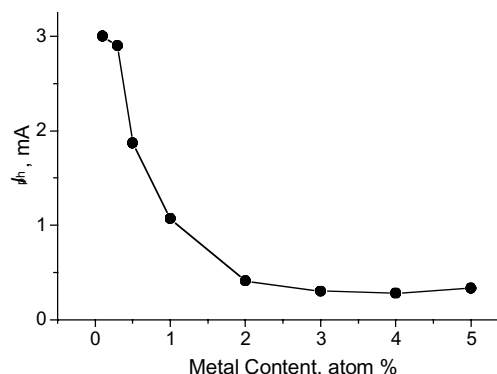


Fig.2. A photocurrent dependence on vanadium content in polycrystalline Ti_{1-x}V_xO₂ electrodes

The main regularities of the structure of paramagnetic coordination centres in the polycrystalline rutile-form TiO₂ doped from 0.1 up to 5.0 at.% with V⁴⁺, Cr³⁺ or Nb⁵⁺ ions, obtained using EPR technique, will be discussed in the paper. Analysis of the peculiarities of

spatial distribution of these ions in the OS matrix allowed to reveal and to characterize quantitatively the nanosized phases, which are existing in the OS material (homogeneous by the XPA data) and are strongly different by the composition. The obtained structural results will be compared with the PEC properties of the doped TiO₂.

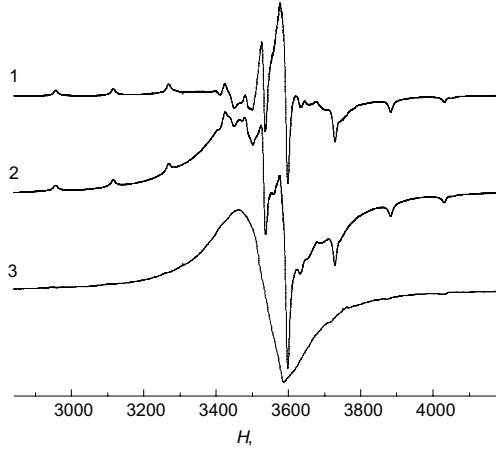


Fig.3. The EPR spectrum of TiO₂ doped with 2 at.% of V⁴⁺ (2) as a superimposition of the multiplet (1) and anisotropic singlet (3). T = 77 K

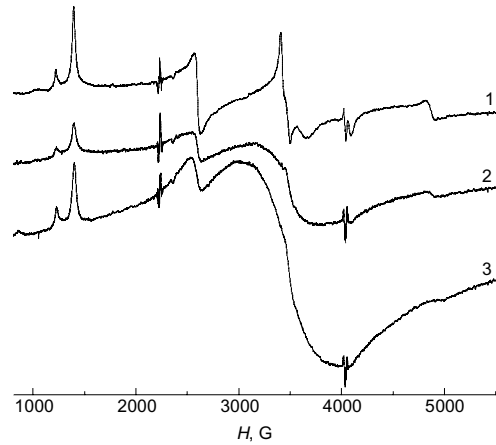


Fig.4. EPR spectra at 77 K of polycrystalline TiO₂ doped with 0.5% Cr³⁺ and 0.5 (1), 1.5 (2) and 4.5 % (3) Nb⁵⁺

It is evident from the EPR spectra (Fig. 3, 4) that a tendency to form the metal ion aggregates in the TiO₂ matrix with high local concentration C_{loc} of the doping ions is typical for V⁴⁺ and Cr³⁺ species. The singlet line in the EPR spectra is usual for paramagnetic centres with strong spin-exchange interaction between them at mean distances less than 0.7-0.8 nm. Simultaneously, the second nanophase with a much lower concentrations C_{loc} of the isolated V⁴⁺ ions (Fig.5), comparing with C_{loc} in aggregates, is also presented in the samples. Fig. 6 shows relative concentrations of the isolated and aggregated V⁴⁺ ions at different vanadium content in the doped TiO₂ matrix.

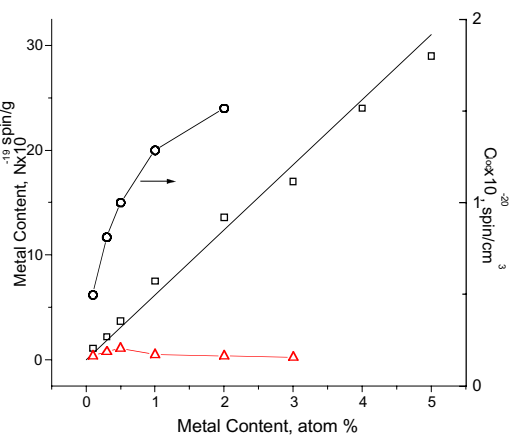


Fig.5. Total amount (Δ) of paramagnetic V⁴⁺ centres in the doped V-1 (Δ) and V-2 (\square) series; local concentrations (O) of the isolated V⁴⁺ ions vs. vanadium content

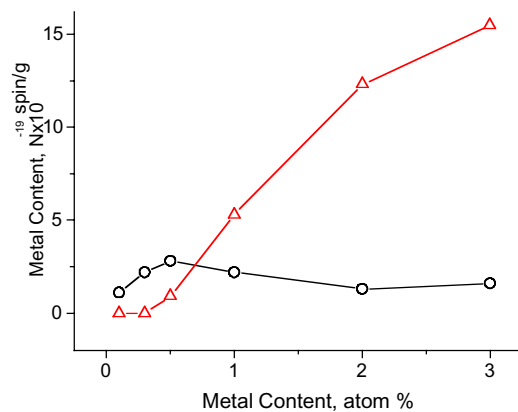


Fig.6. Relative concentrations of the isolated (O) and aggregated (Δ)V⁴⁺ ions at different content of VO₂ in the doped TiO₂

Thus, the metal-doped polycrystalline TiO₂ systems, being homogeneous at a microscopic level, seems to be rather heterogeneous by their structure at the nanoscopic level. The nature, structure and spatial distribution of the metal centres in the TiO₂ matrix will be discussed in the report in comparison with electro- and photoelectrochemical behaviour of such TiO₂ systems.

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