Synthesis and properties of Cu/TiO_2 photocatalytic films and powders

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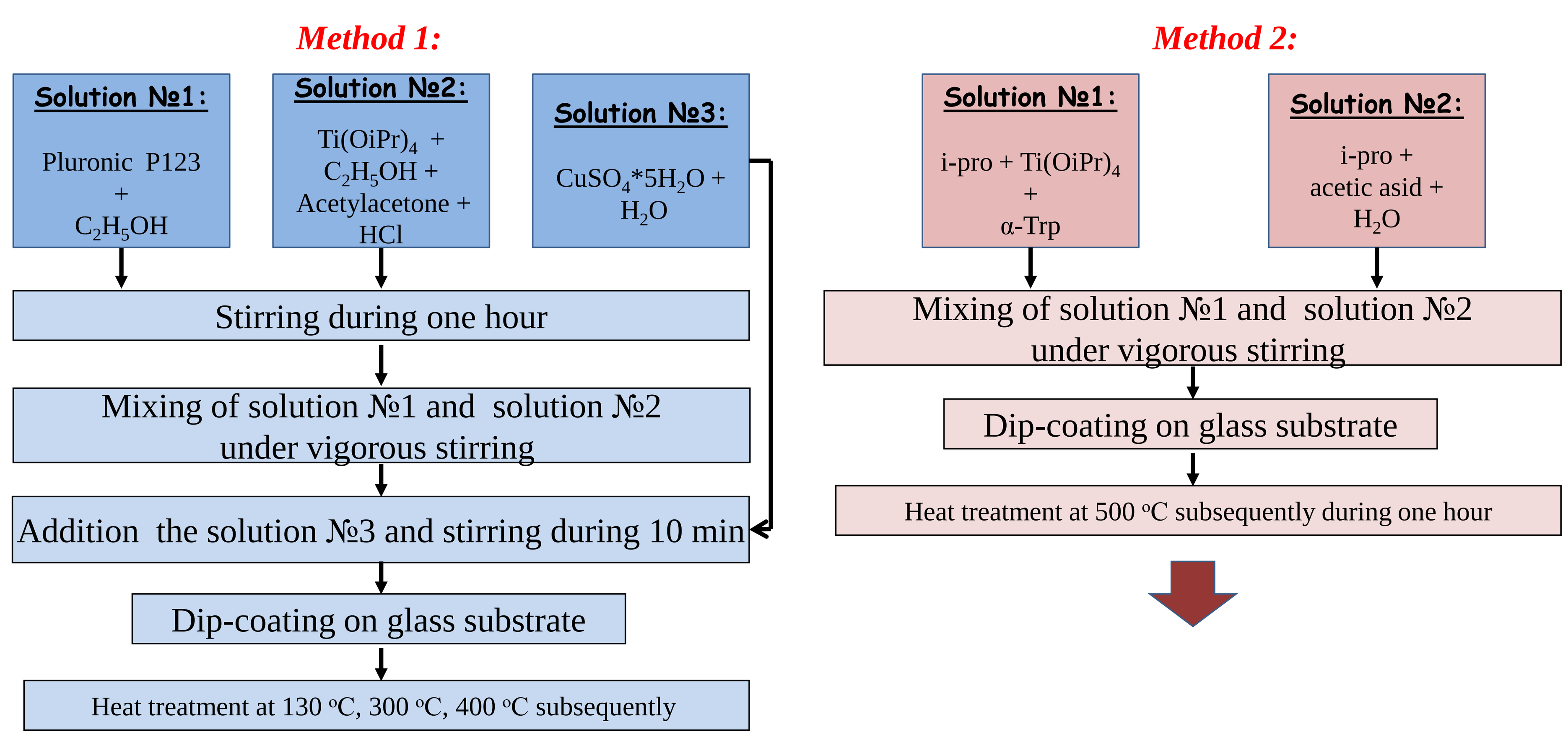
TiO_2/Cu^{n+} Films Preparation via Sol-Gel Method



