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Dispersions of TiO_2 containing Fe^{2+}, Co^{2+} and Cu^{2+} ions as catalysts for plastic metallization

I.M.Kobasa, Ya.S.Mazurkevich, N.I.Zozula

Department of Chemistry, Yu.Fedkovych National University,
2 Kotsiubinsky St., 58012 Chernivtsi, Ukraine

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It has been found that TiO_2 modified with Fe^{2+}, Co^{2+}, and Cu^{2+} salts increases significantly (up to 6–8 times) its catalytic activity in the reaction of copper metal deposition from its salt solutions. Exposure to the light provides a further increase of the catalytic activity. Some electron processes resulting in the improved catalytic activity have been considered. The use of the double-modified catalysts has been shown to provide a higher quality of the copper coatings on dielectrics.

Установлено, что каталитическая активность TiO_2 в процессе осаждения металлической меди из растворов ее соединений увеличивается в 6–8 раз при модифицировании этого полупроводника нанесением на дисперсии солей Fe^{2+}, Co^{2+} и Cu^{2+}. Облучение полученных материалов приводит к дальнейшему увеличению эффективности их каталитического действия. Рассмотрены электронные процессы, благодаря которым может возникать повышенная каталитическая активность. Показано, что использование разработанных катализаторов, содержащих два модификатора, в практически важном процессе металлизации диэлектриков обеспечивает получение высококачественных покрытий медью.

Semiconducting catalysts and photocatalysts for chemical deposition of metals are quite important functional materials. Such deposition processes are of a significant importance from the fundamental standpoint because they involve formation of nano-particles that possess many unique properties and are under intense investigation now [1–4]. The nano-particle formation processes are used widely in various silver-free photography processes [5], in deposition of the uniform metal coatings [6, 7], and in selective metallization of dielectrics for the printed circuit board production [8, 9]. Thus, development of novel effective catalysts for the metal deposition is very topical problem. Some photocatalytic materials have already been put into use for various purposes. For instance, TiO_2 modified with palladium has been proposed to catalyze the metallization in the printed circuit board production [10].

This paper reports results of modification with less expensive admixtures (Cu(II), Fe(II) and Co(II)) as well as effect of UV irradiation. Catalytic activity of our experimental examples has been tested in the process of copper deposition onto dielectric substrate. It has been shown that less expensive substances also provide an improved catalytic activity of TiO_2.

TiO_2 with specific surface S_{sp} = 18 m^2/g was used. The material was synthesized by the acidic hydrolysis of $TiCl_4$. The following salts: $Cu(CH_3COO)_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, and $Co(CH_3COO)_2 \cdot 4H_2O$ were used to modify TiO_2 dispersions by impregnating. The catalytic activity has been determined for the reaction of Cu(II) reduction from the mixture containing $CuSO_4 \cdot 5H_2O$ (22 g/l), $NaKC_4H_4O_6$ (140 g/l), NaOH (60 g/l), Na_2CO_3 (22 g/l), and the modified titanium dioxide (15 g/l). We also added 1.5 ml of formaldehyde to 50 ml of the mixture.

There was no indication of any reaction run for 10 to 20 min without the catalyst.

The amount of Cu^{2+} ion reduced during 1 min was used to assess the catalytic activity of various materials. In this way, the catalytic activity percentage is calculated as $A = (1 - C_2/C_1)\times100$, where C_1 and C_2 are Cu^{2+} concentrations prior to and after the reaction, respectively.

All the dispersions were exposed to UV light in air using a DRT-230 mercury lamp. For better comparison, we kept the same distance from the lamp (15 cm) and exposition time (25 min) through all experiments. An epoxy resin composition was used as the initial material to obtain the dielectric samples for copper deposition. Our catalysts were embedded into the composition (20 mass %). The reaction solution contained 12 g/l of $CuSO_4 \cdot 5H_2O$, 15 g/l Trilon B, 10 g/l NaOH, 10 mg/l $K_3[Fe(CN)_6]$, 10 mg/l α, α′-dipyridyl and 10 ml/l formaldehyde. Copper deposition was carried out at 60°C for 2 h in the presence of various dielectric samples.

