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Semi-Conductive Materials Based on the Titanium Dioxide Doped with Zinc: Catalytic Activity for Copper Deposition and Effect of UV-Irradiation

by I.M. Kobasa

Chernivtsi National University, Kotsiubinsky St. 2, Chernivtsi, 58012, Ukraine
E-mail: igorw@lenta.ru

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Novel semiconductive materials containing TiO_2 dispersion, doped with zinc and additional modifying salts of Cu^{2+}, Fe^{2+}, and Co^{2+}, have been obtained. Such materials can be used as effective catalysts in the Cu^{2+} reduction. Exposition to UV-light followed by the dark storage leads to complex changes of the catalytic activity of TiO_2 products. Detailed character of the changes depends on the presence of a doping agent and on the nature of modifying salts' anion. The scheme of the electron transfer processes has been proposed to describe changes of the activity.

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

Reductive deposition of metals from the solutions of their salts is quite an interesting example of semiconductors' participation in the catalytic and photocatalytic processes. Such processes have many practical applications, such as silver-free photography, making of solid metal covering on various substrates. They can also be used for selective copper deposition for the production of printed plates [1–6]. Besides that, investigation of such processes has significant fundamental importance, because they involve formation of nano-particles possessing quantum dimensional effects and many unique properties [7–10]. So, development of effective catalysts and photocatalysts for the electrolysis-free metals deposition is quite a topical problem. Numerous investigations prove, that properties of the semiconductive materials depend on many factors: synthesis conditions; presence or absence of doping ions, additional modifiers, activators or electron carriers; further oxidizing or reductive treatment; and formation of heterostructures, containing various semiconductors [11–20]. For example, it has been shown [21], that the catalytic activity of titanium dioxide in the copper(II) ions reduction can be increased drastically through the treatment of TiO_2 dispersion with some salts.

Catalytic action of the titanium dioxide after its doping with zinc, additional modification with Cu^{2+}, Fe^{2+}, Co^{2+} salts and exposure to UV-radiation has been investigated for the reaction of the metal copper deposition.

EXPERIMENTAL

Source titanium dioxide with specific surface $S_{sp} = 20\ m^2/g$ has been synthesized in the reaction of titanium sulfate and zinc acetate hydrolysis. Initially TiO_2 dispersions were being impregnated with various salts solutions and stirred for 1 hour. Then the mixture was steamed off and the dispersion was dried up. Afterwards, the dispersion was being annealed either in inert atmosphere (in N or Ar) or in the air at 450°C to achieve zinc acetate decomposition. Finally we modified the product using salt impregnation and dried up the examples. $CuSO_4 \cdot 5H_2O$, $CuC_6H_6O_7$, $Cu(CH_3COO)_2 \cdot H_2O$, $FeSO_4 \cdot 7H_2O$, $FeC_2O_4 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$ were used as modifying salts.

The reaction of copper(II) ions reduction by formaldehyde was used to determine the level of catalytic activity of the materials under investigation. This reaction has been carried out in the alkali media. Cu^{2+} ions were protected by tartrate ligands according to the original method [3]. The procedure of the catalytic activity determination took following operations: we added 1.5 ml of formaldehyde to 48.5 ml of the reaction mixture containing 0.75 g of TiO_2 material, 22 g/l of $CuSO_4 \cdot 5H_2O$, 140 g/l of $NaKC_4H_4O_6$, 60 g/l of NaOH and 22 g/l of Na_2CO_3. Then the mixture was being well-stirred for 1 min. The semiconductor was promptly centrifuged afterwards and the content of Cu^{2+} was determined in the filtrate. Lowering of Cu^{2+} content gave us way to determine the catalytic activity of modified TiO_2 samples according to formula $A = (1 - C_2/C_1) \cdot 100$, where A – activity (%), C_1 and C_2 – concentration of Cu^{2+} before and after contact with the catalyst respectively. Powder products were exposed to UV-radiation in the air without any side materials and lamp DRT-230 was used as the source of radiation. For better comparison all examples were placed in the similar conditions: lamp distance was 15 cm and exposition time was 25 min.

Results of determination of photo-catalytic and catalytic activity, electroconductivity and magnet perceptibility of the modified samples proved, that they stayed stable for at least 2,5 months if there was no effect of UV-radiation or additional temperature processing.

Atom-absorption spectrophotometer C-115-M-1 has been used to determine the catalytic activity of TiO_2 – based materials. Relative inaccuracy of such measurements has not been higher than 0.15–0.24%. This value defined the results' repeatability.