Method 1		Method 2
TiO_2, Cu_2TiO_3, Cu_3TiO_4	Crystal structure	TiO_2, Cu_2O
+	Photocatalytic activity compared to pure TiO_2	–
+	Desorption of copper ions from the surface	–

Structure Characteristics

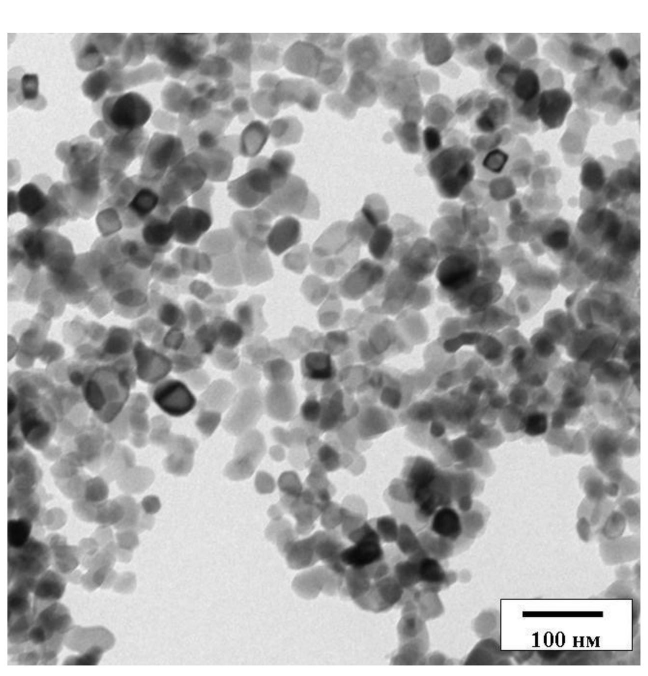


Fig. TEM image of TiO_2/Cu^{2+} (1 % Cu) powder.

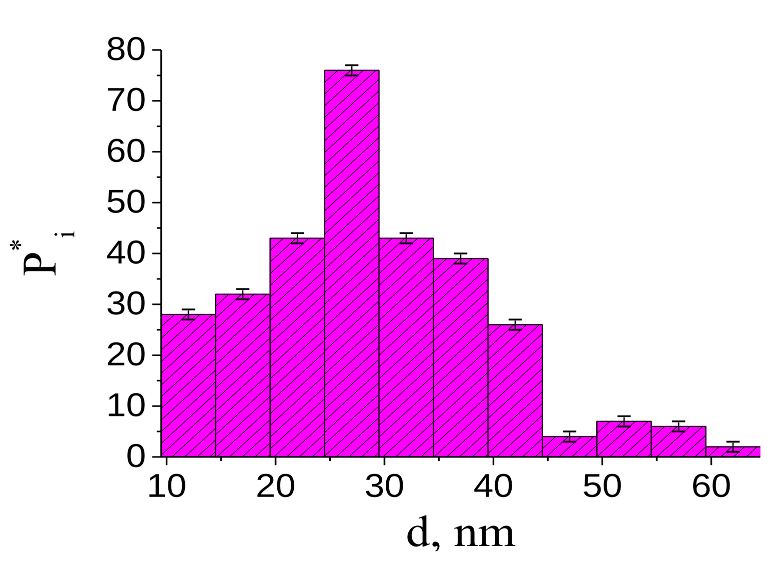


Fig. The histograms of the anatase crystal size distribution for TiO_2/Cu^{2+} powder.

