

Supplementary Material

Comparative study: catalytic activity and rhodamine dye luminescence at the surface of TiO₂-based nanoheterostructures

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Since defects in semiconductors actively interact with photoexcited charge carriers, we performed studies of the samples by the ESR method. ESR spectra of nanoheterostructures TiO₂-WO₃, TiO₂-V₂O₅, TiO₂-MoO₃, TiO₂-MoO₃-V₂O₅, TiO₂-MoO₃-WO₃ are shown in Figure S1 and represent a ESR signals superposition of from various radicals. The program "Symphony" (the company "Bruker") was used to determine the parameters of the radicals. The next ESR line parameters were obtained: g -tensor – $g_1 = 2.0082$, $g_2 = 2.0039$, $g_3 = 2.0036$ and hyperfine interaction constants – $A_1 = 1.6$ G, $A_2 = 1.1$ G, $A_3 = 22.5$ G. ESR signals with such parameters, in accordance with the literature data, can be attributed to nitrogen atoms N• (nuclear spin $I = 1$) with uncompensated electron spin, which were implemented into TiO₂ structure during the synthesis process. We have also identified the centers Ti³⁺/oxygen vacancy – $g_1 = 1.9935$, $g_2 = 1.9328$; Mo⁵⁺ radicals – $g_1 = 1.943$, $g_2 = 1.863$, $A_1 = 45$ G, $A_2 = 15$ G; W⁵⁺ radicals – $g_1 = 1.78$, $g_2 = 1.56$, $g_3 = 1.4$; V⁴⁺ radicals – $g_1 = 1.993$, $g_2 = 1.949$, $A_1 = 53$ G, $A_2 = 150$ G.

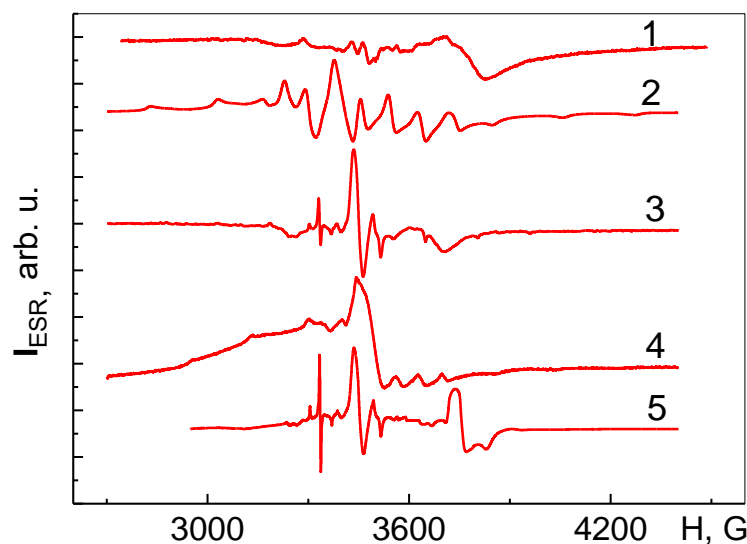


Figure S1. ESR spectra of nanoheterostructures $\text{TiO}_2\text{-WO}_3$ (1), $\text{TiO}_2\text{-V}_2\text{O}_5$ (2), $\text{TiO}_2\text{-MoO}_3$ (3), $\text{TiO}_2\text{-MoO}_3\text{-V}_2\text{O}_5$ (4), $\text{TiO}_2\text{-MoO}_3\text{-WO}_3$ (5).

