ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 1070–1080. © Pleiades Publishing, Ltd., 2008.
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Free Charge Carrier Repartition over the Surface of Photosensitive Materials: Why and How to Manage?

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Received August 22, 2007

Abstract—The free charge carrier repartition over the surface of the photosensitive solids can be efficiently managed by selective elimination of the "parasite" free charge carriers (FCCs) from the exited body. This makes it possible to "correct" the natural FCC repartition law represented by the well-known fifty-fifty ratio (1 generated electron in conduction band versus 1 hole formed in valence band) and to better protect the FCCs against recombination. The chemical design principles of the FCC selective photo-generators (FCCP-Ss) were formulated. The functioning mechanism of the hole selective nanocomposite photo-generators (Sh^+-FCCPs) was examined. This type of active materials generating mainly the most powerful oxidation agents (OH^0 radicals) is suitable for application in oxidation photocatalysis, microbiological object sterilization, and self-cleaning surface development.

DOI: 10.1134/S107036320805040X

INTRODUCTION

The first demonstration of the generation of free charge carriers (FCCs), electrons and "holes," as mobile electron vacancies under semiconductor surface activation with electromagnetic radiation in the near ultraviolet and at the high end of the visible frequency range of the optical spectrum dates back to the late 1930s [1]. The first publications on the use of photosensitive materials in heterogeneous catalysis in the 1950s generated real interest in this phenomenon and initiated studies into solid photocatalysts [2–5].

It is believed that photocatalytic properties are generally exhibited by some crystalline solids with the energy structure of semiconductors, having forbidden band widths ranging from 2.5 to 3.5 eV. Examples can be found primarily in oxides, sulfides, and some other compounds of transition metals, TiO_2, ZnO, CdS, $SrTiO_3$, etc., both in the chemically pure form and with promoters (oxides, noble metals) [6].

In determining whether a photosensitive material is suitable as heterogeneous photocatalys, due consideration should be given to the specific features of its band structure, which makes crystalline solids inherently relevant to the subject of interest. It is commonly recognized that the band structure of a high-performance photocatalyst, on the one hand, should provide transition of valence band electrons to an excited ("free") state under exposure to photons with energies corresponding to $\lambda = 350$ nm and, on the other, prevent instantaneous recombination of free charge carriers, i.e., serve as a kind of a barrier separating oppositely charged FCCs. An average lifetime of FCCs in modern crystalline photosensitive materials with the optimal band structure parameters is $(30–100) \times 10^{-12}$ and $(10–250) \times 10^{-9}$ s for free electrons and electron holes, respectively [7, 8]. In this study, we will deliberately omit the nature of the "hole memory" in discussion. This phenomenon is manifested in the clear inconsistency between the lifetimes τ of free electrons e^-_{CB} and electron holes h^+_{VB} in electromagnetically excited photosensitive materials ($\tau_{h+} >> \tau_{e-}$). Hereinafter, e^-_{CB} and h^+_{VB} symbolize a free electron in the conduction band and an electron vacancy in the valence band, respectively.

In electromagnetically excited solids, a photon transmits to an electron the energy sufficient for its overcoming the forbidden band barrier and passing from the valence to the conduction band, with an electron vacancy, or a “hole,” remaining in the valence band. Thus, an FCC pair is generated, which strictly obeys the $1e^-_{\mathrm{CB}}$–$1h^+_{\mathrm{VB}}$ repartition law and is preserved till recombination or entering of one or both its components into interaction with foreign agents, e.g., oxygen, water, and other molecules adsorbed on the solid surface, occurring as intermediate (activated) complexes.

The very concept of electron hole h^+_{VB} as a “reflection” of a free electron that left the valence band, at the first sight, rules out domination of free carriers of positive, over those of negative, charge, and vice versa, and, theoretically, the fifty:fifty repartition law for FCCs in the bulk and on the surface of an excited photosensitive solid should always be strictly obeyed.

We will forestall further discussion with a note that, in the general case of electromagnetic excitation of an individual photosensitive material not subjected to powerful external physical fields other than the electromagnetic field, the $1e^-_{\mathrm{CB}}$–$1h^+_{\mathrm{VB}}$ law unambiguously predicted by the theory is strictly obeyed in practice. We demonstrated this experimentally for the first time [9], taking as an example a commercial Degussa P-25 photocatalyst, a chemically pure finely divided crystalline titanium dioxide comprised of tentatively 80% anatase and 20% rutile, with the average particle size of about 50 nm [10]. Thus, the physical principle of FCC generation by a solid, which implies the absolutely symmetric charge carrier repartition in an excited body, seems to preclude speculations about possible management of the FCC repartition in photosensitive solids.

At the same time, this seems extremely attractive from the practical viewpoint. The knowledge of how to selectively generate free carriers of positive or negative charge on the surface of an active material would afford much progress in improvement of the basic physicochemical and performance characteristics of this type of materials. We suggest that the latter be broadly termed free charge carrier photo-generators (FCCPs).