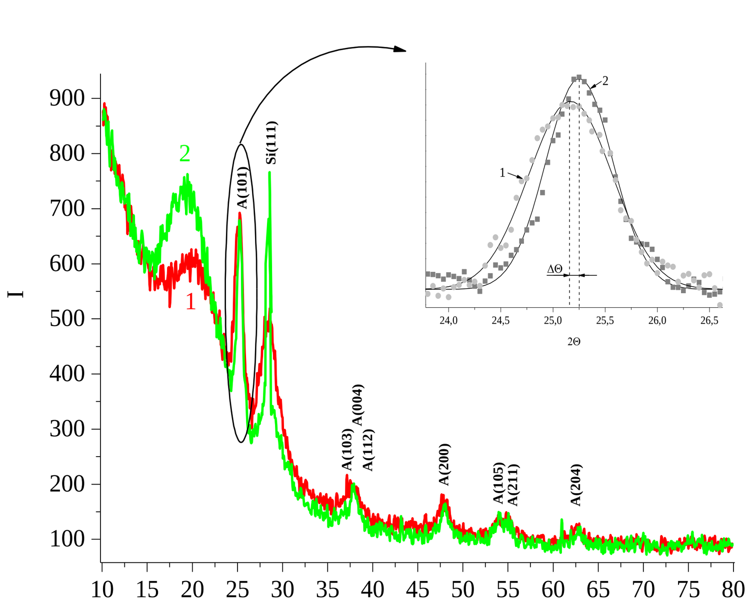


Fig. XRD profiles of TiO_2 (1), TiO_2+5.5%Cu^{n+} (2), with typical anatase peaks.

