Nanocomposites and nanomaterials

Effect of tungsten doping on photo- and electrocatalytic properties of titania films

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Abstract

Doping with metal ions is a well known strategy to increase the photocatalytic activity of titania based materials. Tungsten has been chosen as one of the promising agents employed to improve not only charge separation but also adsorption processes due to the high surface acidity of TiO_2/W^{n+} photocatalysts.

Mesoporous nanoscale TiO_2 and TiO_2/W^{n+} (0,1% до 10%) films were synthesized by the sol-gel method using titanium tetraisopropoxide, $(NH_4)_{10}W_{12}O_{41}\cdot 11H_2O$, nonionic triblock copolymer Pluronic (P123) as a templating and acetylacetone as a complexing agent at pH=3-4 (adjusted by $HClO_4$), and deposited on glass and steel substrates via the dip-coating procedure.

The structural and optical properties, phase composition of the synthesized films and powders, obtained after precursors gelation were investigated by XRD, Raman and UV-Vis spectroscopy. Band gap energy and the position of flat band potentials were estimated by direct photoelectrochemical measurements.

The structural and optical properties

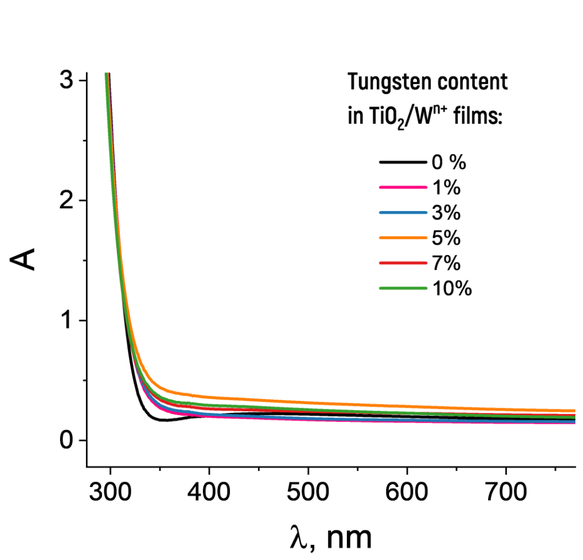

Fig. 1. Absorption spectra of TiO_2 films doped with W^{n+} ions on a glass substrate.

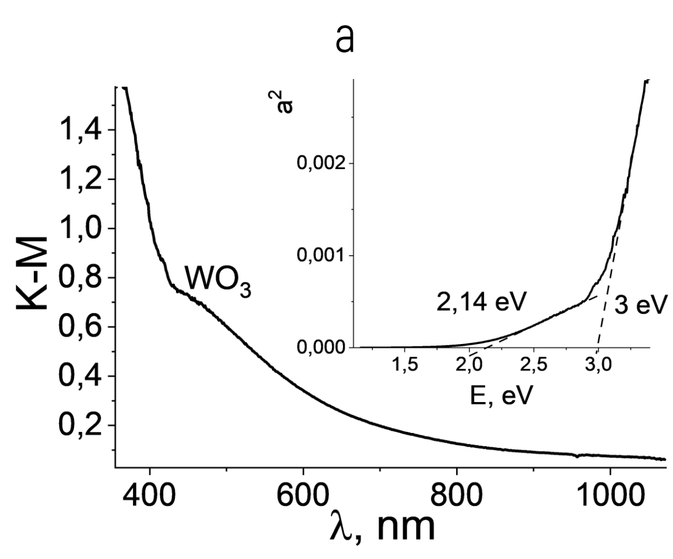

Fig. 2. Absorption spectra of TiO_2/W^{n+} powders:
a) TiO_2/W^{n+} 10 % (ageing of the sol for 6 months);
b) TiO_2/W^{n+} with dopant concentrations of 3%, 5% and 10% (fast drying procedure for 3 days).

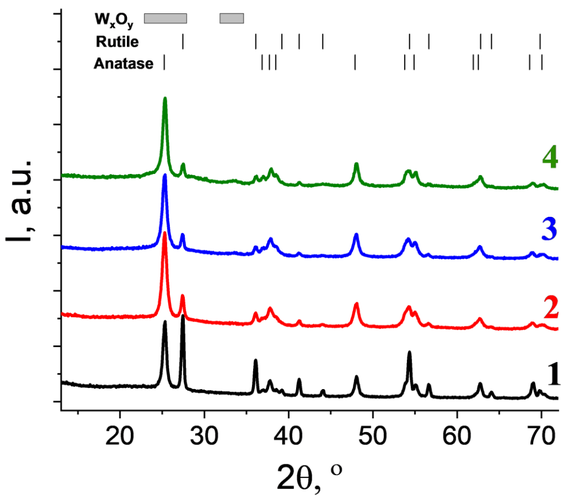

Fig. 3. X-ray diffraction of TiO_2 (*1*), TiO_2/W^{n+} 3 % (*2*), TiO_2/W^{n+} 7 % (*3*), TiO_2/W^{n+} 10 % (*4*) powders, calcined at 500 °C.