First, selective generation of free carriers of either charge would mitigate to a considerable extent the problem of catastrophically fast recombination of oppositely charged FCCs, which would allow, in turn, increasing both the average lifetime of the carriers and their concentration on the solid surface, as well as high performance of FCCPs with larger active phase aggregations. Second, this would allow radically improving the performance characteristics of photosensitive materials: A considerably decreased risk of recombination of free carriers would make selective photo-generators of electron holes (Sh^+_{VB}–FCCP) highly demanded as powerful oxidation agents and sterilization agents for microbiological objects. At the same time, selective photo-generators of free electrons (Se^-_{CB}–FCCP) would be highly attractive for heterogenic catalytic water photolysis applications [11, 12].

In particular, analysis of the prospects of application of photosensitive materials of one of the types considered, Sh^+_{VB}–FCCP, suggests that, according to published data, the electron hole h^+_{VB} and, especially, hydroxy radical HO. formed by the reaction

$$\mathrm{H_2O_{ads}} + h^+_{\mathrm{VB}} \rightarrow \mathrm{H^+} + \mathrm{HO^{\cdot}},$$

belong to the most powerful oxidants (see Table 1). Also, there exist no mechanisms of biological protection against HO. radicals [13], which makes HO. an ideal sterilizing agent. By contrast to the hydroxy radical, the product of transformation of e^-_{CB} on the FCCP surface in the oxygen medium, the $\mathrm{O_2^-}$ superoxide anion formed by the reaction $\mathrm{O_{2ads}} + e^-_{\mathrm{CB}} \rightarrow \mathrm{O_2^-}$ is actively neutralized via the action of protective enzymatic mechanisms initiated by cellular membranes [13, 14].

Thus, in our opinion, the key task to be accomplished in an attempt of managing the FCC repartition over the surface of photosensitive materials should be formulated as follows: To design selective photo-generators of free carriers of positive, or negative, charge to fit the expected application. This poses a question, to which extent this is real for free carriers obeying the natural repartition law, $1e^-_{\mathrm{CB}}$–$1h^+_{\mathrm{VB}}$, taking into account the above-mentioned restrictions. Another question is what principles should underlie the techniques proposed. We attempted answering these questions in this study.

PREPARATION OF TEST SAMPLES OF PHOTOSENSITIVE MATERIALS

We examined six samples of photosensitive materials, of which five were synthesized at the Laboratory of the LGEI (Laboratoire de Génie de

Table 1. Oxidation potentials vs. hydrogen electrode for selected chemical agents

Agent		Oxidation potential, V	Oxidation power against Cl_2
Oxidants	HO•	+2.80	2.1
	h^+_{VB}	+2.70	1.9
	O_3	+2.07	1.5
	H_2O_2	+1.78	1.3
	MnO_4^-	+1.70	1.2
	ClO_2	+1.15	1.1
	Cl_2	+1.40	1.0
	O_2	+1.20	0.9
Reducing agents	O_2^-	–0.33	—
	e^-_{CB}	–0.50	—

l'Environnement Industriel) Center, Ecole Nationale Superieure des Techniques Industrielles et des Mines d'Ales (France). These are composite nano- and microstructures of amorphous and partly crystallized titanium dioxide, chemically bound to the surface of the carriers: silica gel for chromatographic separation with an average pore size of 6 nm and specific surface area of 350 m^2 g^{-1} (available from ACROS Organics) and AA 1.5/3.0 finely porous reactive alumina with the specific surface area of 300 m^2 g^{-1} (available from AXENS). The sixth sample, a commercial Degussa P-25 photocatalyst (available from ACROS Organics), was chosen as the reference.

The samples were synthesized by the molecular layer deposition method [16] (also known as Atomic Layer Deposition (ALD) from English-language publications [17]) whose foundations were laid down in the 1960s at the St. Petersburg Institute of Technology (former Lensovet Leningrad Technological Institute) under supervision of Prof. V.B. Aleskovskii (1912–2006).

A TECHNIQUE FOR ELUCIDATION OF THE FEATURES OF FREE CHARGE CARRIER REPARTITION

As model processes we took the reactions of photoelectrochemical deposition of silver, gold, and lead from aqueous solutions onto the surface of a photosensitive materials:

$$Ag^+ + e^-_{CB} \rightarrow Ag^0, \qquad (1)$$

$$Ag^{3+} + 3e^-_{CB} \rightarrow Ag^0, \qquad (2)$$

$$Pb^{2+} + 2H_2O + 2h^+_{VB} \rightarrow PbO_2 + 4H^+. \qquad (3)$$

The standard electrochemical potentials (SEPs) for these reactions are +0.80, +1.52 and +1.455 V, respectively [18, 19]. Reactions (1) and (2) were chosen for testing the presence and estimating the concentration of free electrons on the FCCP surface, and reaction (3), for revealing electron holes. With two reactions of the same type [reactions (1) and (2)] we intended to obtain more reliable data from examination of the surface redox processes presumably involving free electrons.

As mother solutions of the metal cations served 0.1 M solutions of silver nitrate AgNO3, available from Fluka, and lead acetate $Pb(C_2H_3O_2)_2$, available from Analyticals Carlo Erba, for Ag^+ and Pb^{2+}, respectively, and 0.005 M solution of gold chloride $AuCl_3$ available from Fluka for Au^{3+}.