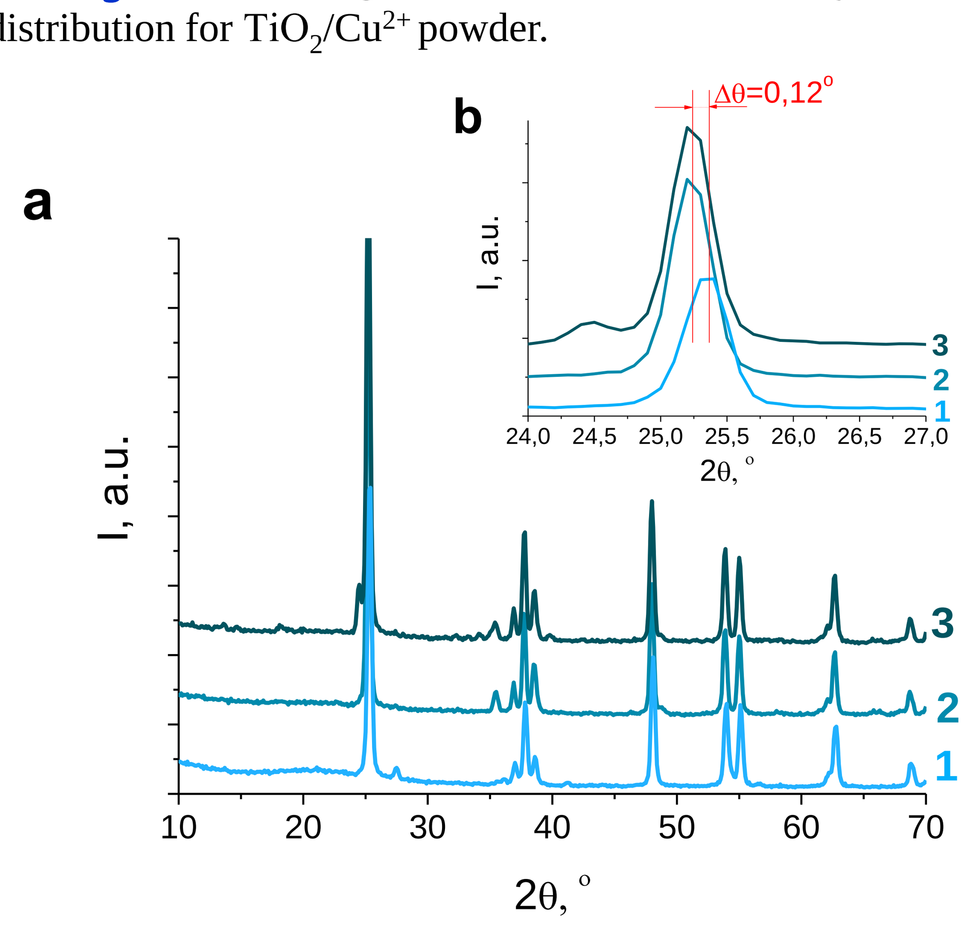


Fig. a) XRD patterns of powders TiO_2 (1), TiO_2/Cu^{n+} 15 % (2), TiO_2/Cu^{n+} 20 % (3), after at 650 °C.
b) Shift of peak 101 anatase in XRD TiO_2 (1), TiO_2/Cu^{n+} 15 % (2), TiO_2/Cu^{n+} 20 % (3).

Photocatalytic Activity

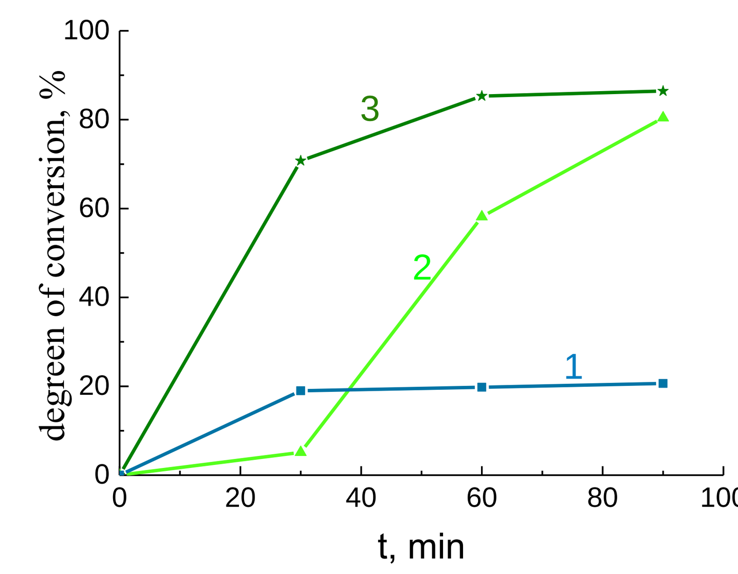


Fig. Kinetic curves of water denitrification in a presence: TiO_2 (1), TiO_2/Cu^{2+} treated at 500°C during 4 hours (2) and TiO_2/Cu^{2+} treated at 500°C during 1 hour (3), $C(Cu^{2+})$=5%. Induction period of NO_3^- photoreduction for sample 2 can be explained by intensive reduction of Cu^{2+} ions to Cu^0.

Reaction of water denitrification:

$$TiO_2 \xrightarrow{h\nu} e^- + h^+$$
$$2NO_3^- + 5HCOO^- + 7H^+ \rightarrow N_2 + 5CO_2 + 6H_2O$$
$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$$
$$HCOO^- + h^+ \rightarrow H^+ + CO_2^{\bullet-}$$
$$2NO_3^- + 12H^+ + 10CO_2^{\bullet-} \rightarrow N_2 + 6H_2O + 10CO_2$$
$$2NO_2^- + 3HCOO^- + 5H^+ \rightarrow N_2 + 3CO_2 + 4H_2O$$
$$2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O$$
$$2NO_2^- + 8H^+ + 6CO_2^{\bullet-} \rightarrow N_2 + 4H_2O + 6CO_2$$

Reaction photoreduction of Cr(VI) to Cr(III):

Cr(VI) → Cr(V) → Cr(IV) → Cr(III)
$0.5H_2O + h^+ \rightarrow 0.25O_2 + H^+$

Summary reaction (for pH=2-4):
$2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 8H_2O + 3O_2$

