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Catalytic Electrolysis-Free Copper Deposition Using Dispersions of Titanium Dioxide with Adsorbed Trespassing Metal Ions

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It has been found that modification of TiO_2 by impregnation with Pd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+} and Co^{2+} salts causes a significant rise of its catalytic activity in the reaction of metal copper deposition. Influence of nature of modifying cation, its concentration, counter-anion concentration and the effect of double modification by two different salts have also been investigated. Comparison of energetic characteristics of all intermediate compounds led us to a possible model of catalytic deposition of copper, explaining the increased catalytic activity of the modified examples.

Key words: titanium dioxide, modification by trespassing metal ions, catalytic copper deposition

Reductive chemical deposition of metals from salt solutions has many fundamental and applicative aspects. Metal nano-particles are being formed at initial stages of the deposition. They can reveal unique properties unlike macro-dimensional samples [1–3] and this fact brings closer the interest to investigation of such particles. Catalyst is usually required for electrolysis-free deposition of metals. Theory of catalysis and, especially, theory of catalytic activity of metal nano-particles can be extended through investigation of such deposition [4]. Let us remark that silver-free photography process is also based on catalytic reduction of dissolved metal ions [5]. The same process can be used for covering of metal films on various plastics [6,7] and for photo-additive technology of selective metallization of printed plates [8–10]. Thus, development and investigation of novel catalysts for chemical deposition of metals from salt solutions is quite a topical problem.

Influence of titanium dioxide suspension modification by Pd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+} and MoO_4^{2-} ions on its catalytic activity has been investigated. Catalytic activity was determined for the reaction of copper deposition, which is one of technological stages for production of printed plates.

EXPERIMENTAL

Catalyst synthesis. Titanium dioxide with specific surface $S_{sp} = 20\ m^2/g$ was obtained as a product of titanium sulfate hydrolysis followed by sediment separation, drying and annealing at 800°C. Then this product was used for synthesis of catalysts and further modification by metal ions. Modifying ions were applied using following steps: TiO_2 dispersion was impregnated by putting into well-stirred salt solutions for 1 hour. Then materials were dried up at 60–80°C. Final concentration of the modifying ions has been calculated basing on the amount of the salts used. Atomic absorption spectroscopy was engaged for the control in the concentration measurement. We used the following salts: $PdCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$, $CuCl_2\cdot 2H_2O$, $Cu(CH_3COO)_2$, $Cu(HCOO)_2$, $FeSO_4\cdot 7H_2O$, $FeCl_3\cdot 6H_2O$, $CoSO_4\cdot 7H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$ and $(NH_4)_2MoO_4$.

Catalyst activity determination. The influence of suspension of TiO_2 modified by metal ion was investigated in the reaction of reduction of Cu^{2+} by formaldehyde. This reaction was used to determine the catalytic activity of TiO_2. Reaction ran in alkaline solution containing tartaric acid. Latter substance and Cu(II) form a complex compound preventing precipitation of $Cu(OH)_2$. Base mixture contains 22 g/l of $CuSO_4\cdot 5H_2O$, 60 g/l of NaOH, 22 g/l of Na_2CO_3, 140 g/l of $KNaC_4H_4O_6$ and 10 g/l of formalin. Such mixture is stable at room temperature until the catalyst is added. Metal copper started to deposit right after adding of the semi-conductive catalyst. To determine the catalytic activity, we added 0.75 g of catalytic suspension to 50 ml of the mixture, stirred it well for 1 min, then filtered out the suspension and determined the content of Cu^{2+} in the filtrate. Quantity of ions taken part in the reaction was used to calculate the catalytic activity: $A = (1 - C_2/C_1)*100\%$, where A – catalytic activity (%), C_1 and C_2 – initial and final concentration of Cu^{2+} correspondingly.

RESULTS AND DISCUSSION

It has been found that pure, non-modified titanium dioxide has a comparatively low activity (A = 8%), while its activity rises drastically after impregnation by palladium(II), copper(II), iron(II), and cobalt(II) salts (Table 1). Sodium salts, having the same acid residual, give no change in the catalytic activity of titanium dioxide. This fact proves, that transient metal cations are responsible for the rise of the catalytic activity. However, experimental data (see Table 1, experiments 3–5 and 6–9) show that for salts A catalytic activity depends on anion as well as on cation nature. Data shown in Table 2 prove that the activation effect starts to appear at very low concentration of metal-activating ions ($\sim 10^{-3}$ atomic % – see experiments 1 and 2; 1 and 8).