In the course of the experiment, the sample examined (1 g) was placed into a reservoir containing an excess of the test solution and illuminated with a Philips R-60W incandescence lamp from a distance of 0.2 m for 90 min. The emission spectrum of this lamp is shifted to long waves and, thus, can simulate the conditions of FCCP activation by a low-energy radiation source. The luminous flux intensity on the surface of the sample–solution system reached 32000 lux, with the sample warming up to 45–50°C during the experiment.

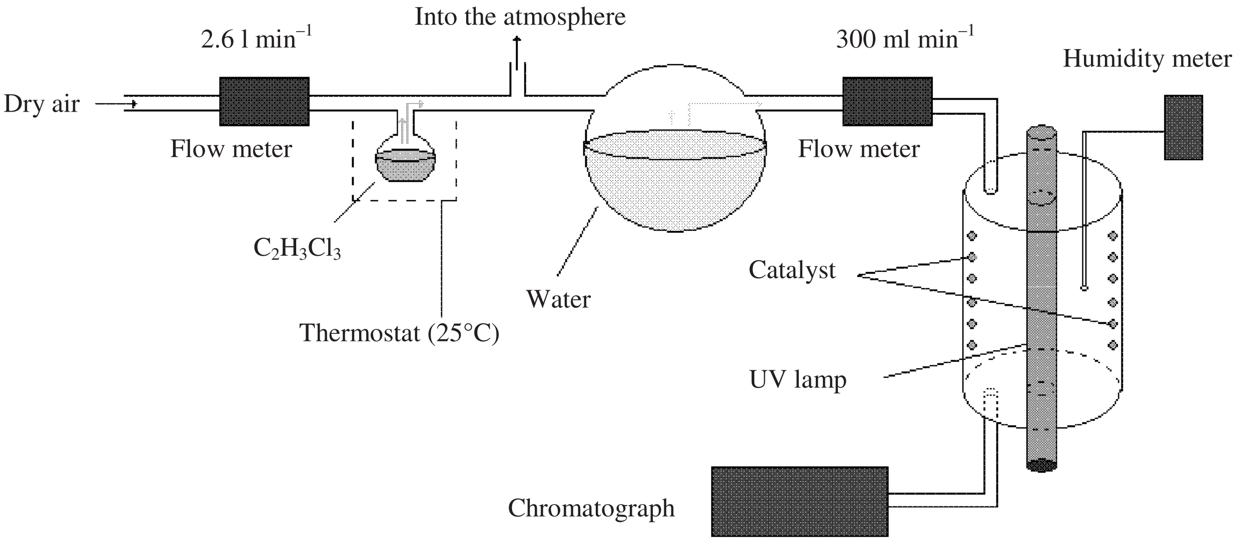


Fig. 1. Schematic of the flow-through laboratory setup for photocatalytic activity examinations.

The material balance for the photoelectrochemical deposition of metals onto the FCCP surface was compiled from the results of the atomic-emission data for the liquid phase (mother solutions) and the solid phase (FCCP samples). The solid phase was analyzed after filtration, washing, drying, and dissolution of the samples in a 65% nitric acid during 1.5 h at 70°C under permanent stirring. A 2000 JY ICP atomic-emission spectrometer served as the analytical instrument.

Upon completion of the photoelectrochemical deposition we examined the morphology and structure of the samples by scanning electron microscopy and energy dispersive X-ray analysis (a Quanta 200 SEM/FEG microscope). The X-ray diffraction patterns of the materials were measured on a BRUKER D8 diffractometer at λ_{Cu} = 1.5405 Å.

A TECHNIQUE FOR SAMPLE ACTIVITY EXAMINATIONS

Examination of the Photocatalytic Activity of the Samples. Figure 1 shows the schematic of the flow-through laboratory setup for examination of the photocatalytic activity of the FCCP samples. Table 2 presents the technical parameters of the trials. As model contaminant of the gas environment served 1,1,1-trichloroethane $C_2H_3Cl_3$. The vapor concentration of this volatile organic substance was measured at the photocatalytic reactor inlet and outlet using a standard gas chromatograph with a flame-ionization detector. In the course of the experiment, the FCCP samples were fixed on a cardboard peace with an adhesive surface layer and placed into a radial reactor

Table 2. Conditions of testing the photocatalytic activity of the FCCP samples

Parameter	Value
Concentration C_0 of $C_2H_3Cl_3$ vapor at the reactor inlet, ppm	35—45
Relative humidity of the gas flow φ, %	0
Gas mixture flow rate G, ml min^{-1}	300
Time of residence of the gas mixture in the reaction zone τ, s	12
Geometric characteristics of the radial reactor, cm	
length	13
diameter	3,5
Mass of the composite samples in the reaction zone M_{sample}, mg	Adapted to $M(TiO_2)$ ≈ const
Mass of the active phase (TiO_2) in the samples examined, mg	60—70

