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Phthalocyanine modified TiO_2 or WO_3-catalysts for photooxidation of sulfide and thiosulfate ions upon irradiation with visible light

V. Iliev*, D. Tomova, L. Bilyarska, L. Prahov, L. Petrov

Institute of Catalysis, Bulgarian Academy of Sciences, Akad. G. Bontchev Str., Bl. 11, 1113 Sofia, Bulgaria

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Abstract

The photooxidation of Na_2S or $Na_2S_2O_3$, catalyzed by Al_2O_3, TiO_2 or WO_3 superficially modified with metal-free phthalocyanine complex (Pc), cobalt phthalocyanine complex (CoPc) and copper phthalocyanine complex (CuPc), has been studied upon irradiation with visible light. The rates of the substrate photooxidation, catalyzed by the phthalocyanine complexes supported on TiO_2 or WO_3, are much higher than those registered with the same complexes, anchored on Al_2O_3. The high photocatalytic activity of the samples is explained by an electron transfer from the conduction band of the excited phthalocyanine semiconductor particles to the conduction band of the TiO_2 or WO_3 supports. The increase of the quantum yield of the photocatalytic redox process comes as a result of the additional formation of superoxide radicals on the TiO_2 or WO_3 conduction bands. A complete oxidation of Na_2S or $Na_2S_2O_3$ to sulfates has been registered in the presence of the studied photocatalysts.

Keywords: Photocatalytic detoxification; Phthalocyanine semiconductors; Oxide semiconductors; Sulfide; Thiosulfate; Visible light

1. Introduction

Semiconductor photocatalysis is an advanced oxidation process to eliminate organic pollutants in water. During the last two decades, there have been a number of studies on this process and it has recently been reviewed [1–3]. Photoinduced electrons and holes can reduce and oxidize species adsorbed on the semiconductor particles during photocatalytic processes [3]. The semiconductors, most widely used as photocatalysts, triggering off the oxidative destruction and mineralization of organic substrates, are TiO_2, WO_3 and SnO_2. Due to the width of the band gap (E_G) of these photocatalysts (TiO_2, $E_G = 3.2\,eV$; WO_3, $E_G = 2.8\,eV$; SnO_2, $E_G = 3.6\,eV$) [2], the processes of catalytic oxidative destruction are accomplished upon irradiation with light of the UV region. The photocatalytic processes do not occur effectively during the irradiation with solar light as only approximately 4% of the total radiation of the solar spectrum is in ultraviolet region. One disadvantage of the particulate systems upon band gap excitation of the semiconductors is the high degree of recombination between the photogenerated charge carriers. As a results of this recombination the photocatalyst effectivity is decreased as well as the quantum yield of the redox process.

In order to overcome this disadvantage, semiconductors [4,5] or coupled semiconductor systems (heterotype “photochemical diodes”) are used, in which one of the components is excited upon visible light irradiation [6,7]. Applying photocatalysts, obtained by coupling two different semiconductor phases, an efficient charge separation can be achieved [7,8]. The anchoring of pigments, especially phthalocyanine complexes on wide-band gap semiconductors [5,9–13], is an alternative method, in which a dye (sensitizer), adsorbed on the support surface, gets excited by absorbing visible light and an intercomponent electron transfer is realized in the couple molecular semiconductor–oxide semiconductor. It was shown in previous studies [12,13] that the rates of the sodium sulfide or phenols photooxidation, catalyzed by the metal-free 29H-, 31H-phthalocyanine complexes, supported on TiO_2, are much higher than those registered with the same complexes, anchored on Al_2O_3.

The catalytic activity of the metal-free phthalocyanine complex (Pc), the cobalt phthalocyanine complex (CoPc) and the copper phthalocyanine complex (CuPc) supported on Al_2O_3, TiO_2 or WO_3, is studied in the present work upon irradiation of the samples with visible light. The oxidation of Na_2S and that of $Na_2S_2O_3$ have been chosen as model reactions. The thiosulfates are the main final products in the

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* Corresponding author. Tel.: +359-2-9792514; fax: +359-2-9712967.
E-mail address: iliev@ic.bas.bg (V. Iliev).

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case of sulfide ion oxidation [14,15]. The aim of the study is to investigate the influence of supports with semiconducting properties, such as TiO_2 and WO_3, upon the quantum yield of the redox process, photocatalyzed by the investigated phthalocyanine complexes. The effect of semiconductor type of supports on the conversion degree of the hidrosulfide and thiosulfate ion is also object of the studies. The photocatalytic activity of the phthalocyanine complex, supported on TiO_2 or WO_3, is compared to that displayed in the case, when the pigments are anchored on a support with dielectric properties (Al_2O_3).