As it is shown in Table 1, titanium dioxide dispersions modified with iron, cobalt, and copper salts, exhibit 6–8 times higher catalytic activity as compared to the initial TiO_2. Some characteristic features of the transition metal ion reduction both in the volume and on the surface should be taken into account in order to explain the drastic rise of the catalytic activity. Metal particles should also play some role in that effect. It is shown [1, 5, 11], that some thermodynamically competent processes may be hindered while running in homogeneous solutions. Such hindrances are caused by formation of high-reactive, easily oxidable free atoms. For example, free copper atom has a lone outer S-electron ($d^{10}s^1$ electron configuration) and is a strong reducing species. The standard ion/atom potential for Cu^{2+}/Cu^0*atom* is $IE^0_{Cu^{2+}/Cu^0atom} = -1.25$ V [11] and standard electron potential for copper metal is $E^0_{Cu^{2+}/Cu^0} = 0.337$ V [12]. The atoms can be adsorbed on the solid surface, resulting in a partial compensation of the unpaired electrons. The latter process causes significant potential shift towards positive values, which improves the reduction process. Metal nano-particles can also be formed as a result of the reduction and such particles catalyze further reduction of the same or other metal ions [1, 5]. Thus, the increased catalytic activity of TiO_2 after its treatment by salts of transition metals seems to be due to the following: Adsorbed Fe^{2+}, Co^{2+}, and Cu^{2+} ions are easily reduced with formaldehyde. Due to that reaction, metal particles are formed depositing on the semiconductor surface, which catalyze the further deposition of copper. The reduction of modifying ions is thermodynamically favored, since the redox potential of formaldehyde $E^0_{HCHO/HCOO^-} = -1.07$ V [1] is considerably more negative than standard electrode potentials $E^0_{Fe^{2+}/Fe^0} = -0.440$ V, $E^0_{Co^{2+}/Co^0} = -0.277$ V, and $E^0_{Cu^{2+}/Cu^0} = 0.337$ V, [12].

Considering energy characteristics of the systems under investigation and possible electron transition processes, one can gain information concerning the mechanisms of the catalytic copper deposition. We have determined the conductivity band location as $E_{CB} = 0.8 \div 0.9$ eV. This value is based on results of the flat band potential (U_{FB}) investigation for pH = 14 involving a number of TiO_2 samples synthesized at various conditions [13]. Little difference between E_{CB} and U_{FB} (no more than 0.1–0.2 eV, [13, 14]) has also been taken into consideration. Thus, we can estimate the position of the valence band upper limit as $E_{VB} = 2.3 \div 2.4$ eV, basing on the found values of E_{CB} and the E_g value of 3.2 eV [13].

It is known that the surface nano-particles of metals may form surface states (SS) on the substrate, positioning them into the band-gap. The SS may take part into electron transfers from the conductivity band to electrolyte ions [14, 15]. The small particles can form SS positioned 2.1–2.2 eV above the valence band upper limit, as it is shown in [16]. At the same time, the SS formed by iron particles are 0.45–0.75 eV below the conductivity band [17]. Combining this information with the E_{CB} and E_{VB} values, we can determine the energy position of the copper nano-particles SS as $E_{SS}(Cu) = 0.1 \div 0.2$ eV and that of iron nano-particles SS as $E_{SS}(Fe) = -0.15 \div -0.45$ eV. Comparing the energy characteristics with redox potentials of reagents ($E^0_{Cu^{2+}/Cu^0}$, $E^0_{HCHO/HCOO^-}$), we can identify the following processes as thermodynamically allowed: (a) Injection of reducing agent electron into the conductivity band of TiO_2; (b) electron transfer from the conductivity band onto SS, e.g. onto metal particles deposited on a semiconductor; and (c) interaction between Cu^{2+} and negatively charged metal particles resulting in formation of copper atoms Cu^0. The freshly formed copper atoms can either instantly react with the metal particles or be captured by ions with a cluster formation. This