Table 1. Catalytic activity (A) of TiO_2 dispersion after impregnation with various salts of iron(II), cobalt(II), copper(II), and palladium(II).

№	Modifying Salt	Modifier content, at. %	A, %
1	–	–	8
2	$FeSO_4$	0.10	17
3	$CoSO_4$	0.30	33
4	$Co(NO_3)_2$	0.30	44
5	$CoCl_2$	0.30	58
6	$CuSO_4$	0.10	36
7	$CuCl_2$	0.10	51
8	$Cu(CH_3COO)_2$	0.10	67
9	$Cu(HCOO)_2$	0.10	71
10	$PdCl_2$	0.010	45

Table 2. Catalytic activity (A) of TiO_2 dispersions with various content of some modifiers (modifying salts: $CuSO_4$, $CoCl_2$, $PdCl_2$).

№	Modifying ions content, at. %			A, %
	Cu^{2+}	Co^{2+}	Pd^{2+}	
1	–	–	–	8
2	0.001	–	–	16
3	0.010	–	–	21
4	0.100	–	–	36
5	–	0.08	–	37
6	–	0.30	–	58
7	–	0.50	–	50
8	–	–	0.005	24
9	–	–	0.01	45
10	–	–	0.02	25

Further increase of activator's concentration initially leads to a rise of A, then A exhibits some decrease. Besides that, the catalytic activity of modified dispersion of TiO_2 can be improved after its treatment by another metal salt. Table 3 shows that activity of TiO_2, modified by Cu^{2+}, became higher after additional treatment with Fe^{3+} as activity of TiO_2 modified by Pd^{2+} became higher after its treatment with Fe^{2+} or Co^{2+}. Increase of additional modifier ions concentration leads to rise of A, then it reaches saturation and even starts to lower at further increase of modifier ions concentration (see experiments 2–5, 8–11, and 13–17). As opposed to this tendency, MoO_4^{2-} ions have been found to be suppressors of activity of the catalyst containing Pd^{2+} (see experiment 10 in Table 1 and experiments 18–20 in Table 3).

Table 3. Catalytic activity (A) of double-modifier TiO_2 dispersions (modifying salts: $CoCl_2$, $FeCl_3$, $PdCl_2$, $CuSO_4$, $FeSO_4$, $(NH_4)_2MoO_4$).

№	Modifying ions content, at. %						A, %
	Cu^{2+}	Pd^{2+}	Fe^{2+}	Fe^{3+}	Co^{2+}	MoO_4^{2-}	
1	–	–	–	–	–	–	8
2	0.1	–	–	–	–	–	36
3	0.1	–	–	0.1	–	–	44
4	0.1	–	–	0.3	–	–	48
5	0.1	–	–	0.5	–	–	59
6	0.1	–	–	0.8	–	–	37
7	–	0.01	0.04	–	–	–	37
8	–	0.01	0.10	–	–	–	49
9	–	0.02	–	–	–	–	25
10	–	0.02	0.02	–	–	–	43
11	–	0.02	0.08	–	–	–	49
12	–	0.02	0.12	–	–	–	43
13	–	0.02	0.14	–	–	–	40
14	–	0.005	–	–	0.08	–	42
15	–	0.02	–	–	0.02	–	62
16	–	0.02	–	–	0.04	–	65
17	–	0.02	–	–	0.08	–	69
18	–	0.02	–	–	0.10	–	60
19	–	0.02	–	–	1.00	–	43
20	–	0.02	–	–	–	0.04	20
21	–	0.02	–	–	–	0.08	15
22	–	0.02	–	–	–	0.10	14

