IMPROVING THE PHOTOCATALYTIC PROPERTIES OF TIN DIOXIDE BY DOPED WITH TITANIUM AND COPPER

Samsonenko M.[1]*, Khalameida S.[1], Sydorchuk V.[1], Zakutevskyy O.[1], Starchevskyy V.[2], Lakhnik A.[3]

[1] *Institute for Sorption and Problems of Endoecology of NAS of Ukraine, Kyiv, Ukraine*
[2] *Institute of Chemistry and Chemical Technologies, Lviv National Polytechnic University, Lviv, Ukraine*
[3] *G.V. Kurdyumov Institute for Metal Physics of NAS of Ukraine, Kyiv, Ukraine*
*E-mail:mashuna.08@gmail.com

One of the ways to *improve the photocatalytic activity of tin dioxide* in the processes of neutralization of organic pollutants in aqueous solutions is the doping with transition metals. At *doping with titanium dioxide,* there is observed the formation of *mutual solid solutions*. *Copper monoxide* is a p-type semiconductor, therefore when used as a tin dioxide dopant, the formation of *"p-n heterojunction transition"* is possible.

The purpose of this work

Investigation of the effect of doping of tin dioxide with titanium and copper on the physical-chemical, especially electronic properties of the obtained samples and, as a result - on their activity in photodergadation of pollutants in water.

EXPERIMENTAL

The high porous *gel* SnO_2 heterogeneously precipitated using ammonia
$SnCl_4 + 4NH_3 + H_2O \rightarrow SnO_2 + 4\,NH_4Cl$
S = 178 m²/g

UST
+5% $TiO(OH)_2$
at 90°C
at 22 KHz
τ = 2 h
+thermal treatment at 300 and 550°C

The low dispersed non-porous *powder* SnO_2
S = 6 m²/g

MChT
+5% Cu_2O
in air
at 300 rpm
τ = 0.5 h

Physical-chemical properties of all samples were studied using the following techniques: X-ray analysis, XPS, nitrogen adsorption-desorption, UV-Vis spectroscopy, TEM, SEM

Photocatalytic activity
Aqueous solution of ***Rhodamine B***, ***Safranin T*** *($C = 1 \cdot 10^{-5}$ mol/L); $C_{photocatal.} = 1$ g/L;*
LED lamp Philips LED Cool daylight
power = 100 W; λ_{max}=580 nm; τ = 10 h.

RESULTS

Both oxides belong to the same crystal symmetry (tetragonal) with the space group D14 4h and two molecular units per primitive unit cell. They both crystallize within the rutile structure. Besides, Sn^{4+} and Ti^{4+} cations have similar radii and electronegativity values. Hence, these oxides can easily form a solid solution. Indeed, a full-profile analysis of diffractograms showed a decrease in the lattice constants a and c for doped samples compared with pure SnO_2 and absence reflexes related to TiO_2 phases after calcinations at 300-550°C. This may mean that the solid solution formed under these conditions.

Table 1. Unit cell parameters of initial and doped SnO_2.

Sample	Lattice parameters		<ε>*	D**, nm
	a=b, nm	*c*, nm		
SnO_2 precipitated	0.4736	0.3188	0.00800	3.2
SnO_2 + TT 300°C	0.4744	0.3189	0.00700	5.2
SnO_2 + TT 550°C	0.4739	0.3188	0.00097	18.0
SnO_2 + 5%Ti UST 90°C	0.4748	0.3202	0.00950	3.0
SnO_2 + 5%Ti UST 90°C +TT 300°C	0.4740	0.3188	0.00640	4.8
SnO_2 + 5%Ti UST 90°C + TT 550°C	0.4737	0.3185	0.00052	16.5

<ε>*- the micro-distortion of crystal lattice; D** – the size of coherent scattering regions

Fig. 1. Data of XRD

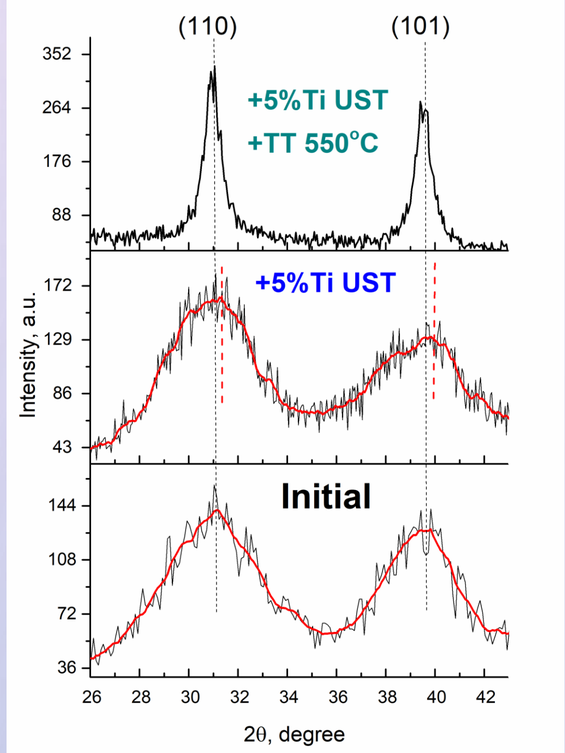

Table 2. Physical-chemical and photocatalytic properties of prepared samples.