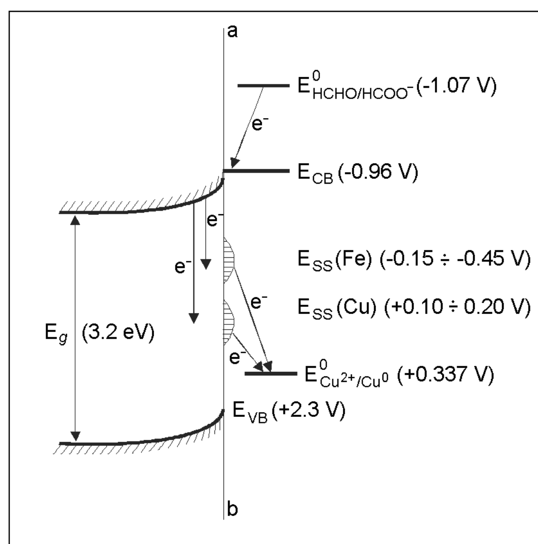

Fig. Energy diagram of the system containing TiO_2 with SS formed by iron and copper nano-particles, and reagent solution (HCHO and Cu^{2+}). Scheme of possible electron transfer processes, which can cause Cu^{2+} reduction and copper metal deposition.

process eliminates hindrances peculiar to the free atom formation. The energy diagram for the system iron and copper modified TiO_2/reagent solution is shown in Fig. together with the scheme of possible electron processes. We assume that copper deposition will run more effectively according to the scheme shown in Fig. than through direct reaction between copper ions and formaldehyde. The latter process requires preliminary adsorption of the ions on neutral metal particles, which is not necessary in our scheme. Our scheme can be especially effective at the initial stages of the process while the freshly formed metal particles are small enough. The interaction between the metal particles weakens in the growth course thereof. This process leads to a narrowed electron capture cross-section [16], which also causes copper deposition to slow down. In fact, our experimental data (see details below) proved a decrease of the catalytic activity under experimental conditions, promoting formation of bigger particles of the activator metal. This suggests that the mechanism of chemical reactions, involving the conductivity band and SS, becomes gradually replaced by direct interaction between the reagents in the course of assertion of metal particles agglomerations. The direct interaction provides a lowered reduction rate of Cu^{2+}. It requires 1 mine to form catalytic centers on the modified TiO_2 and to attain the Cu^{2+} deposition extent of 26–41 % (see Table 1). But it requires about 2 h and higher temperature to accomplish the metallization even if we use highly active irradiated catalysts.

Exposure to UV radiation results in a significant catalytic activity improvement of the initial material and its dispersions containing modifying salts (see Tabl. 1). It is known [13, 18–20], that photoinduced generation of the electron-hole pairs is followed by a regular recombination process involving substances adsorbed previously on the semiconductor particles. However, electron capturing from the conductivity band by the lattice ions can also take place. The latter process provides the formation of the donor structure defects, for example, Ti^{3+}. Interaction between such defects and Cu^{2+} forms the metal copper nano-particles on the TiO_2 surface even without involving of any reducing agent admixture [16].

As a rule, multi-electron processes are not observed at the photoexcitation of a semiconducting particle [19]. Thus, reduction

Table 1. Catalytic activity of TiO_2 dispersions modified with Fe^{2+}, Co^{2+} and Cu^{2+} salts ($A_{mod.}$). Catalytic activity of the same materials exposed to UV radiation ($A_{rad.}$) and change of the activity during storage of the materials (A_{stor})