2. Experimental

Merck $Na_2S·9H_2O$ and $Na_2S_2O_3$ were used without any further purification. The concentration of Na_2S solutions, before the catalytic oxidation, has been determined in accordance with the method described in [16] by means of selective precipitation of the sulfide ion as CuS in excess of $CuCl_2$ and titration of the filtrate with a Titriplex III solution. Aldrich non-metallic 29H-, 31H-phthalocyanine complex, cobalt phthalocyanine complex and copper phthalocyanine complex were used without any further purification. Al_2O_3 (Merck, 150, Typ T), TiO_2 (Riedel-de Haen) and WO_3 (Aldrich) were used as supports. The specific surface areas of Al_2O_3 (60 $m^2\,g^{-1}$), TiO_2 (4 $m^2\,g^{-1}$) and WO_3 (14 $m^2\,g^{-1}$) were measured using nitrogen adsorption method at 77 K and BET analysis. The X-ray diffraction patterns of TiO_2 powder were measured using Co Kα radiation. The TiO_2, used as support, is 100% anatase, which is proved by the presence of a peak at $2\theta = 29.5$ (Fig. 1), which is the major peak for this type of structure.

The anchoring of the phthalocyanine complexes (Pc, CoPc or CuPc) on Al_2O_3, TiO_2 and WO_3 was carried out by impregnation of the supports with a solution of the phthalocyanine complex in concentrated sulfuric acid. One gram of the support is impregnated with 1 ml concentrated H_2SO_4, containing 90 mg of the respective phthalocyanine complex. The crystallization of the phthalocyanine complexes deposited on the supports is realized by a slow addition of water upon stirring. The catalysts are washed with distilled water to pH = 7 and dried at temperature 393 K under vacuum. The supported phthalocyanine complexes on Al_2O_3, WO_3 or TiO_2 amount to 0.16 $mmol\,g^{-1}$ of support. The photocatalytic studies were carried out with 70 mg of the obtained catalysts, containing 11 μmol phthalocyanine complex. The rate of water addition exerts some effect on the strength of anchoring of the phthalocyanine complexes and on the catalyst activity. The deposition of CoPc and CuPc complexes on the supports is more difficult to achieve, compared to that of the metal-free Pc complex.

It was impossible to evaluate the size of the phthalocyanine microcrystallites, attached to the supports by SEM (JEOL model JSM-5300) due to their high degree of dispersion. By ESR spectroscopy (Bruker ER 200D SRC) a qualitative estimation was made in regard to the distribution of anchored non-metallic 29H-, 31H-phthalocyanine complex, CoPc complex and CuPc complex on the surface of Al_2O_3, TiO_2 or WO_3. Typical ESR spectra are represented in Fig. 2. The ESR investigations showed the formation of microcrystals of the phthalocyanine complexes in all the samples. In the case of Pc diamagnetic complex, anchored on supports, the evidence for the formation of microcrystals is the registering of a narrow ESR singlet at $g = 2$ (Fig. 2c and d). The ESR singlet at $g = 2$ is specific for the presence of a

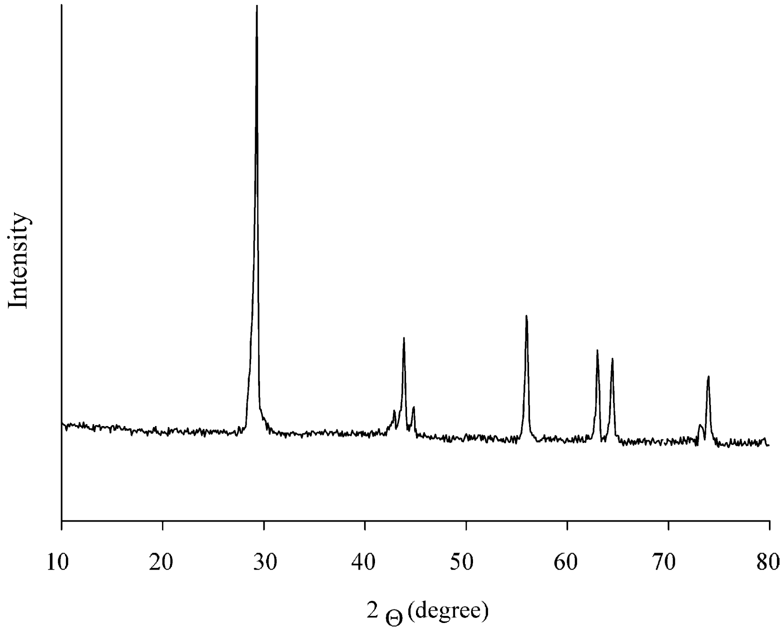

Fig. 1. X-ray powder diffraction pattern of TiO_2.

