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Surface nanocrystal hydrogen-bonded complex for photochemical water splitting

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Abstract

Photocatalytic splitting of water in the heterogeneous system consisting of photosensitizer, intermediate electron carrier and catalyst for hydrogen evolution was studied. Molecules and nanocrystals of Mg phthalocyanine were used as photosensitizer; *p*-benzoquinone served as intermediate electron carrier, and finely dispersed platinum as catalyst for hydrogen evolution. With finely dispersed platinum in the system, the quantum efficiency by the hydrogen formation in the presence of molecules and nanocrystals of the MgPc sensitizer increased by an order of magnitude. It was found that the new adsorption centers are formed on the platinum-modified surface of silicon dioxide (SiO_2). Adsorption of sensitizing molecules of Mg phthalocyanine on them increases the lifetime of the excited states of the latter. The luminescence characteristics of the adsorbates of Mg phthalocyanine nanocrystals on SiO_2 were studied.

Keywords: Heterogeneous catalysis; Finely dispersed platinum; Photosensitized water splitting; Magnesium phthalocyanine; Magnesium phthalocyanine nanocrystals

1. Introduction

Hydrogen production by the photocatalytic splitting of water under solar radiation has received attention of many researches [1,2]. In our works [3–5], the water splitting photosensitized to the solar radiation wavelengths has been studied in the heterogeneous system modeling the Photosystem II. This system consists of adsorbates of phthalocyanine (Pc) and *p*-benzoquinone (Q) on the surface of silicon dioxide. Different metal phthalocyanines having high photo- and thermal stability were photosensitizes. For electron transfer served *p*-benzoquinone, intermediate electron acceptor. The molecules of adsorbates and water are hydrogen bonded to hydroxyl cover of the substrate surface and to each other. The water splitting is a multistage process. The water photosplitting in this system has the quantum efficiency of 5×10^{-3}.

To increase the efficiency of water splitting, we introduced finely dispersed platinum into the system. Platinum possesses high catalytic activity in oxidation–reduction reactions owing to existence of the manifold of oxidative states with close energies [6]. Platinum having weakly bound electrons catalyses well all the electron transfer reactions. This is especially true for the case when adsorbed water is present on the platinum surface in the course of the catalysis. H_2O binds to a metal as electron-donating molecule. Therefore, the electron charge transfer from the water molecule to the platinum takes place. As a result, the work function of a metal decreases. Moreover, the VIII-group metals are the best catalysts in hydration and dehydration, because the heats of hydrogen chemisorption on them are minimal [7]. The surface of both finely dispersed and nanocrystalline platinum has d-orbital of various types of symmetry. Therefore, it is reasonable to use platinum as catalyst in multistage processes.

Also, we have attempted to increase the quantum efficiency of the water splitting using phthalocyanine nanocrystals as photosensitizer. As known, conversion of some phthalocyanines from molecular to a crystalline state drastically changes the

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photophysical and photochemical properties. Nanocrystals consisting of non-luminescent molecules start luminesce. For luminescent phthalocyanines, the luminescence spectra of nanocrystals and those of individual molecule were found to differ markedly. In the case of different metal phthalocyanine derivatives having virtually coinciding luminescence spectra, the luminescence spectra of nanocrystals differ very considerably from each other [8]. In the case of our heterogeneous system, it was necessary to study the change in the phthalocyanine spectral properties on going from nanocrystals to adsorbates.

2. Experimental

2.1. Materials and reagents

Phthalocyanine and *p*-benzoquinone (99% purity) were purchased from Merck and used in the study after vacuum recrystallization. Silica gel (SiO_2) grade 62, 150 Å, Pt $(C_5H_7O_2)_2$, acetone were supplied by Aldrich. The SiO_2 surface was purified in successive many-hours heating in oxygen atmosphere and vacuum at 400 °C [9]. Bidistilled water was additionally sublimated in vacuum. Platinum(II) 2,4-pentanedionate, Pt $(C_5H_7O_2)_2$ was used as precursors for preparing platinized silica. The Pt/SiO_2 adsorbent was prepared by the sol–gel method.