The electrochemical properties

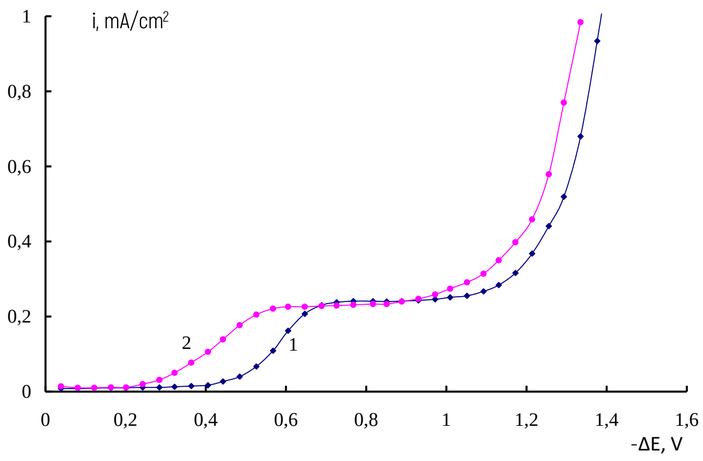

Fig. 4. Polarization curves of oxygen electroreduction on TiO_2/W^{n+} electrodes: 1 - TiO_2/W^{n+} 0%; 2 - TiO_2/W^{n+} 10%. The potential sweep rate is 20 $mV{\cdot}s^{-1}$.

Composition	$E_{1/2(O2)}$, V	E_0, V	ΔE, V
TiO_2	-0,58	-0,06	-0,52
3% TiO_2/W^{n+}	-0,52	-0,01	-0,51
7% TiO_2/W^{n+}	-0,48	-0,01	-0,47
10% TiO_2/W^{n+}	-0,50	-0,08	-0,42

Table 2. Dependence of the oxygen reduction half-wave potential $E_{1/2(O2)}$, the steady-state electrode potential E_0 and the oxygen reduction overvoltage ΔE on the tungsten content.

C_W, %	Rutile content, %	d_r, nm	d_a, nm
0	59	40	27
3	26	40	22
7	21	34	22
10	18	37	25

Table 1. Rutile content and crystal sizes of anatase and rutile in TiO_2 and TiO_2/W^{n+} powders with different dopant concentrations.

Photocatalytic activity

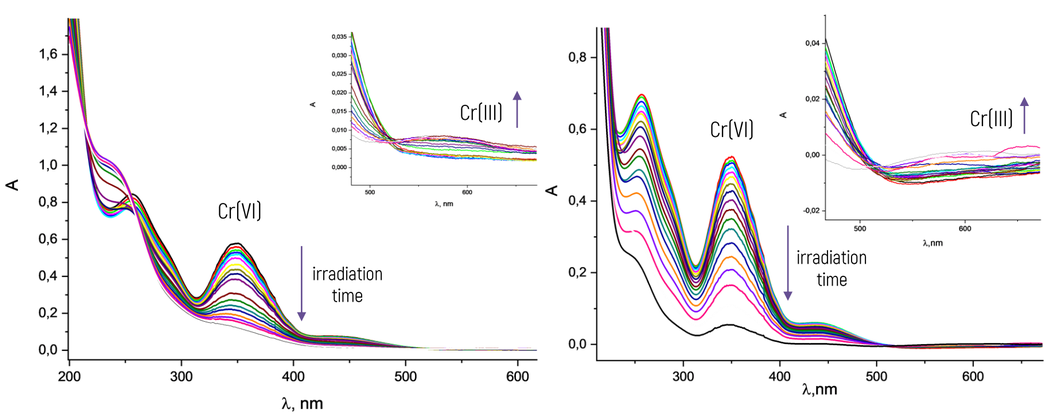

Fig. 5. Spectra of irradiated solution Cr on TiO_2/W^{n+} 0,1% (left) and TiO_2/W^{n+} 10% (right) films.

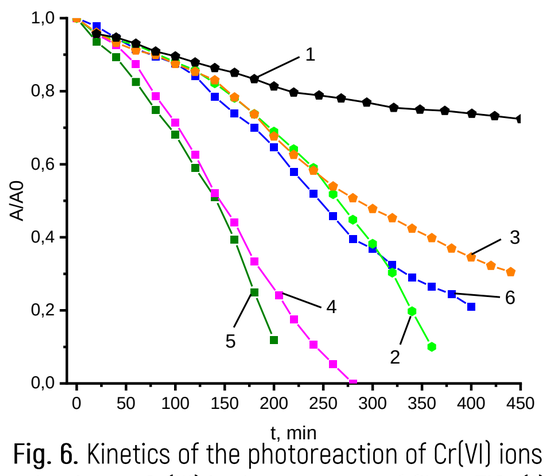

Fig. 6. Kinetics of the photoreaction of Cr(VI) ions reduction to Cr(III) in the presence of films: TiO_2 (1), TiO_2/W^{n+} 0,1% (2), TiO_2/W^{n+} 0,5% (3), TiO_2/W^{n+} 5% (4), TiO_2/W^{n+} 7% (5), and TiO_2/W^{n+} 10% (6).

Conclusions

XRD patterns of TiO_2/W^{n+} powders showed anatase (20-25 nm) and rutile (35-40 nm) nanocrystalline phases. A lower degree of anatase to rutile transformation was observed for tungsten-doped films compared to pure titania. The most effective in the photoreaction of Cr^{6+} ions reduction to Cr^{3+} in the presence of EDTA as an electron donor under UV irradiation were TiO_2 films with a content of 5-7% W^{n+}. When the dopant concentration was increased to 10%, the activity decreased but remained higher than to pure TiO_2. The electrocatalytic properties of TiO_2 and TiO_2/W^{n+} electrodes were investigated in the process of oxygen electroreduction. The potential of oxygen reduction changes with the film composition. With increasing tungsten content in the films from 0 to 10%, the electrocatalytic activity of the electrodes increased. The maximum electrocatalytic activity was shown by electrodes with tungsten content equal to 10% (ΔE =-0,42V).

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