The following radicals were found during ESR investigation in $\text{TiO}_2\text{-WO}_3$ samples: $\text{N}\bullet$; Ti^{3+} /oxygen vacancy and W^{5+} . The next centers were detected in $\text{TiO}_2\text{-V}_2\text{O}_5$: $\text{N}\bullet$, Ti^{3+} /oxygen vacancy and V^{4+} . In $\text{TiO}_2\text{-MoO}_3$ nanoheterostructures the defects $\text{N}\bullet$, Ti^{3+} /oxygen vacancy and Mo^{5+} were found. Nanoheterostructures $\text{TiO}_2\text{-MoO}_3\text{-V}_2\text{O}_5$ have shown the superposition of the next spin centers as $\text{N}\bullet$, Ti^{3+} /oxygen vacancy, Mo^{5+} and V^{4+} . The next radicals were found in $\text{TiO}_2/\text{MoO}_3/\text{WO}_3$ samples: $\text{N}\bullet$, Ti^{3+} /oxygen vacancy, Mo^{5+} and W^{5+} . We have calculated the defect concentrations N_s . They had the following values: $1.2 \cdot 10^{18} \text{ g}^{-1}$ ($\text{TiO}_2\text{-WO}_3$), $2.2 \cdot 10^{18} \text{ g}^{-1}$ ($\text{TiO}_2\text{-V}_2\text{O}_5$), $2 \cdot 10^{18} \text{ g}^{-1}$ ($\text{TiO}_2\text{-MoO}_3$), $1.5 \cdot 10^{19} \text{ g}^{-1}$ ($\text{TiO}_2\text{-MoO}_3\text{-V}_2\text{O}_5$), $1.3 \cdot 10^{19} \text{ g}^{-1}$ ($\text{TiO}_2\text{-MoO}_3\text{-WO}_3$).

An example of dye degradation on nanostructured individual titanium and molybdenum oxides is shown (Fig. S2, curves 1a and 1b). After turning off illumination, the process of dye degradation in such samples ceased.

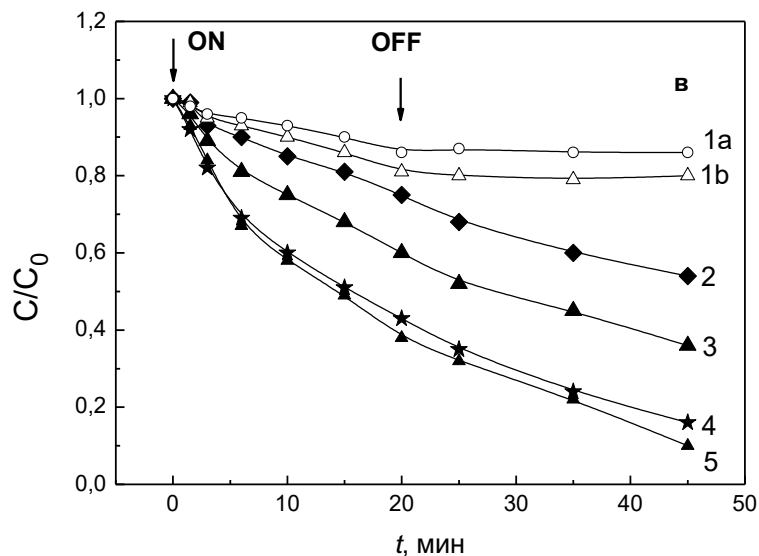


Figure S2. Kinetic curves of photocatalysis for MoO₃ (1a) and TiO₂ (1b) nanooxides, and nanoheterostructures TiO₂-WO₃ (2), TiO₂-MoO₃ (3), TiO₂-MoO₃-V₂O₅ (4), and TiO₂-MoO₃-WO₃ (5) under photoexcitation in the visible spectral region (450–750 nm). Arrows show the moments of switching illumination on ($t = 0$) and off ($t = 20$ min). C_0 is the initial dye concentration at the moment $t = 0$ and C is the dye concentration at the moment t . TiO₂ doped with nitrogen was used.

At the samples of nanoheterostructures the rate of photocatalysis in the visible spectral region was higher than that at the surface of individual nanooxides. This may be due to both the high concentration of radicals participating in catalytic reactions at the surface and the lower rate of photoexcited electrons and holes recombination. After illumination is turned off, the process of dye degradation in the nanoheterostructures

continues (Fig. S2). This is the evidence of electrons and holes recombination suppression. Actually, one can presume that, after the electron–hole pairs generation in titanium dioxide under illumination, electrons are injected to other metal oxides present in the samples (MoO_3 , V_2O_5 , WO_3) and are trapped at defects in them (molybdenum, vanadium, or tungsten ions). And the holes remaining in TiO_2 no longer have pairs for recombination. This way, in the nanoheterostructures, the accumulation of the photoinduced charge occurs. And this charge is gradually spent for the formation of oxygen and hydroxy radicals from oxygen and water molecules adsorbed at the nanooxide surface (after illumination is turned off). The formed radicals continue taking part in the redox reactions at the surface of the samples, thus prolonging the process of dye degradation, i.e., the catalytic activity of the obtained nanoheterostructures.