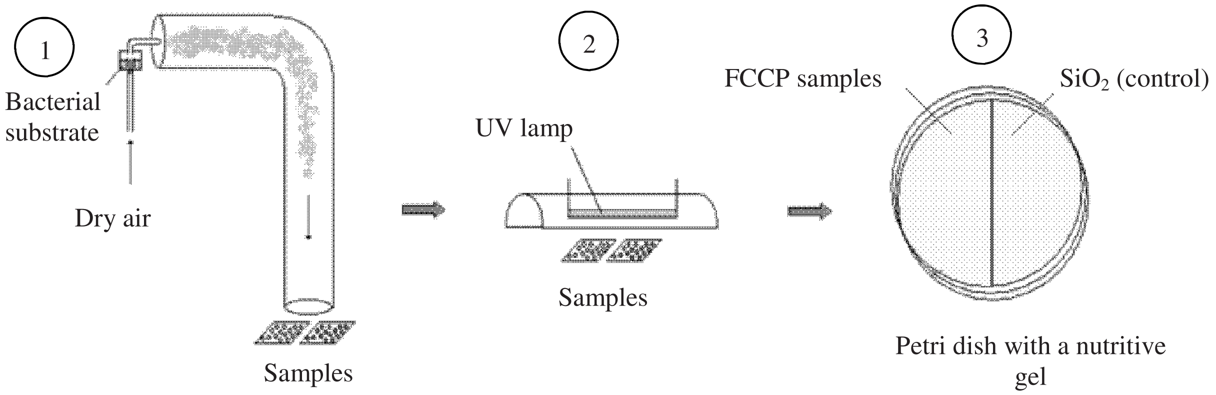


Fig. 2. A laboratory setup for examination of the sterilizing power of the samples.

with an UV radiation source (a lamp with a power of 6 W, λ_{rad} = 365 nm) in the middle.

Examination of the Sterilizing Power of the Samples

Figure 2 shows the schematic of the laboratory setup. As the test culture we used a genetically modified stable biocenosis of *Escherichia Coli Gr+*. After 1-min residence in a bacterial aerosol (Fig. 2, unit 1) the samples were UV-irradiated for 10 min (unit 2). The irradiated FCCP samples and the samples of an inert material (SiO_2), prepared by the same technique, with the *Escherichia Coli Gr+* biocenosis, inoculated onto the surface and also irradiated, were transferred to Petri dishes with a nutritive gel, divided into two, left (test) and right (control), sections (unit 3). The resulting samples were placed into a thermostat at 35.5°C for 20 h so that the viable part of the biocenosis grew under the optimal conditions. The number of the bacterial colonies grown was further determined by direct counting.

Examination of the Surface Self-Cleaning Power of the Samples

In the flow-through photocatalytic reactor, the FCCP samples were treated with an air–toluene vapor mixture till exhaustive deactivation (saturation) of the surface acid (Lewis) sites with the compaction products. The spent samples were further placed onto a laboratory table near the window pane in a way such that direct solar illumination was avoided. The oligomeric organic compaction products on the surface of the acceptor mineral substrates (silica gel, aluminosiliates, etc.), having a Bronsted acid nature [20], were monitored on the FCCP sample surface by pH-metering.

A MODEL OF SELECTIVE PHOTOGENERATOR OF ELECTRON HOLES: A NANOCOMPOSITE MATERIAL WITH A PHOTOSENSITIVE ACTIVE PHASE ON A LEWIS ACID TYPE SUBSTRATE

We showed previously [9, 21–23] that selective free charge carrier photo-generators can be created by exposure to a permanent electric field of an electromagnetically excited photosensitive material. The role of the electric field consists in selective elimination of the desired type of “parasite” FCCs, so as to decrease the intensity of recombination of the carriers in the bulk and on the surface of the solid and to increase the lifetime and the surface concentration of FCCs.

In out opinion, the most promising sources of external electric field are active mineral substrates with prominent electron donating (Lewis base) or, on the contrary, electron accepting (Lewis acid) properties [21]. The reactive “Lewis” carriers favorably compare with other sources of permanent electric field in that only they can offer real prospects for designing objects of any shape and size, since the electric field source occurs inside the object at the photosensitive compound–active carrier interface and needs no external power supply. Moreover, with conventional sources of permanent electric field, generation of the field intensity required for effective separation of FCCs at distances exceeding tens or hundreds of nanometers is an extremely difficult technical task,

Table 3. Intensity and selectivity of photoelectrochemical deposition of Pb^{2+}, Ag^+, and Au^{3+} cations onto the surface of model FCCP sample

Run no.	Sample[a]	TiO_2 content in 1 g sample, mg	Physical mass m_i, mg (numerator) and number of milligram-equivalents of metal or its cation, q_i (denominator), deposited onto 100 mg of TiO_2 in the active phase			Selectivity of the surface of the sample in generation of electron holes, Sh^+_{VB}, %
			Pb^{4+} [c]	Ag^0	Au^0	
1	$1TiO_2$-AA	32	582/5.62	206/1.92	20.3/0.31	74.4
2	$3TiO_2$-AA	54	373/3.60	100/0.94	2.4/0.036	79.2
3	$1TiO_2$-SiO_2	29	617/5.96	176/1.64	31.3/0.48	78.4
4	$3TiO_2$-SiO_2	64	240/2.32	100/0.94 (estimation)	2.5/0.038	71.2
5	Degussa P-25	100	38/0.37	37/0.34	1.5/0.023	52.1
6	Amorphous titanium-silicate ($ATS_{L\&B}$)[b]	105	188/1.81	16/0.15	Not determined	92.3

[a] The TiO_2 formula is prefixed with the number of the molecular layer deposition cycles; [b] The active component in this sample is represented by two morphological types, the layer and spherical (bubbles) aggregates; [c] For Pb in the PbO_2 dioxide.

whose accomplishment entails inputs making the materials examined unsuitable for application.