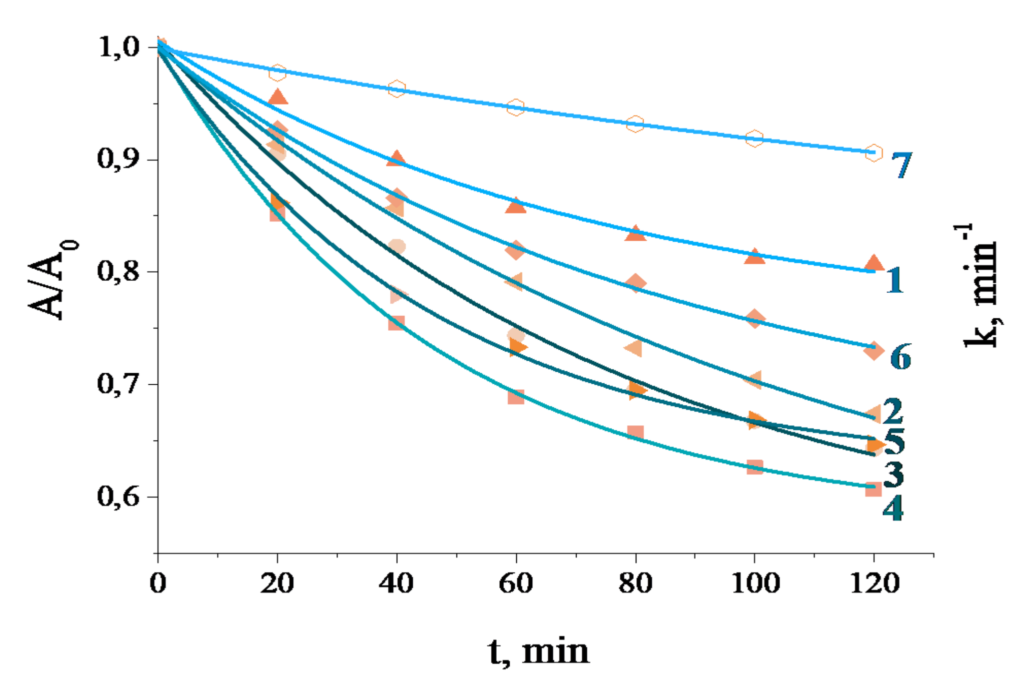


Fig. Photoreduction of Cr(VI) ions to Cr(III) in the presence of films: TiO_2 (1), TiO_2/0.25%Cu^{n+} (2), TiO_2/2.5%Cu^{n+} (3), TiO_2/5.5%Cu^{n+} (4), TiO_2/10%Cu^{n+} (5), TiO_2/30%Cu^{n+} (6), without photocatalyst (7).