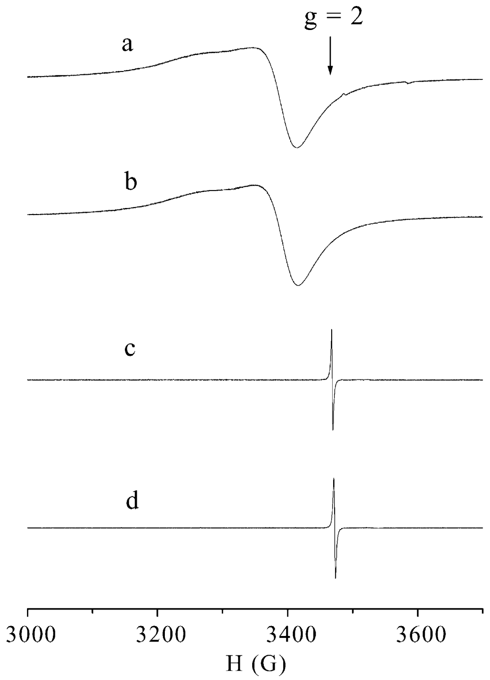

Fig. 2. Typical ESR spectra of phthalocyanine complexes, anchored on supports: (a) CuPc/TiO_2; (b) CuPc/Al_2O_3; (c) Pc/TiO_2; (d) Pc/Al_2O_3.

crystalline phase and it is associated with the presence of defects in the crystal lattice of the phthalocyanine complexes [17–20]. The formation of phthalocyanine microcrystallites on the surface of TiO_2, WO_3 or Al_2O_3 was registered directly in the case of the paramagnetic CuPc complex. The registering only of a broad singlet ESR signal from CuPc complexes (Fig. 2a and b) in which the hyperfine splitting from $^{63,65}Cu$ ($I = 3/2$) and the superhyperfine splitting from ^{14}N ($I = 1$) was missing, is a direct evidence for the exchange dipole–dipole interactions between the paramagnetic molecules in the phthalocyanine crystallites, anchored on the surface of the supports [20–22]. Obtaining such information from the ESR spectra of the paramagnetic CoPc complex is more difficult because of the short spin-lattice relaxation times and the high sensitivity to exchange interactions.

The rates of sodium sulfide and sodium thiosulfate catalytic and photocatalytic oxidation were evaluated on the basis of the consumption of pure oxygen, which was measured using a gas burette. The oxidation process was performed at 293 K, pH $= 9$ and atmospheric pressure in a glass static reactor, upon stirring the catalyst suspension with an electromagnetic stirrer. The irradiation was carried out with a halogen lamp (12 V, 50 W), the illumination being 38 mW/cm^2. The lamp output was filtered to eliminate UV light by using a 400 nm glass filter (Schott). The formation of $Na_2S_2O_3$ after the termination of the catalytic process was registered quantitatively by means of high performance liquid chromatography (HPLC) equipped with a Hewlett-Packard 89500 UV-Vis detector [16]. The amount of sulfate ions formed upon oxidation and photooxidation of Na_2S was determined gravimetrically by precipitation with $BaCl_2$. The accuracy of the analysis was ±7 wt.%.

3. Results and discussion

Recently, it has been established that the oxidation of the sulfide ion in the presence of O_2, catalyzed by cobalt phthalocyanine complexes and semiconductors (MoS_2, CdS and $NiPS_3$), excited by visible light, is proceeding via a series of parallel and consecutive reactions in accordance with the following supposable scheme [15,16] (Fig. 3).