Below, we present the major experimental findings on the functioning mechanism of the model selective photo-generators of electron holes, specifically, nanocomposite oxide structures (TiO_2) of various degrees of crystallization, chemically grafted to the surface of electron-accepting substrates, silica gel and reactive alumina.

Table 3 summarizes the intensities and selectivities of the photoelectrochemical deposition of metals by reactions (1)–(3) on the surface of FCCP samples with different compositions. The electron hole generation selectivity of the samples was calculated by the expression:

$$Sh^+_{VB} = [q_{Pb^{4+}}/(q_{Pb^{4+}} + q_{Ag})] \times 100\%, \quad (4)$$

where $q_{Pb^{4+}}$ and q_{Ag} are the respective numbers of milligram-equivalents of lead dioxide and silver deposited onto the sample surface, as indicated in the fourth and fifth columns of Table 3, respectively.

The q_i parameter in expression (4) was determined taking into account the equivalence relationships between the physical masses of the deposited metals m_i (in the elemental or cationic form), their atomic masses AM_i, and the valences of their cations n_i in test reactions (1–3): $q_i = (m_i n_i)/AM_i$, where AM_i/n_i ratio corresponds to the mass, mg-equiv, of each of the cations, specifically, 107, 65.7, and 103.5 mg for Ag^+, Au^{3+}, and Pb^{2+}, respectively.

Data in Table 3 fully validate the theoretically predicted generation of free charge carriers in the fifty:fifty ratio by an individual FCCP, not exposed to an external perturbation such as an electric field (sample no. 5). At the same time, the composite FCCPs whose photosensitive components, in our case, are exposed to a powerful electron-accepting carrier exhibit enhanced selectivity of the surface in generation of electron holes: For partly crystallized FCCPs with an aggregate morphology of the active component (sample nos. 1–4), $70\% < Sh^+_{VB} \leq 80\%$ holds. At the same time, for completely amorphous sample no. 6, this parameter exceeds 90%. In the limiting case, Sh^+_{VB} can reach 100%, when the active surface of FCCP is morphologically homogeneous and formed entirely by an amorphous "molecular" layer of the photosensitive component chemically bound to the electron-accepting substrate. In the case when internal energy barriers are virtually lacking, free electrons generated by electromagnetic excitation of the active phase are quantitatively immobilized by Lewis acid sites of the carrier, which control the layered noncrystalline structure of the 2D type but are no more fully able of selective elimination of e^-_{CB} from large surface aggregates, even if the latter are also represented by amorphous formations.

Figure 3 illustrates the presumptions we made; Fig. 4 provides information about the degree of crystallization of a number of the samples examined (according to the X-ray diffraction patterns). The