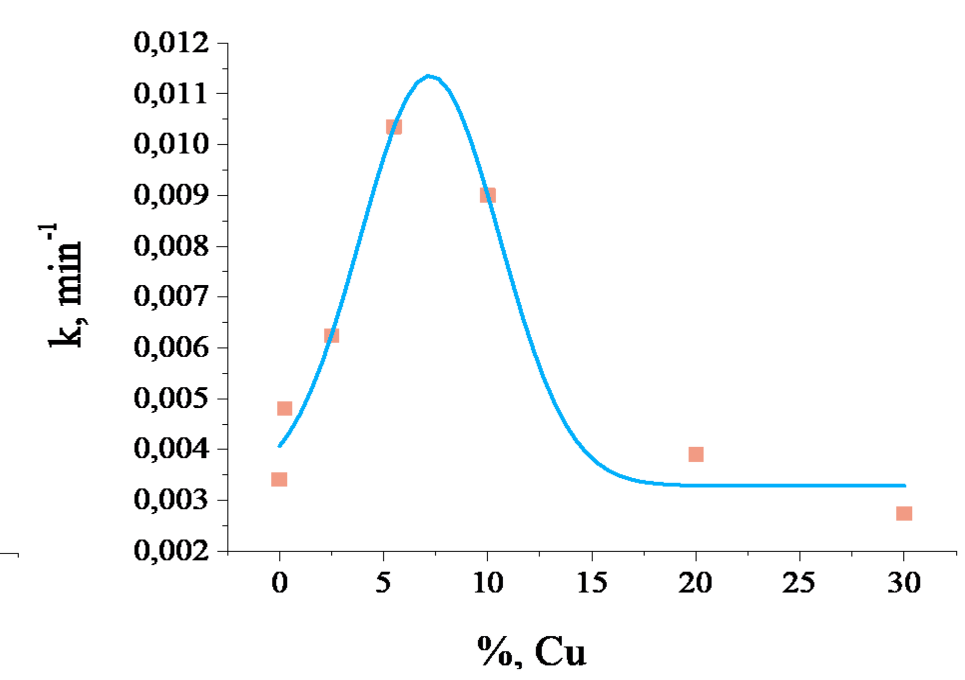


Fig. Dependence of the photoreduction reaction rate constant of Cr(VI) ions to Cr(III) in the presence of TiO_2/Cu^{n+} films on the concentration of Cu^{n+} ions.

Bactericidal Activity

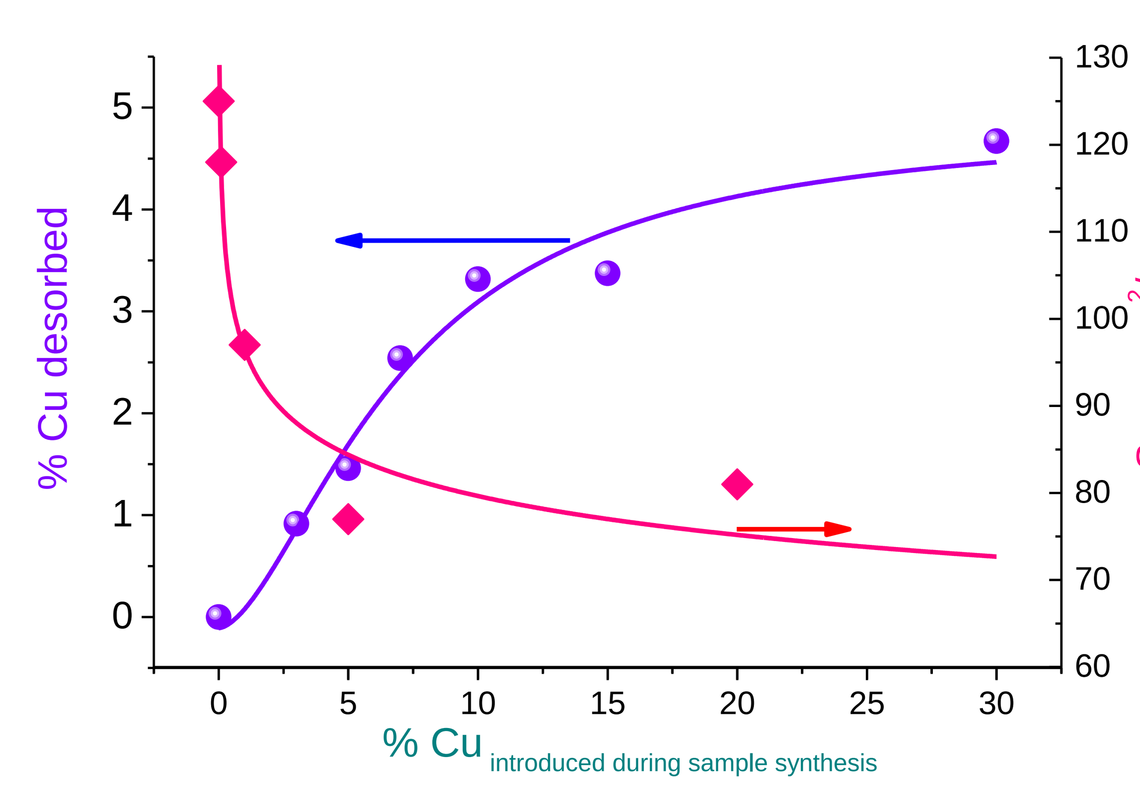


Fig. The percentage of copper ions released into the aqueous solution and the specific surface area of sol-gel TiO_2/Cu^{n+} powders containing Cu_2TiO_3 and Cu_3TiO_4 copper titanates in their structure.