The redox process, occurring in the presence of both types of catalysts, is connected with a transfer of electron from the substrate to the oxygen molecule, coordinated to or adsorbed on the catalysts. As a result of this a radical is formed from the substrate and a superoxide radical in the first step of the redox process. The oxidation of H_2O is energetically unfavorable with all of these catalysts and photocatalysts [23]. The oxidation of Na_2S in the presence of this type of catalysts is not complete. The final products of the sulfide ion oxidation or photooxidation at pH $= 9$, catalyzed by cobalt phthalocyanine complexes or metal chalcogenides of semiconductor type are about 70% thiosulfate and ≈30% sulfate ions [15]. It has been established that no oxidation

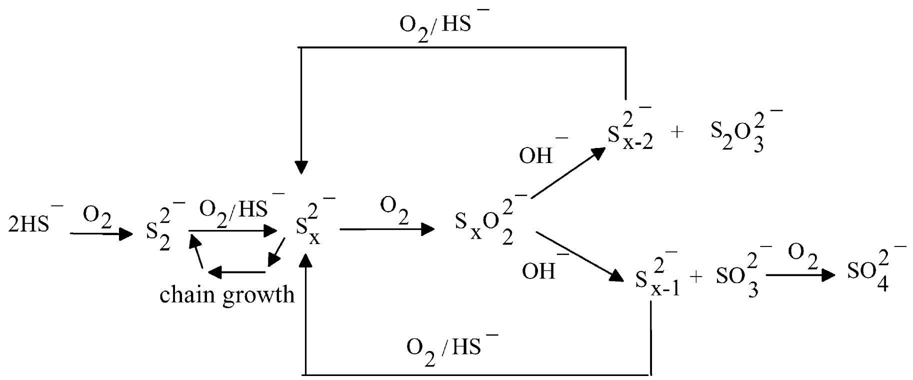

Fig. 3. Reaction scheme of catalytic oxidation of sulfide ion.

Table 1
Catalytic and photocatalytic oxidation of Na_2S (2 mmol) and $Na_2S_2O_3$ (20 mmol) in an aqueous solution. Temperature 298 K, pH = 9.2, O_2 partial pressure = 1 atm

No.	Catalyst[a]	Na_2S		$Na_2S_2O_3$
		µmol O_2 min^{-1}	O_2 consumption[b] (µmol)	µmol O_2 min^{-1}
1	–	0.31	–	0.79
2	CoPc/TiO_2[c]	27.53	2.61	1.86
3	CoPc/WO_3[c]	21.92	2.55	1.51
4	CoPc/Al_2O_3[c]	16.11	2.45	1.25
5	CoPc/TiO_2[d]	13.82	2.0	0.67
6	Pc/TiO_2[c]	13.43	2.65	2.17
7	Pc/TiO_2[d,e]	0.35	–	0.71
8	Pc/TiO_2[f]	10.21	2.55	1.77
9	Pc/WO_3[c]	11.43	2.50	1.92
10	Pc/WO_3[f]	8.79	2.53	1.65
11	CuPc/TiO_2[c]	10.22	2.55	1.72
12	CuPc/WO_3[c]	7.82	2.50	1.58
13	Pc/Al_2O_3[c]	5.32	2.35	1.36
14	Pc/Al_2O_3[f]	4.20	–	1.05
15	CuPc/Al_2O_3[c]	4.11	–	0.97

[a] 11 µmol phthalocyanine complexes.
[b] After 500 min of oxidation.
[c] Upon irradiation.
[d] In the absence of irradiation.
[e] No catalytic oxidation in the presence of: Pc/Al_2O_3; Pc/TiO_2; Pc/WO_3; CuPc/Al_2O_3; CuPc/TiO_2; CuPc/WO_3.
[f] Photocatalytic test in the presence of 1% isopropanol.

and photooxidation of $Na_2S_2O_3$ is occurring in the presence of this type of catalysts [15,24–26].

The results of Na_2S or $Na_2S_2O_3$ catalytic and photocatalytic oxidation in the presence of the investigated samples are represented in Table 1. Standard calculation methods were applied to determine the initial rates of sulfide or thiosulfate conversion. The catalytic and photocatalytic activity of the samples is expressed by the rate (mol O_2 min^{-1}).