It is known [11,12] that there are some electron donor defective areas, such as oxygen vacancies or various admixtures (for example, Ti^{3+} ions) on the surface of titanium dioxide. Such defective areas or electrons can react with easily reducible ions (Ag^{+}, Pt^{2+}, Pd^{2+}, Cu^{2+} and Cu^{+}). Corresponding atoms deposit as a result of reaction, then they combine into nano-particles and form "islands" of nano-particles [13]. It is also known [3,5], that small metal particles can be an effective catalyst for reaction between the same or other metals and reducing agent. Such reactions are normally stopped in homogeneous solutions, because atoms, clusters and nano-particles of metals possess a highly reductive chemical activity and a short lifetime. Reductive chemical activity of these particles significantly exceeds the activity of larger particles or macro-dimensional metals [14]. Nano-particles can be stabilized on a surface, and this makes the metal deposition easier. Free nano-particles do not form under such conditions, and the reaction runs through consecutive joining new metal ions and electrons from reducing agent to the stabilized atoms and particles. Then the particles grow and may be aggregated. Metal particles from a solution containing another metal ions also can act as catalysts [5]. In our opinion, the same processes cause an increase of catalytic activity of TiO_2 after its modification by application of metal salts. Indeed, reduction of ions to metals is thermodynamically justified, as it is seen from comparison of standard electrode potentials of modifying metals $E^{o}_{Pd^{2+}/Pd^{o}} = +0.987$ V, $E^{o}_{Cu^{2+}/Cu^{o}} = +0.337$ V, $E^{o}_{Fe^{2+}/Fe^{o}} = -0.440$ V, $E^{o}_{Fe^{3+}/Fe^{o}} = -0.036$ V and $E^{o}_{Co^{2+}/Co^{o}} = -0.277$ V [15] and redox potential of formaldehyde in alkali media ($E^{o} = -1.07$ V [3]).

Thus, one can assume two types of processes occurring after modified TiO_2 has been applied into solution of Cu^{2+}. Initially the modifying ions are being reduced, forming nano-particles of metals. Then, these nano-particles start to act as catalysis centers and macro-dimensional metal copper continue to deposit onto these centers. Easily reducible ions (Pd^{2+}, Cu^{2+}) can interact with electron-donor defects of semiconductor and form some catalytically active nano-particles, even at a previous stage of semiconductor's modification.

Titanium dioxide can act in two ways. First, it can act as a stabilizing surface for reduced atoms and nano-particles formed from these atoms. Besides that, titanium dioxide possesses semi-conductive properties and can stay unchanged, while taking part directly in the process of reduction. Last assumption is proved by comparison of the thermodynamic data of compounds forming system "TiO_2 – metal ions – solution of formaldehyde". Estimation of location of conduction band has been made basing on data of flat band potential (U_{FB}) for series of TiO_2 samples [16]. Obtained values of E_{CB} were found within the range from –0.8 to –0.9 V. E_{CB} and U_{FB} are very close and differ no more than 0.1–0.2 V [11,16]. Both processes – injection of electrons into conduction band and further electron transfer onto adsorbed metal ions are thermodynamically justified, as it is seen from data of Fig. 1. Such route of reduction seems to be more preferable than direct transfer of electron from formaldehyde. It is known [13], that minor surface parts of metal can form surface states (*SS*) located in a band gap.

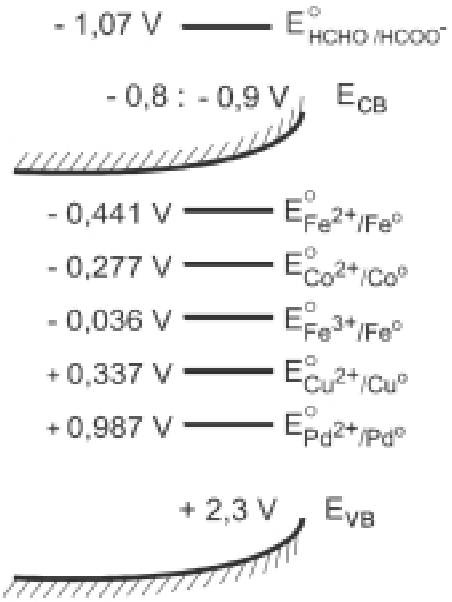

Figure 1. Diagram of energetic characteristics of titanium dioxide, standard potentials of modifying metals and redox compounds of metal copper deposition system.