RESULTS AND DISCUSSION

We were determining the doped products' activity while annealing. Experimental data showed initial rise of the activity followed by its saturation and, later, some decrease effect. The most active examples were obtained after annealing at 450°C for 3 hours. Data shown in Tab. 1 proves that minimal addition of zinc leads to significant rise of the activity (up to 4 times). Further addition of zinc leads to slower rise of the activity, which reaches saturation and then starts to decrease after reaching ZnO concentration of 5 atom %. One can see that annealing in the inert atmosphere produces more active catalysts comparing to the examples processed in the air (see Tab. 1, experiments 3 and 5). This effect was taken into account in further experiments. All experiments mentioned hereinafter were carried out using most optimal dispersions of TiO_2/ZnO (5 atom % of ZnO; annealing in the inert gas (nitrogen) atmosphere at 450°C for 3 hours).

Tab. 2 proves that impregnation of TiO_2/ZnO with $CuSO_4$, $FeSO_4$ and $CoCl_2$ leads to different changes of the catalytic activity. 0.01 mass % of copper salt is enough to give significant rise of the catalytic activity. Further addition of copper leads to decrease of A. Activity of the modified product drops lower than A of pure TiO_2 if concentration of Cu^{2+} exceeds 1.0 mass %. Impregnation with Fe(II) exhibits similar tendency. Although significant rise of the catalytic activity requires addition of 0.5

mass % of Fe^{2+}. Further addition of iron ions causes decrease of *A* but it drops slowly than in the case of using copper addition. TiO_2 containing 5.0% of Fe^{2+} still has higher catalytic activity than initial non-modified material. Cobalt salts influence catalytic activity in more complex way. Catalytic activity of the materials containing 0.01–0.10% of Co^{2+} is lower than activity of initial TiO_2. Further addition of the salt causes rise of *A*, which reaches maximum value, then drops down to 40% comparing to initial *A*.

Table 1. Catalytic activity (A) of semiconductive materials containing zinc acetate (initial A = 8%) after annealing at 450°C for 3 hours.

No	Zinc contents (converting to ZnO), atom %	A, % after annealing	
		in nitrogen	in the air
1	0.01	30	–
2	0.10	32	–
3	5.0	40	34
4	10.0	38	–
5	20.0	36	25

Table 2. Catalytic activity (A) of TiO_2 dispersions after their doping by zinc (5.0 atom % converting to ZnO) and additional modification with $CuSO_4$, $FeSO_4$, $CoCl_2$.

No	Content of the modifying ion, atom %			A, %
	Cu^{2+}	Fe^{2+}	Co^{2+}	
1	–	–	–	40
2	0.01	–	–	50
3	0.10	–	–	49
4	0.50	–	–	48
5	1.00	–	–	26
6	5.00	–	–	21
7	–	0.01	–	40
8	–	0.10	–	45
9	–	0.50	–	49
10	–	1.00	–	48
11	–	5.00	–	47
12	–	–	0.01	20
13	–	–	0.10	30
14	–	–	0.50	45
15	–	–	1.00	42
16	–	–	5.00	37

Tab. 3 shows influence of modifying anions, UV-radiation and long-term storage of the materials in the air out of the light. One can remark following characteristics: a) Same trespassing cation but various anions salts cause different values of *A* though alkali elements salts give no evident change of *A*. b) Exposure to the light causes significant lowering of *A* of TiO_2/ZnO examples modified with Cu^{2+}, Fe^{2+}, and Co^{2+} salts with inorganic anions. Same modifying salts containing organic anions exhibit slight rise of *A* of TiO_2/ZnO examples after the exposure. c) Storage of irradiated materials modified with inorganic salts causes significant rise of *A*. It reaches the maximum value in a week, then lowers. The materials containing organic modifiers exhibit the same, but less significant changes. In this case *A* reaches its maximal value in about 24 hours, then it lowers.

Table 3. Influence of additional modifying salt (A_{mod}), exposition to UV-radiation (A_{rad}), and dark storing (A_{stor}) on the catalytic activity of TiO_2 doped with Zn.

No	Modifying salt	Content of the modifying cation, atom %	A_{mod} %	A_{rad} %	A_{stor}, %					
					storage time, days					
					1	2	3	7	15	30
1	$CuSO_4$	0.01	50	35	43	54	64	72	48	46
2	$CuSO_4$	0.5	48	29	57	59	67	68	50	49
3	$CuC_6H_6O_7$	0.5	54	57	58	61	58	50	48	48
4	$Cu(CH_3COO)_2$	0.5	50	51	55	59	54	44	42	41
5	$CoCl_2$	0.5	47	37	48	49	49	58	51	50
6	$Co(CH_3COO)_2$	0.5	55	56	65	67	57	53	50	50
7	$FeSO_4$	0.5	49	42	50	51	52	54	50	49
8	FeC_2O_4	0.5	55	56	65	65	53	50	49	48