Phthalocyanine complexes deposited on the supports, do not display any catalytic activity in the dark in the Na_2S oxidation reaction (Table 1). The only exception are the samples containing cobalt phthalocyanine complexes (CoPc) (Fig. 4). The catalytic activity of the CoPc complexes in the oxidation of thiols and hydrosulfides by dioxygen and the mechanism of the redox processes have been extensively studied [14,15,18,25,27–29]. Due to the high activity and chemical stability these complexes have found wide application in the catalytic oxidation of mercaptans in oil fractions [30]. The catalytic oxidation of Na_2S (2 mmol) in the presence of the studied CoPc complexes, deposited on supports, is not complete (Table 1). $Na_2S_2O_3$ is the main final product of the substrate conversion. This fact is confirmed by the analysis of the converted mixture by means of HPLC equipped with an UV-Vis detector [16]. The total O_2 consumption after the termination of the catalytic process is ≈2 mmol (Fig. 4c), which is in accordance with the stoichiometry of Eq. (1):

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (1)$$

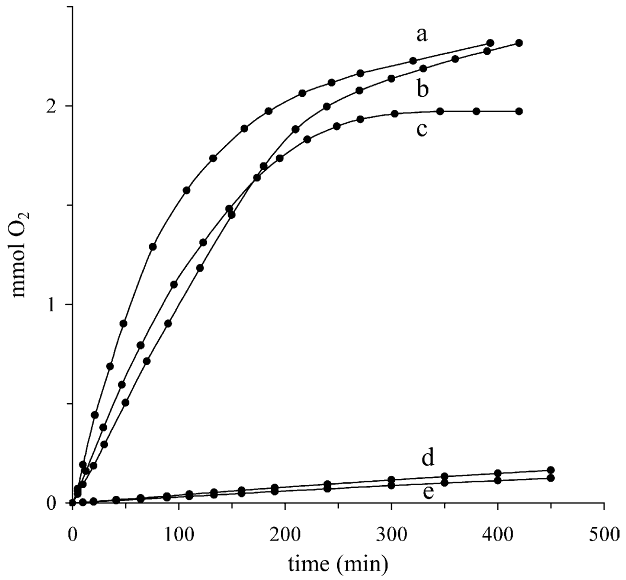

Fig. 4. Oxidation of Na_2S (2 mmol) in the presence of: (a) 11 µmol CoPc/TiO_2, upon irradiation; (b) 11 µmol Pc/TiO_2, upon irradiation; (c) 11 µmol CoPc/TiO_2, without irradiation; (d) 11 µmol Pc/TiO_2, without irradiation; (e) in the absence of catalysts.

Upon irradiation with visible light (λ ≥ 450 nm) the catalytic activities of all the catalysts grows up substantially (Table 1). Fig. 5 represents the results of the Na_2S photooxidation catalyzed by some of the studied samples. The rates of hydrosulfide ion oxidation in the presence of the phthalocyanine complexes, anchored on TiO_2 or WO_3 are higher than those of the samples, prepared by anchoring of

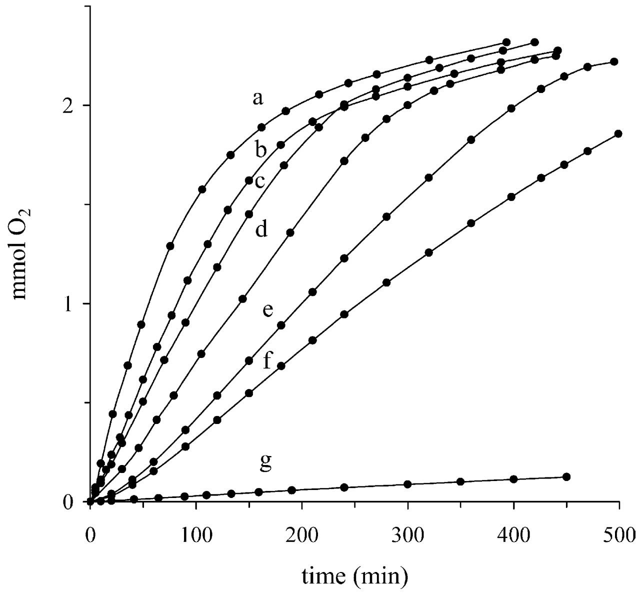

Fig. 5. Photooxidation of Na_2S (2 mmol) in the presence of: (a) 11 µmol CoPc/TiO_2; (b) 11 µmol CoPc/Al_2O_3; (c) 11 µmol Pc/TiO_2; (d) 11 µmol CuPc/TiO_2; (e) 11 µmol Pc/Al_2O_3; (f) 11 µmol CuPc/Al_2O_3; (g) in the absence of catalysts.