They may be located in various depths depending on the metal. It has been reported in [17,18] that oxidation of donor defects of TiO_2 leads to formation of hetero-particles containing nano-particles of Pd and Cu, which also form *SS*. Such *SS* are located respectively 2.40 and 2.10–2.20 eV over the threshold of the valency band. Nano-particles of Fe lead to formation of *SS* located 0.45–0.75 eV below the threshold of conduction band [19]. Using these values and above mentioned value $E_{CB} = -0.9$ V, we found the following values for nano-particles-formed *SS*: –0.20 V (Pd), +0.10 ÷ +0.20 V (Cu) and –0.15 ÷ –0.45 V (Fe). All these values and, probably cobalt-*SS* potential, are located between potentials $E^{0}_{HCHO/HCOO^-}$ and $E^{0}_{Cu^{2+}/Cu^{0}}$. It should be noted that capturing and releasing of charge carriers in semiconductors is a common property of various *SS*. Consequently they can also promote charge transfer towards ions in electrolytes [20]. Hence, our model of metal copper deposition can include injection of formaldehyde electrons to TiO_2 conduction band, followed by transfer of electrons to *SS*, their accumulation on nano-particles transforming them into catalytic centers. Finally, Cu^{2+} ions are being reduced on such centers (see Fig. 2). Our model can explain the effect of modifying ion (see Table 2) and additional modifier (see Table 3) on activity of TiO_2. Higher number of nano-particles formed in corresponding examples can cause a rise of their catalytic activity with increase of adsorbed Pd^{2+}, Cu^{2+} and Co^{2+} content (see Table 2, experiments 2–4, 5, 6, 8, and 9). Further lowering of activity can be caused by two other factors. First, a higher content of modifying ions causes a more preferable formation of macro-dimensional metal particles. Corresponding *SS* have more positive potentials [13]. Then potential gap

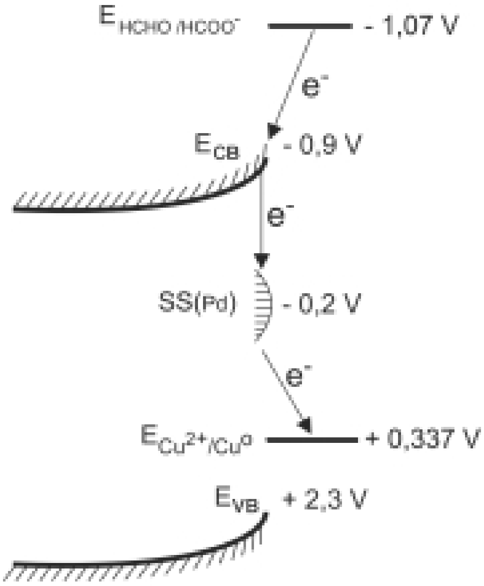

Figure 2. Energetic diagram of catalytic system containing titanium dioxide with nano-particles of palladium-*SS* and solution containing formaldehyde and Cu^{2+}. Scheme of metal copper deposition electron processes.

between E_{SS} and $E^0_{Cu^{2+}/Cu^0}$ narrows and the reduction of Cu^{2+} slows down. Second, bigger particles interact with TiO_2 matrix slowly and the velocity of electrons capturing diminishes for such particles as well. Finally, reaction of copper reduction turns to another way. Formaldehyde starts to interact directly with adsorbed Cu^{2+}. This reaction route requires the adsorption of metal ions onto neutral particles and, in our opinion, is less effective.

The same approaches can also be applied to consideration of double-modifier dispersion of TiO_2. Activity of TiO_2 first rises, passes through maximum, then lowers at increase of second modifier concentration (at constant concentration of first modifier) as it is seen from Table 3. Double-modifier dispersions have higher catalytic activities (compare example 15 with examples 5 and 10, Table 2). Pd^{2+} and MoO_4^{2-} modified examples demonstrated another shape of dependence of their activity on modifier concentration. MoO_4^{2-} leads to constant lowering of catalytic activity (see examples 18–20, Table 3 and example 10, Table 2). Some electrons are being injected to conduction band, but MoO_4^{2-} ions intercept part of them causing a lower catalytic activity of corresponding examples.

Various salts with the same metal ion form different values of catalytic activity (see Table 1). This is natural, because redox properties of ions of trespassing metals are in strong dependence on nature of counter-anion and the possibility of complex formation. Besides that properties of nano-particles-formed *SS* may depend on chemical properties of surface-based counter-anion as well.

Our paper reports significant increase of TiO_2 catalytic activity through application of salts of Pd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Co^{2+}. Simplified phenomenological examination of activation processes, based on comparison of energetic properties, may be useful for pre-evaluation of activation values of other modifying ions.

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