Catalytic action of the doped titanium dioxide without modifying salts. Chemical deposition of metals starts from formation of nano-dimensional metal particles. Such particles can effectively catalyze the following deposition [6,7]. Catalytic activity of TiO_2 is also caused by the presence of metal nano-particles. They can appear after the interaction between easily reducible ions (such as Cu^{2+}) and electron-donoring defects of the structure (such as oxygen vacancies) [22]. Source titanium dioxide has low catalytic activity ($A = 8\%$) before doping, because it had not been exposed to the special treatment aimed to formation of defects [13,14,18,20]. Hence, only few catalyzing copper metal particles could appear on its surface.

Adding of Zn gives wider opportunities for formation of the nano-particles and rising of the catalytic activity. Atoms of Zn appear in the internodes of TiO_2 grade and this effect causes formation of donor levels positioned 0.23 eV lower the conductivity band [13]. Such levels can take part in the reduction of the copper ions. Formation of zinc oxide becomes an important factor at rising of the doping agent concentration because this factor is favorable for the origination of new catalytic centers. ZnO contains some internode atoms contributing the formation of donor level positioned just 0.05 eV lower the conductivity band. This effect provides some free electrons to the semiconductor. Let us remark, that annealing of the materials at the stage of doping can also lead to formation of some oxygen vacancies. Various activities of examples after their annealing in the air or in the inert atmosphere (see Tab. 1, experiments 3 and 5) prove effect of the oxygen vacancies. *A* exhibits some tendency to lower at increase of zinc content, which can be explained through the possibility of formation of zinc metatitanate $ZnTiO_3$ at such conditions [23]. This compound is probably less defective.

Catalytic process with modified materials. Catalytic copper deposition in the system containing TiO_2 dispersion modified by trespassing metals ions, Cu^{2+} ions, and formaldehyde starts from the reduction of the surface copper ions [24]. The reduction involves adsorbed ions rather than ones from the solution, because the first way excludes the stage of free atom formation. Free atoms are highly reactive [6,7,25] and can be easily oxidized to adsorbed atoms, followed by the metal particles. Further stages of the deposition include alternate processes of electron transfer to newly formed catalytic nano-particles and interaction between these catalytic centers and Cu^{2+} from the solution [24]. In our opinion, the similar scheme can also describe processes, taking part in the system under our investigation. Salt modification of the zinc-doped materials can lead either to increase or decrease of the catalytic activity (see Tab. 2, experiments 5, 6, 12, 13, 16 and compare to experiment 1). Internode zinc atoms can be oxidized by Fe^{2+}, Co^{2+}, and Cu^{2+} ions at the impregnation of the doped semiconductor with salts. This oxidizing forms new catalytic centers with different potential positioning. It is known [24], that catalytic activity of the nano-particles depends on the metal nature and dimension of the particle. The same reference also proves, that this dependence passes through a maximum value. These reasons give us ground to suppose a lower activity of the cobalt nano-particles, comparing to the same size particles of copper (see Tabl. 2, experiments 12, 13 and 2–4). Lower activity of the doping agent free TiO_2 [24] and of the examples containing higher amount of the modifying agent (experiments 4, 5, and 16) can be justified by formation of bigger particles. Such particles are characterized by weaker interaction with the semiconductive substrate and lower catalytic activity in the copper(II) ions' reduction.

It is known [14], that exposition to radiation leads to partial reduction of titanium dioxide and formation of Ti^{3+} ions. If such exposition acts on the material, containing easily reducible ions such as Pd^{2+}, Ag^{+} or Cu^{2+}, nano-dimensional parts of corresponding metal can appear on the surface of TiO_2. This way we can increase the catalytic activity of TiO_2 dispersions covered by salts of iron, cobalt or copper. Our experiments proved, that exposition to the light actually led to significant rise of the catalytic activity of such dispersions containing no zinc. The same materials, containing a doping agent, show different behavior. As it is seen from the data of Tab. 3, their activity either stays practically unchanged (see experiments 3, 4, 6, and 8) or significantly decreases (see experiments 1, 2, 5, and 7). Exposition to light leads to decrease of the activity of the doped TiO_2, as well (from initial $A = 40\%$ down to 34% for the examples containing 5% of the doping agent).