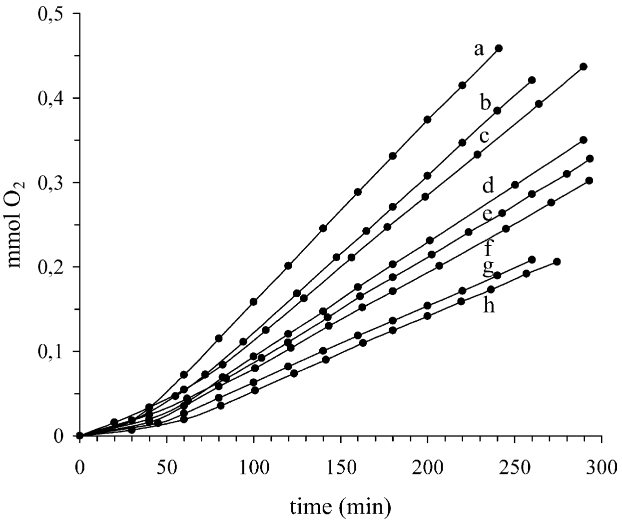

Fig. 6. Oxidation of $Na_2S_2O_3$ (20 mmol) in the presence of: (a) 11 μmol Pc/TiO_2, upon irradiation; (b) 11 μmol CoPc/TiO_2, upon irradiation; (c) 11 μmol CuPc/TiO_2, upon irradiation; (d) 11 μmol Pc/Al_2O_3, upon irradiation; (e) 11 μmol CoPc/Al_2O_3, upon irradiation; (f) 11 μmol CuPc/Al_2O_3, upon irradiation; (g) in the absence of catalysts; (h) 11 μmol CoPc/TiO_2, without irradiation.

the phthalocyanine complexes on Al_2O_3 (Table 1). No catalytic oxidation of Na_2S is registered in the presence of TiO_2 or WO_3 upon illumination with light of $\lambda \geq 450$ nm. This is explicable in view of the band gap energy of these photocatalysts (TiO_2, $E_G = 3.2$ eV; WO_3, $E_G = 2.8$ eV) of the semiconductor type.

The complete oxidation of Na_2S to sulfates occurs upon irradiation with visible light in the presence of all the studied catalysts (Table 1) following the general equation:

$$HS^- + 2O_2 + OH^- \rightarrow [S_2O_3{}^{2-}] \rightarrow SO_4{}^{2-} + H_2O \qquad (2)$$

This is confirmed by the analysis of the products. The photooxidation of the sulfide ion occurs at a high rate at the beginning of the redox process. The oxidation rate changes by an order of magnitude within the time interval 200–500 min since the start of the photocatalytic oxidation of Na_2S, which is specific for each catalyst sample (Fig. 5). The change in the rate is attributed to accumulation of thiosulfate anions, whose oxidation is more difficult. The analysis of the products by HPLC within the 200–500 min interval (Fig. 5) shows absence of sulfide ions in the converted mixture. Upon increasing the duration of the redox process it was established by HPLC and gravimetric methods that the ratio sulfate–thiosulfate grows up. The complete conversion of Na_2S into sulfates has not been investigated due to the prolonged duration of the studied redox processes.

The photooxidation of $Na_2S_2O_3$ has been studied aiming at a more detailed investigation of the catalytic properties of the studied catalysts in the course of converting the sulfide ion to sulfate. The thiosulfate anion (Eq. (2)) is an intermediate product in the process of complete oxidation of Na_2S. Fig. 6 represents the typical curves of O_2 consumption (mmol) during photooxidation of $Na_2S_2O_3$. Neither of the studied samples catalyzes the oxidation of $Na_2S_2O_3$ in the dark. No catalytic oxidation of $Na_2S_2O_3$ occurs in the presence of cobalt phthalocyanine complexes, deposited on supports, as it was shown by our previous studies [25]. Upon irradiating all the samples with visible light they catalyze the $Na_2S_2O_3$ oxidation to sulfate (Table 1) according to the following equation:

$$S_2O_3{}^{2-} + 3O_2 + H_2O \rightarrow 2SO_4{}^{2-} + 2OH^- \qquad (3)$$

The proceeding of photocatalytic oxidation of $Na_2S_2O_3$ after Eq. (3) is evidenced by the decrease of the thiosulfate ion concentration with the time, registered by HPLC and accumulation of sulfate ions, determined gravimetrically as $BaSO_4$.