№	Samples	S, m^2/g	V_Σ, cm^3/g	V_{me}, cm^3/g	V_{mi}, cm^3/g	d_{me}, nm	E_g, eV	*RhB* $K_d \cdot 10^5$, s^{-1}	*ST* $K_d \cdot 10^5$, s^{-1}
1.1	SnO_2 precipitated	176	0.10	0.02	0.08	2.4	4.2	3.3	2.9
1.2	SnO_2+ TT 300°C	149	0.11	0.05	0.04	4.6	3.2	2.2	2.6
1.3	SnO_2+ TT 550°C	26	0.10	0.08	-	12.6	3.3	1.6	1.0
1.4	SnO_2+ 5%Ti UST 90°C	201	0.21	0.03	0.08	2.4	2.8	6.0	3.9
1.5	SnO_2+ 5%Ti UST 90°C+ TT 300°C	122	0.23	0.09	0.01	4.7	2.9	7.7	3.2
1.6	SnO_2+ 5%Ti UST 90°C+ TT 550°C	19	0.18	0.08	0.01	13.9	2.7	8.1	5.6
2.1	SnO_2 powder	7	0.02	0.02	-	41.5	3.8	-	1.2
2.2	SnO_2+ 5%Cu MChT air 300 rpm	10	0.09	0.09	-	4.7	3.7	-	4.2

S - specific surface area, V_Σ - pore volume, V_{me} - mesopores volume, V_{mi} - micropores volume; d_{me}- mesopores sizes; E_g - band gap ; $K_d \cdot 10^5$ - rate constant of Rhodamine B and Safranin T degradation

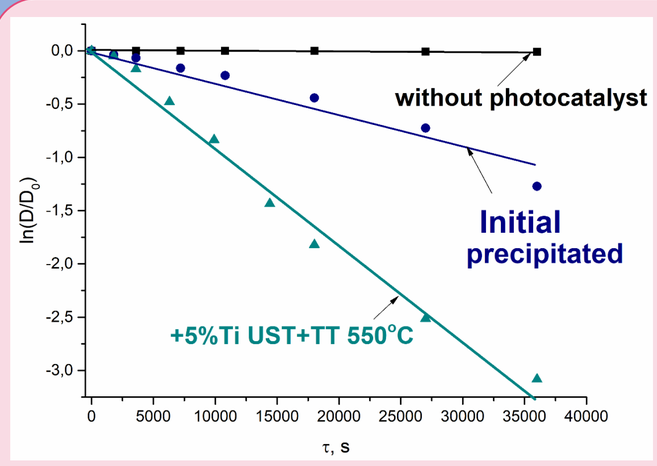

Fig. 2. Kinetic curves for the degradation of Rhodamine B in the presence of prepared samples

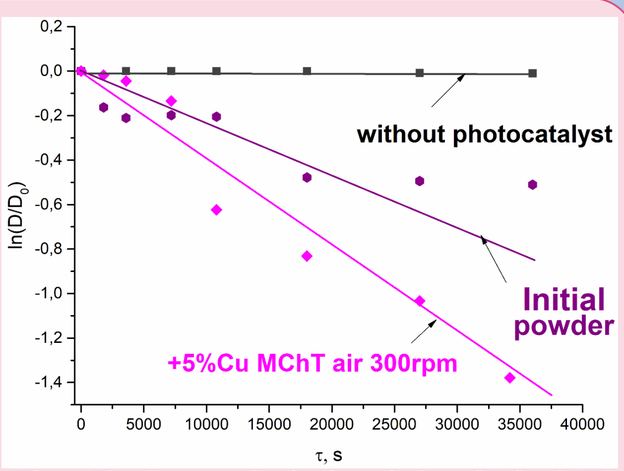

Fig. 3. Kinetic curves for the degradation of Safranin T in the presence of prepared samples

All doped precipitated and commercial SnO_2 samples are characterized an increase in the specific surface area and total pore volume, and following thermal treatment assist to reduce the specific surface area and micropores volume. The formation of meso-macroporous structure of doped and calcined samples is observed. In addition, for doped samples there are a decrease in the band gap E_g and an increase in visible light absorption of up to 50%. For example, the band gap for the initial precipitated sample is 4.2 eV, and for SnO_2 doped with titanium and after TT at 550° C - 2.7 eV. Doping of tin dioxide with titanium and copper increases the photocatalytic activity under the action of visible light in several times.