Let us describe possible electron processes, which can take place at the exposition of doped materials to light. Electron-hole pair originates in the semiconductor, then electrons are being used in the recombination or in the capturing by oxygen molecules. Besides that, some electrons can be used for the reduction of the grade-located ions Ti^{4+} or, for the examples containing Cu^{2+}, for the reduction of copper. Both processes lead to the increase of the catalytic activity. Hole-involving processes (electron-hole recombination, capturing of the holes by hydroxyl ions located on the surface of TiO_2 or by adsorbed molecules of water or by anions of the applied salts) makes no direct impact on the catalytic activity. However, oxidizing of the surface atoms and metal particles by the holes is thermodynamically competent. This process leads to decrease of the catalytic activity. Thus, activity-decreasing processes would prevail over activity-increasing ones for the materials containing no effective donors of electrons (for example, non-modified semiconductor or the dispersion containing inorganic salts with SO_4^{2-} and Cl^- anions). We suppose that such phenomena cause a decrease of the catalytic activity of the examples previously exposed to the light (see Tab. 3, experiments 1, 2, 5, and 7).

Atoms and nano-particles are being oxidized less effective in the materials containing organic hole-accepting anions (experiments 3, 4, 6, and 8). That is why such materials reveal only slight decrease of the activity after the irradiation.

Storage of the irradiated catalysts. Activity of the irradiated catalysts can have different temporal changes, depending on the nature of the doping agents used. Doping agent free examples reveal steady decreasing of the activity, caused by slow (running about 1 month) process of oxidizing of the electron-donor defects (for example, Ti^{3+} ions) previously formed during the irradiation. Zinc-doped and irradiated examples initially reveal increase of the activity, which then turns to decrease. Peak activity can be achieved after various intervals of time depending on the nature of the doping salt anion (see Tab. 3). These data lead us to conclusion, that there are two opposite processes, occurring in such catalysts. First, the air oxygen oxides the donor defects, leading to decrease of the activity. Second, there is another process, generating new catalytic centers or their electron-donoring precursors' formation on the surface of TiO_2. The latter process causes an opposite effect of the increase of catalytic activity. All the examples were being stored out of influence of any reducing agents. This fact gives us ground to suppose that some kind of inner process, like redistribution of the electron density in semiconductive particles, can cause occurrence of the two processes mentioned above. Most probably, this process involves transfer of electrons between oxidized (cation-like) surface catalytic centers (formed after capturing of the holes generated by the light irradiation) and internodal atoms of metal located in the body of the disperse particle. Spontaneous deposition of new nano-particles on TiO_2 always involves the process of electron transferring from the donor defects (not even necessary from the nearest ones) [22]. This fact also proves the possibility of the electron transferring between the surface catalytic centers and internodal atoms.

Assumption of the electron transfer occurrence gives us way to ground all the changes of the irradiated catalysts' activity while dark storing. Velocity of the electron transfer is probably higher than the velocity of the donoring defects' the oxidation. In the case of sulfate or chloride containing examples, the process of the activity change takes about 7 days to finish (see Tab. 3, experiments 1, 2, 5, and 7). The examples, containing organic salts, are less subjected to the oxidation by the holes and, in this case, the same process takes only about two days to finish (see Tab. 3, experiments 3, 4, 6, 8). The sharpest changes of the activity can be achieved for the examples modified by copper sulfate. After reduction of such materials, they contain Ti^{3+} ions together with Cu^{+} and Cu^{0}. Copper formation in the reaction $Cu^{+} + Cu^{+} \rightarrow Cu^{0} + Cu^{2+}$ also improves the catalytic activity of such examples.

Thus, the examples containing higher amount of Cu^{2+} (0.5%) reveal more significant decrease of the catalytic activity at irradiation and its increase during the dark storage than the examples with lower content of Cu^{2+} (0.01%) (see experiments 1, 2). This difference can be expressed in the following way: Most electrons from the conductivity band of the higher content of Cu^{2+} examples are being used in the reduction. The examples with lower content of Cu^{2+} ions have more complicated conditions for the reaction $Cu^{2+} + e^{-} \rightarrow Cu^{+}$ and it runs much slowly.

Similar single electron reactions are not energetically justified for $CoCl_2$ and $FeSO_4$ containing catalysts. In this case all electrons from the conductivity band take part in the reduction of titanium ions only. Correspondent examples reveal much lesser changes of the activity after their exposition to the light followed by dark storage (see Tab. 3, experiments 2, 5, and 7).

To sum up we can emphasize following results. a) It has been proved that doping of titanium dioxide by zinc leads to significant increase of its catalytic activity in the reaction of copper deposition from the solutions of its salts. Additional doping of titanium dioxide by copper, iron or cobalt salts also leads to some increase of the catalytic activity. b) Influence of UV-irradiation, anion residual or storing on different catalysts has been determined. c) Some electron schemes have been proposed in order to clarify changes of the catalytic activity.

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