The increase of the catalytic activity of the phthalocyanine complex, anchored on supports, upon irradiation with visible light is associated with the semiconductor properties in the solid state of these organic systems. The phthalocyanines in the solid state behave as p-type semiconductors, characterized by energy of the band gap about 2 eV [10,31–34]. This enables the excitation of the molecular semiconductor with visible light. Considering the earlier reports on the dye-sensitized photocatalytic oxidation of pollutants [5,12,13,35], the following working mechanism is proposed for the first step of the photocatalytic oxidation of Na_2S upon applying non-semiconductor oxides (MeO) as supports (Eqs. (4)–(10)).

$$\text{MeO–(Pc)}_S \xrightarrow{h\nu} \text{MeO–(Pc}^*)_S \qquad (4)$$

$$\text{MeO–(Pc}^*)_S \rightarrow \text{MeO–(Pc}^+ + e^-_{CB})_S \qquad (5)$$

$$\text{MeO–(Pc}^+ + e^-_{CB})_S + HS^- \rightarrow \text{MeO–(Pc} + e^-_{CB})_S + HS^\bullet \qquad (6)$$

$$\text{MeO–(Pc} + e^-_{CB})_S + O_2 \rightarrow \text{MeO–(Pc)}_S + O_2{}^{\bullet -} \qquad (7)$$

$$2O_2{}^{\bullet -} + 2H_2O \rightarrow 2OH^\bullet + 2OH^- + O_2 \qquad (8)$$

$$HS^- + OH^\bullet \rightarrow HS^\bullet + OH^- \qquad (9)$$

$$2HS^\bullet + 2OH^- \rightarrow {}^-S\text{–}S^- + 2H_2O \qquad (10)$$

In the case of photocatalytic $Na_2S_2O_3$ oxidation, the following working mechanism is proposed for the first step of the photocatalytic process upon applying non-semiconductor oxides (MeO) as supports (Eqs. (11)–(16)).

$$\text{MeO–(Pc)}_S \xrightarrow{h\nu} \text{MeO–(Pc}^*)_S \qquad (11)$$

$$\text{MeO–(Pc}^*)_S \rightarrow \text{MeO–(Pc}^+ + e^-_{CB})_S \qquad (12)$$

$$\text{MeO–(Pc}^+ + e^-_{CB})_S + {}^-S\text{–}S(O_2)\text{–}O^- \rightarrow \text{MeO–(Pc} + e^-_{CB})_S + {}^\bullet S\text{–}S(O_2)\text{–}O^- \qquad (13)$$

$$\mathrm{MeO{-}(Pc + e_{CB}^{-})_S + O_2 \rightarrow MeO{-}(Pc)_S + O_2^{\bullet -}} \quad (14)$$

$$\mathrm{2O_2^{\bullet -} + 2H_2O \rightarrow 2OH^{\bullet} + 2OH^{-} + O_2} \quad (15)$$

$$\mathrm{^{\bullet}S{-}S(O_2){-}O^{-} + OH^{\bullet} \rightarrow S^{-} + SO_4^{2-}} \quad (16)$$

In the case of phthalocyanine complexes, deposited on supports with dielectric properties (Al_2O_3), illumination with visible light ($h\nu$) results in the excitation of the surface-adsorbed phthalocyanine particles (Eqs. (4) and (11)), which effects charge transition into the conduction band in the excited state (Eqs. (5) and (12)). The hydrosulfide or thiosulfate anions serve to reduce the oxidized surface-adsorbed dyes (Eqs. (6) and (13)), while the electron in the conduction band (e_{CB}^{-}) is transferred to molecular oxygen (O_2) leading to the formation of superoxide/hydroxide radicals ($O_2^{\bullet -}/HO^{\bullet}$) in the system (Eqs. (7), (8) and (14), (15)). The formation of $OH^{\bullet}$ radicals has been proved qualitatively by conducting a photocatalytic experiment in the presence of isopropanol 1% (Table 1), which is known as a good $OH^{\bullet}$ quencher [36]. The hydroxyl radicals interact with the hydrosulfide or thiosulfate anions (Eqs. (9) and (16)) and hydrosulfide or thiosulfate radicals are obtained as a result. The first step of the photocatalytic oxidation of the sulfide ion, catalyzed by the molecular semiconductor (Pc), ends with the formation of a stable disulfide (Eq. (10)). In the case of thiosulfate ion the first step of the photocatalytic oxidation most probably ends with formation of equimolar mixture of sulfide and sulfate ions (Eq. (16)). The next steps of the photocatalytic redox process occur through a series of parallel and consecutive reactions (Fig. 3) studied earlier [12,15,16].