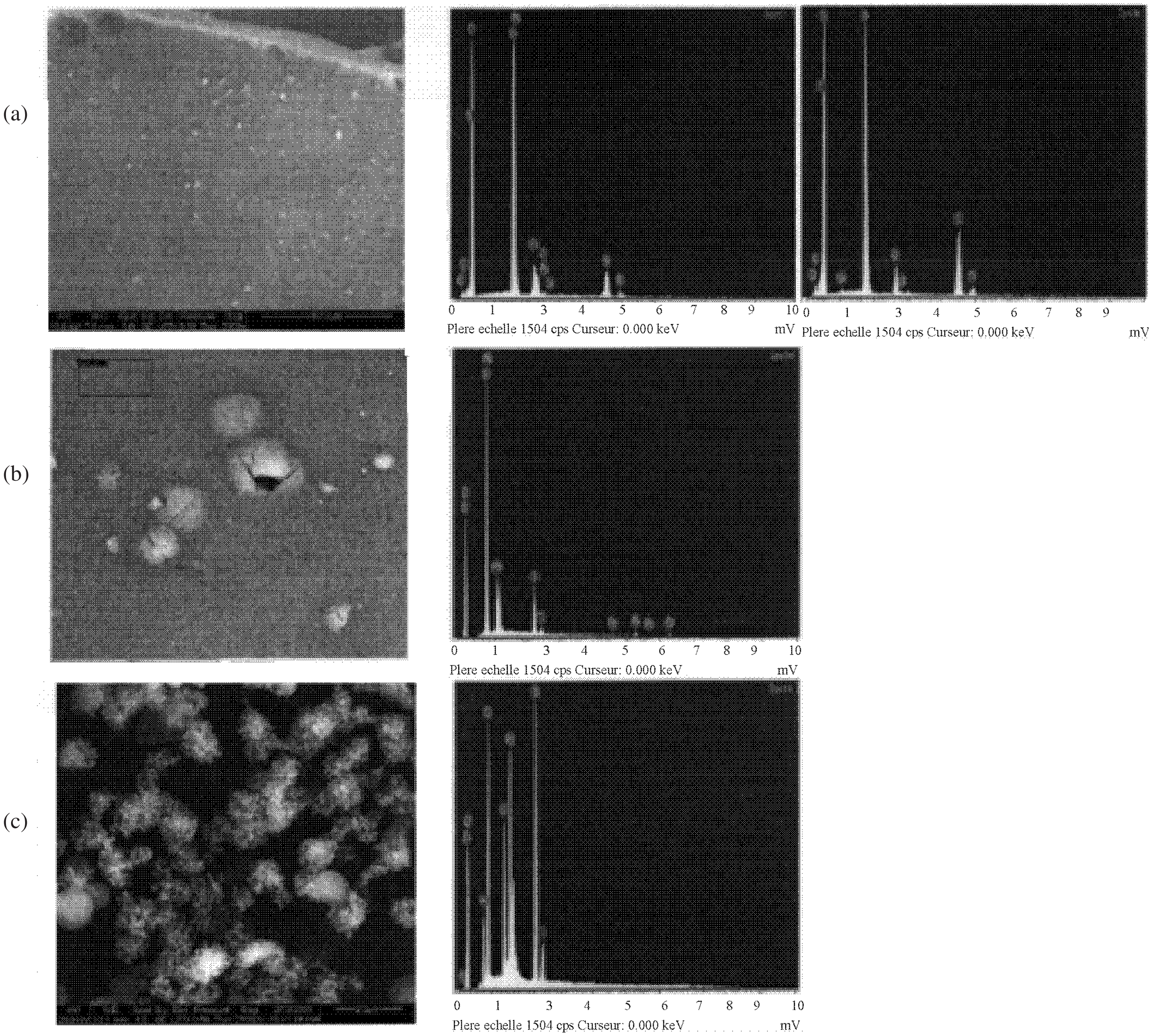


Fig. 3. SEM images and EDX patterns of samples upon completion of the surface photoelectrochemical deposition of lead and silver from solutions: (a) amorphous sample of the ATS_L type with a 2D active component layer (no silver deposition) and (b, c) amorphous sample no. 6 from Table 3 (intensive deposition of lead dioxide, predominantly on the layered structure surface, and weak silver deposition, predominantly on the surface of large aggregates)

noncrystalline 2D layered structures of photosensitive materials on the surface of the carriers with pronounced Lewis acid properties represent an ideal model of a selective photogenerator of electron holes (Sh^+–FCCP). This is supported by the facts that free electrons are virtually lacking on the surface of 2D composite of the ATS_L type (Fig. 3a) and that the active surface is incapable of silver reduction from solution. The e^-_{CB} deficit is accompanied by mass egress of positive charge carriers onto the active surface. As a result, reaction (3) proceeds very actively, with its main product, lead dioxide, deposited predominantly on the surface segment occupied by the photosensitive 2D structure (Fig. 3b).

The specific surface concentrations of electron holes in the partly crystallized and completely amorphous composite FCCPs significantly exceed

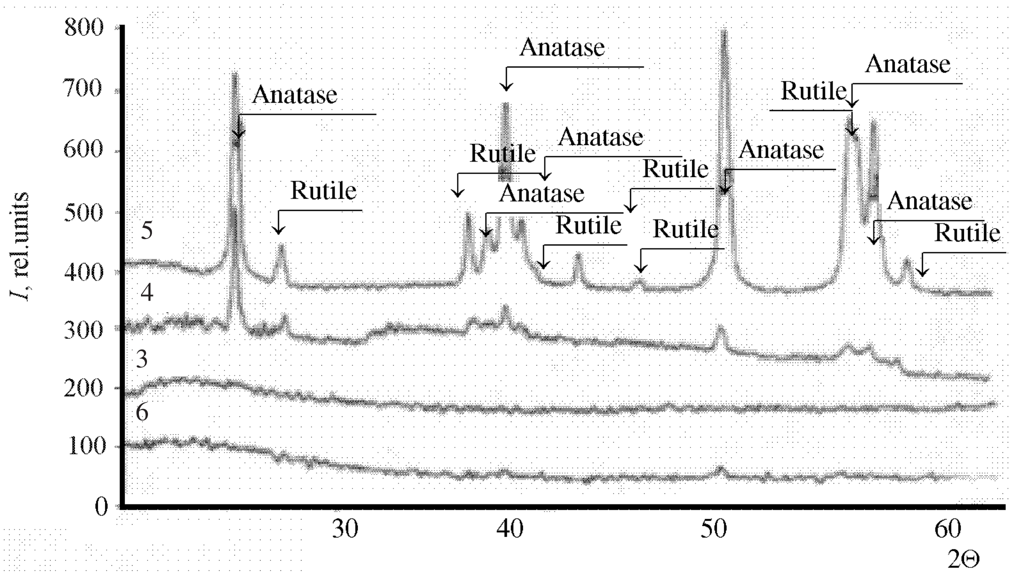


Fig. 4. X-ray diffraction patterns of sample nos. 3–6 (samples are numbered as in Table 3).

those in the noncomposite samples. All other condition being the same, the amount of the photoelectrochemically deposited lead per 100 mg of the active component on the surface of sample no. 6 is approximately 5 times its amount in the sample of crystalline FCCP with an individual chemical composition (sample no. 5). This effect is due to an additional influence of the external electric field promoting separation of oppositely charged carriers (Table 3). The use of an additional tool for FCC separation, a change to composite structures with a crystallized photosensitive active component, allows further increase in the specific surface concentration of h^+_{VB} relative to the noncrystallized FCCPs (sample nos. 1–4 and 6 in Table 3).