No.	Modifying ion content, mass.%			$A_{mod.}$, %	$A_{rad.}$, %	$A_{stor.}$, %					
						Storage time, days					
	Fe^{2+}	Co^{2+}	Cu^{2+}			1	3	5	10	20	30
1	–	–	–	5	31	30	25	18	42	7	5
2	0.5	–	–	29	49	46	40	36	30	30	30
3	0.5	–	0.1	41	60	57	47	43	40	40	40
4	–	0.3	–	26	58	54	52	44	40	30	29
5	0.1	0.3	–	38	53	50	47	44	39	38	37
6	–	1.0	1.0	34	61	52	45	39	37	34	34

Table 2. Properties of copper coatings on epoxy rubber composites. Catalyst: UV-irradiated dispersions of TiO_2, modified with Fe^{2+}, Co^{2+} and Cu^{2+} ($A_{rad.}$-catalytic activity after the material illumination. Metallization result is indicated as "+ ")

No.	Modifying ion and content of the added salt, mass.%	$A_{rad.}$, %	Metallization result	
			Uniform and unbroken coating	Broken coating, containing some copper-free areas
1	Fe^{2+} (0.5)	49		+
2	Fe^{2+} (0.5) and Cu^{2+} (0.1)	60	+	
3	Fe^{2+} (0.1) and Co^{2+} (0.3)	53	+	
4	Co^{2+} (0.3)	58		+
5	Co^{2+} (1.0) and Cu^{2+} (1.0)	61	+	

of the adsorbed ions or molecules runs via the single-electron mechanism instead. For example, illumination of the Cu^{2+}-added semiconductor results in Ti^{3+} formation and additional deposition of copper atoms and nano-particles. The latter process runs via consecutive reactions: $Cu^{2+} + e^- \rightarrow Cu^+$ ($E^0 = 0.153$ eV); $Cu^+ + e^- \rightarrow Cu^0$ ($E^0 = 0.521$ eV) [13, 16]. Unlike Cu^{2+}, single-electron reduction of Fe^{2+} and Co^{2+} is significantly hindered and effective electron-hole recombination occurs as a result of electron transfer from the conductivity band. That is why there is no cation reduction at the illumination of TiO_2 dispersions containing iron and cobalt salts. The photo-generated charge carriers are consumed in the same process as in the unmodified semiconductor (including formation of Ti^{3+}). Thus, electron donor structure defects cause increase of the catalytic activity of the semiconductor materials after light exposure thereof. Copper atoms deposit on such defects forming additional nano-particles. Such particles can act as catalytic centers for the metallization process. Storing of the illuminated materials in air turns conditions for the active center formation worse because the air oxygen oxidizes Ti^{3+} ions, Cu^0 atoms and few-atom clusters. This process lowers the catalytic activity down to pre-exposure value (see Table 1).

Investigation of the metallization process has shown that there are only two salts which form catalysts ensuring high quality coatings (see Table 2, experiments 2, 3, 5). Copper-free parts of the metal coating indicate areas with zero catalytic activity formed because of non-uniform distribution of the modifying agent.

Thus, our results can be easily explained basing on the assumption that particles of two modifying agents give more uniform coating in comparison to a single modifier. However, verification of this assumption requires further specialized investigation.

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Дисперсії TiO_2, що містять іони Fe^{2+}, Co^{2+} та Cu^{2+}, як каталізатори процесу металізації діелектриків

І.М.Кобаса, Я.С.Мазуркевич, Н.І.Зозуля

Встановлено, що каталітична активність TiO_2 в процесі осадження металічної міді з розчинів її сполук зростає в 6–8 разів під час модифікування цього напівпровідника нанесенням на дисперсії солей Fe^{2+}, Co^{2+} та Cu^{2+}. Опромінювання одержаних матеріалів УФ-світлом приводить до подальшого збільшення ефективності їх каталітичної дії. Розглянуто електронні процеси, завдяки яким може виникати підвищена каталітична активність. Показано, що використання розроблених каталізаторів, які містять два модифікатори, в практично важливому процесі металізації діелектриків забезпечує одержання високоякісних покриттів міддю.