The photocatalytic behavior of the phthalocyanine complex supported on TiO_2 or WO_3 can be explained considering the position of the energy levels of each couple molecular semiconductor–oxide semiconductor. At pH 7 the band gap energy of the studied phthalocyanine complexes is about 2 eV [37,38], while those of the oxide semiconductors are TiO_2 ($E_G = 3.2$ eV) and WO_3 ($E_G = 3.6$ eV). The conduction band of the investigated phthalocyanine complexes is estimated to be at least 500–600 mV more cathodic than the conduction bands of TiO_2 or WO_3 while the valence bands of TiO_2 and WO_3 are significantly more positive than the corresponding band of supported phthalocyanine complexes [9,38,39].

Upon irradiation with visible light $\lambda \geq 460$ nm it is possible to excite only the phthalocyanine particles, supported on TiO_2 or WO_3, which effects a charge transition into the conduction band in the excited state inside them. The photoinduced redox process occurs in accordance with Eqs. (6), (7), (13) and (14) involving the participation of adsorbed HS^{-}, $S_2O_3^{2-}$ and O_2 on the surface of the phthalocyanine particles. The quantum yield of the redox process, catalyzed by the molecular semiconductor is not high [9], which is a prerequisite for accomplishing the electron transfer over to the conduction band of TiO_2 or WO_3. The probability of realizing an electron transfer from the conduction band of the excited phthalocyanine particle, to the conduction band of TiO_2 or WO_3 is higher, taking into account the investigations on this process [6,9,10,38]. The intercomponent electron transfer in the couple: molecular semiconductor–oxide semiconductor and the occurring of the catalytic redox process are represented schematically in Fig. 7. As it is shown, the oxygen molecule O_2 may interact with the conduction bands of both molecular and oxide semiconductors (Fig. 7), as a result of which the quantum yield of the photoprocess and the respective formation of superoxide anion radical ($O_2^{\bullet -}$), are increased. Therefore, the promotion of the photocatalytic activity in the system phthalocyanine particles–oxide semiconductor (Table 1) could be explained by the formation of superoxide anion radical ($O_2^{\bullet -}$) on the TiO_2 or WO_3 conduction bands (Fig. 7) and by the additionally occurring redox process in accordance with Eqs. (8)–(10), (15) and (16).

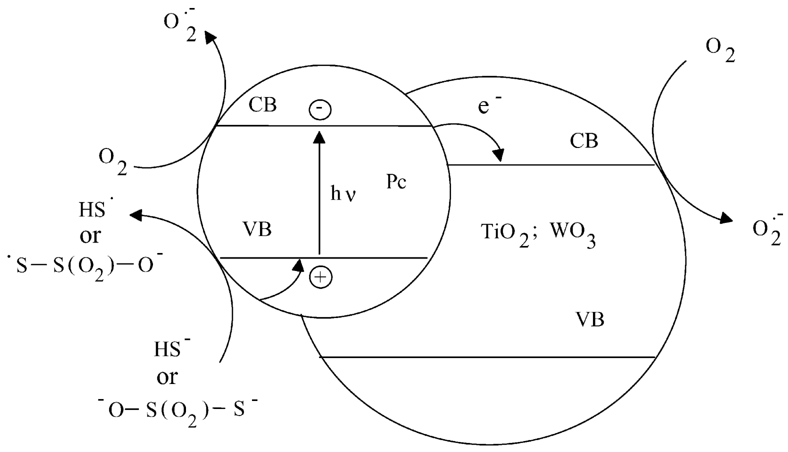

Fig. 7. Schematic diagram representing the intercomponent electron transfer in a phthalocyanine/inorganic semiconductor system.

4. Conclusions

The metal-free phthalocyanine complex, the cobalt phthalocyanine complex and the copper phthalocyanine complex, anchored on TiO_2 or WO_3, are much more effective catalysts for the oxidation of Na_2S and $Na_2S_2O_3$ upon irradiation with visible light compared to the samples obtained by anchoring the same phthalocyanine complexes on Al_2O_3. The high photocatalytic activity of the phthalocyanine complexes, deposited on the supports with semiconductor properties is explained by the realization of an electron transfer from the conduction band of the excited phthalocyanine semiconductor particles to the conduction band of the supports. The increase of the quantum yield of the redox process and the higher degree of oxidation of the substrate in the former case comes as a result of the additional formation of superoxide radicals on the TiO_2 or WO_3 conduction band.

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