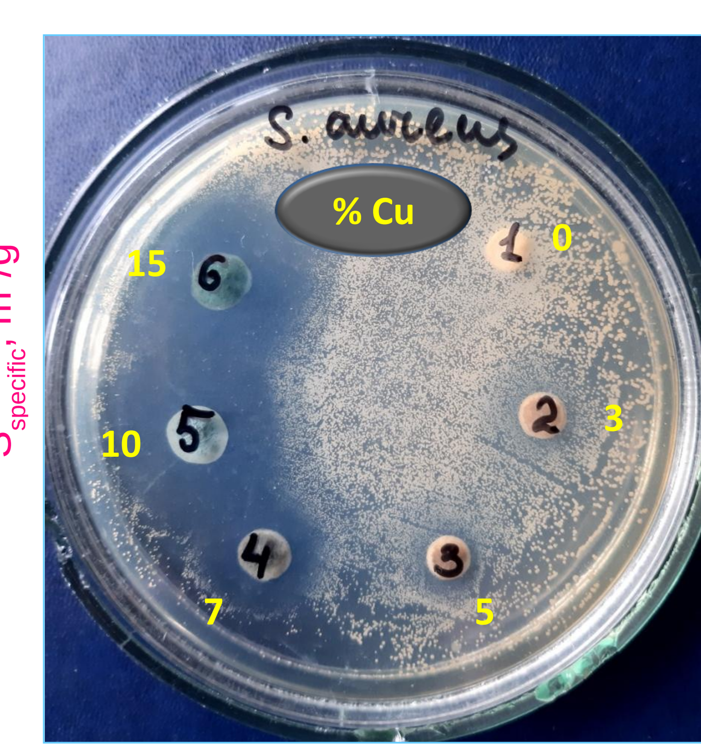


Fig. Antimicrobial activity of TiO_2/Cu^{n+} powders against gram-positive bacteria *S. aureus*

The amount of desorbed copper ions from powders obtained by the second method is negligibly small. For a sample TiO_2/Cu^{n+} 30 %, it is 0.13 %.

Conclusions

Due to the difference between the ionic radii of Ti(IV) and the modifier ion, the unit cell of TiO_2 is slightly deformed, the band gap of TiO_2 decreases, and the photocatalytic activity increases under the influence of visible light. As we showed earlier, the content of up to 7% of Cu^{n+} ions in the structure of films and powders leads to acceleration of photocatalytic reactions of water denitrification, reduction of Cr^{6+} ions to Cr^{3+}, etc. Bactericidal activity arises from the release of ions from the surface of metal NPs upon contact with water or biological fluid. The release of ions from the surface of NPs (or their oxides) critically depends on their localization in the TiO_2 structure, which is related to the method of synthesis. It is found that in an aqueous environment, metal ions are released from the surface of sol-gel powders synthesized using method 1, which determines the ability to decontaminate effluents from organic toxic substances. Copper-containing crystalline films and Cu-TiO_2 dispersions have a high redox photocatalytic effect in relation to heavy metals and their adsorption removal. In the case of using method 2, stable oxide phases of the dopant are formed in the TiO_2 structure, from the surface of which metal ions are not desorbed. The studies have shown a high bactericidal activity in relation to Escherichia coli (*S. aureus*). The desorption of Cu^+, Cu^{2+} ions from the surface of the composites quantitatively correlates with the bactericidal properties of the obtained powders.

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