Figure 5 shows the activity and selectivity of FCCPs in generation of electron holes in relation to the type of the samples and degree of crystallization of the photosensitive active component. For composite Sh^+–FCCPs, the selectivity of the samples with partly crystallized active phase is generally lower than in the case of completely amorphous composites. The reason is that, with increasing structural organization level and arising in the structure of real energy barriers (forbidden band analogs), the accepting potential of the carrier becomes insufficient for complete immobilization of free electrons of the excited active phase. Nevertheless, as long as the acceptor substrate significantly affects the photosensitive component, free electrons are preserved to a certain extent, specifically owing to a decrease in the FCC recombination intensity under exposure to an electric field of the carrier (Table 3, fifth and sixth columns, sample nos. 1, 3). With weakening influence of the substrate on the active component, the surface concentrations of e^-_{CB} and h^+_{VB} sharply decrease because of an increase in their recombination frequency. This concerns especially the deficient free electrons that are actively attacked by the excess electron holes (Table 3, fourth, fifth, and sixth columns, sample nos. 2, 4). As a result, the surface concentration of e^-_{CB} in the samples of

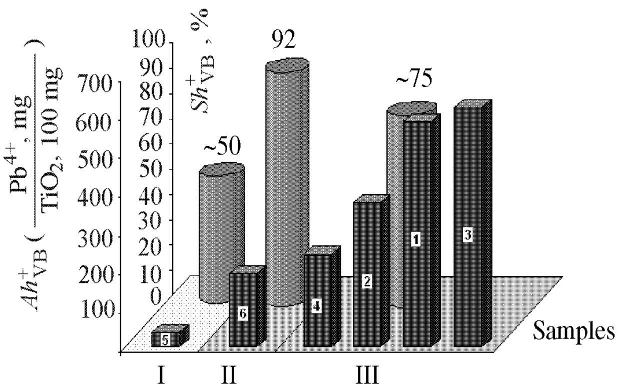


Fig. 5. Activity and selectivity of FCCPs of different types in h^+_{VB} generation: (I) noncomposite crystalline materials; (II) composite amorphous materials with mixed morphology (2D and 3D structures); and (III) partially crystallized composite materials (samples are numbered as in Table 3).

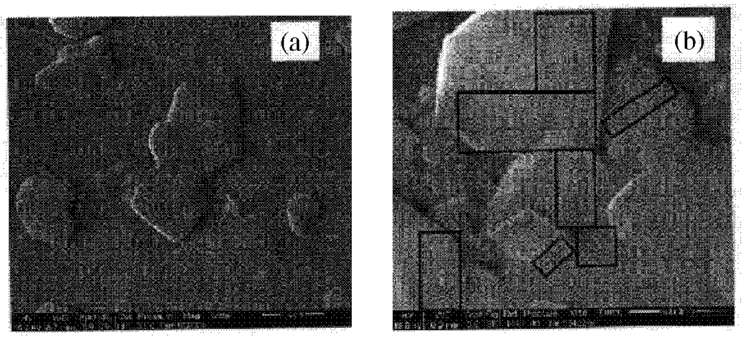


Fig. 6. SEM image of sample no. 3 (a) before and (b) after Au^0 deposition by reaction (2).

composite FCCPs with the "nTiO$_2$–accepting carrier" formulation approach those in "classical" FCCPs (Table 3, sixth column, sample nos. 2, 4, 5).

Figure 6 illustrates the selective contribution of elements from the active surface of the composite Sh^+–FCCPs into photoelectrochemical reduction of metals from solutions. Comparison of the electron images in Figs. 6a and 6b suggests that gold nanoparticles are deposited onto selected faces of the TiO_2 structures at certain sites only, predominantly at the sites of egress of e^-_{CB} onto the surface at the conduction band boundaries coinciding with the crystal sites for the titanium cations. A roughness of the faces of the titanium dioxide aggregates arises at the accumulation sites of the gold nanoparticles with the average diameter of 10–20 nm (the location sites of these zones are shown with rectangles). The faces of egress onto the surface of the valence bands, chemically represented by oxygen anions and, by definition, containing h^+_{VB}, remain chemically inert in this reaction system.

APPLICATION OF Sh^+–FCCPs (OXIDATION PHOTOCATALYSIS, STERILIZATION OF MICROBIOLOGICAL OBJECTS, SELF-CLEANING OF SURFACES)

Figures 7–9 illustrate some possible applications of selective photo-generators of electron holes. Under the experimental conditions, the Sh^+–FCCPs essentially surpass the conventional nonselective photocatalyst in the photocatalytic activity. Also, Sh^+–FCCPs exhibit a very high sterilizing potential and are able of self-cleaning of heavily contaminated surfaces.

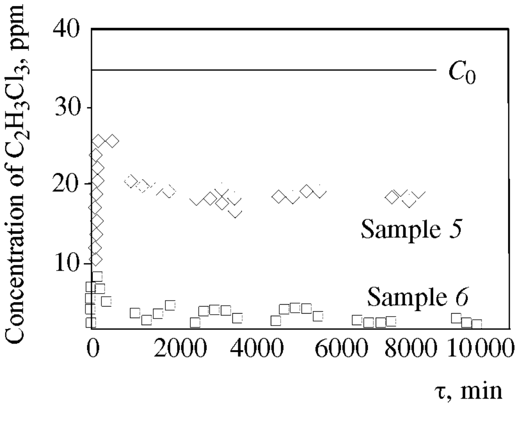
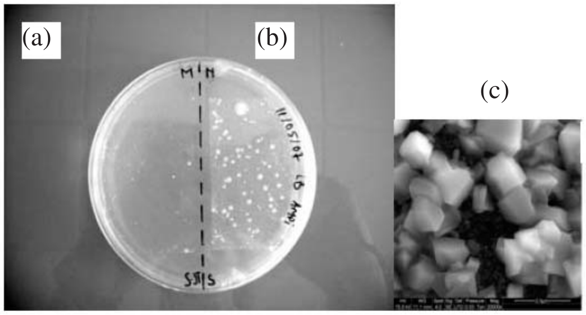
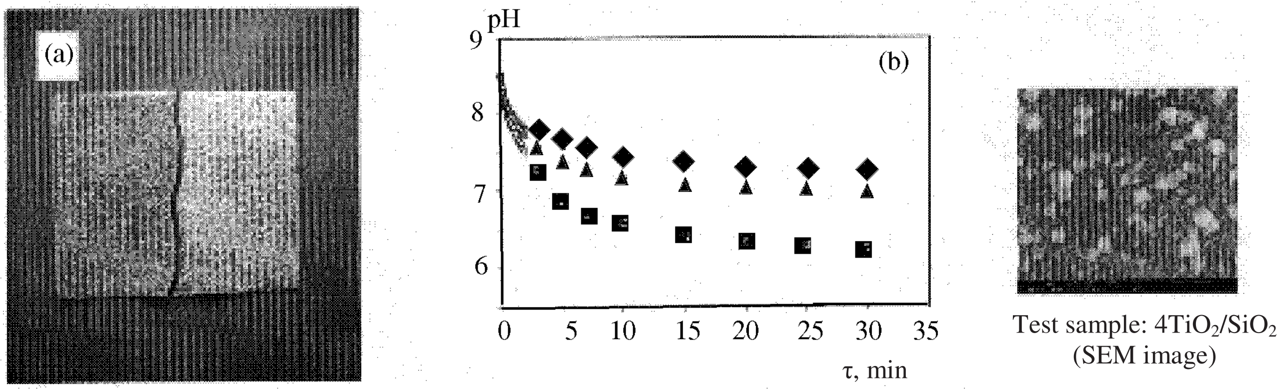


Fig. 7. Trends in variation of the $C_2H_3Cl_3$ vapor concentration at the photoreactor outlet for sample nos. 5 and 6: (C_0) initial concentration; (◊) sample no. 5; and (□) sample no. 6.



2 (sample no. 3) and 77 (control) *e.q.* colonies after incubation

Fig. 8. Sterilization power of sample no. 3 with respect to *Escherichia Coli Gr*$^+$ biocenosis: 97% efficiency; (a) sample no. 3, 2 colonies; (b) control, 77 colonies after incubation; and (c) sample no. 3, SEM image.



Test sample: $4TiO_2/SiO_2$ (SEM image)

Fig. 9. Self-cleaning power of the Sh^+–FCCP sample: (a) surface upon (left) complete deactivation and (right) 83-day illumination with scattered natural light in air and (b) pH measured for the Sh^+–FCCP sample–H_2O_{dist} system: (♦) initial sample, (■) deactivated surface, and (▲) sample after self-cleaning.

CONCLUSION

Designing simple and practically convenient photo-generators of free charge carriers, capable of selective generation of positive or negative charge carriers, will improve the performance characteristics and extend the application field of photosensitive materials. This task can be accomplished by designing nanocomposite materials in which the amorphous or partly crystallized active component is chemically bound to the substrate with prominent Lewis base or acid properties. The role played by the substrate as a powerful source of a permanent electric field consists in deceleration of recombination of FCCs via selective elimination of "parasite" carriers. This, in turn, increases the total surface concentration of the free charge carriers and allows directed variation of the natural $1e^-_{CB}$–$1h^+_{VB}$ ratio for FCC repartition. Selective photo-generators of the "hole" type, in full agreement with the above presumptions concerning the mechanism and features of their functioning, exhibit high performance characteristics as oxidation photocatalysts, as well as materials for sterilization of microbiological objects and self-cleaning surfaces.

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