2.2. Preparation of the samples

The molecular Mg phthalocyanine was adsorbed by vacuum sublimation. A monomeric MgPc coating was formed by prolonged heating in vacuum at 380 °C [10]. MgPc nanocrystals were prepared, according to the method proposed in [11]. Into a saturated molecular solution of a dye, the second fluid that is mixed with the first but does not dissolve the dye was added. As a result, the dye was salted out to form a colloid solution, in which formation of the dye crystals started. The size of the forming crystals was controlled with a salting out liquid, heating temperature, and crystallization time. In preparing MgPc nanocrystals acetone was solvent, and water, salting out liquid. The dye crystallization was controlled spectroscopically, i.e., by appearance of new absorption bands belonging to the crystalline form of a given dye. The sizes of the nanocrystals obtained were from 20 to 50 nm. The sorbent was kept in a suspension of phthalocyanine nanocrystals and then dried, and MgPc nanocrystals were adsorbed. In order to prepare the Pt/SiO_2 samples 0.01 g of $Pt(C_5H_7O_2)$ was dissolved in 40.0 ml of ethanol and 12 drops of nitric acid to form a gel solution. 2.7 g of SiO_2 was then dipped into the gel solution. Afterwards, the silica was dried at 100 °C for 40 min, followed by calcination at 300 °C for 5 h.

2.3. Vacuum reactor for photosensitized water destruction

The photosensitized water splitting was performed on a grease-free stainless steel vacuum reactor at a pressure of 10^{-6} to 10^{-7} Pa. The scheme of the reactor was described in the previous work [5]. The vacuum was achieved by two vacuum pumps of the magnetodischarge type (NORD). The samples were irradiated by high-pressure 1000 W xenon and 600 W halogen incandescent lamps. The requisite portions of the spectrum were separated out by standard glass filters. A circulating water quartz cell was used to filter infrared waves.

2.4. Analytical methods

The hydrogen evolution was recorded with an IPDO-2A ion-resonance mass-spectrometer.

The luminescence and excitation spectra were determined on a Hitachi-4010 spectrofluorimeter. The kinetic characteristics of the luminescence of magnesium phthalocyanine adsorbates on silica were recorded under the excitation of a second harmonic radiation of a pulsed yttrium–aluminum garnet laser ($\lambda = 532$ nm) [4].

3. Results and discussion

3.1. Luminescence spectra of MgPc photosensitizes

To determine the spectral characteristics of investigated photosensitizes on the SiO_2 surface the luminescence spectra of molecular MgPc and MgPc nanocrystals adsorbates on pure and platinized silica has been studied.

A decrease in intensity of the 672 nm maximum that is associated with the physisorbed MgPc on the platinized surface shows that platinum quenches the photosensitizer excited state (Fig. 1, curve 2).

New bands in the luminescence and excitation spectra (Figs. 1 and 2, respectively) suggest that the new adsorption centers are formed on the surface of silicon dioxide owing to the interaction with the metal. This suggestion is confirmed by the kinetic characteristics (Table 1).

As follows from Table 1, the MgPc adsorbates exist in the form of two radiative centers with different lifetimes, τ_1 and τ_2: $I = A_1\, e(-t/\tau_1) + A_2 e(-t/\tau_2)$. With platinum introduced, the

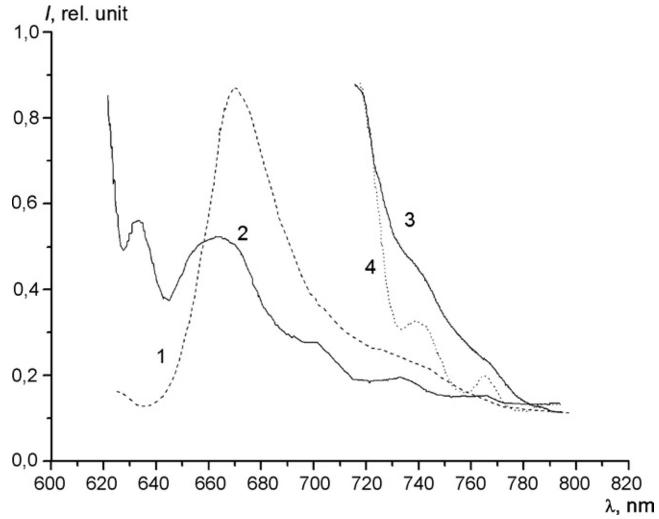

Fig. 1. Luminescence spectra of MgPc adsorbates at surfaces of SiO_2 (1 and 3) and Pt/SiO_2 (2 and 4); $\lambda_{exc} = 600$ nm (1), 590 nm (2), and 690 nm (3 and 4).

Table 1
Kinetic data of luminescence of MgPc adsorbates

Adsorbent	A_1	τ_1 (ns)	A_2	τ_2 (ns)
SiO_2	0.79	1.73	0.21	6.67
$SiO_2 + H_2O$	0.95	2.32	0.05	15.3
Pt/SiO_2	0.93	2.25	0.07	13.44
$Pt/SiO_2 + H_2O$	1.00	7.51	–	–

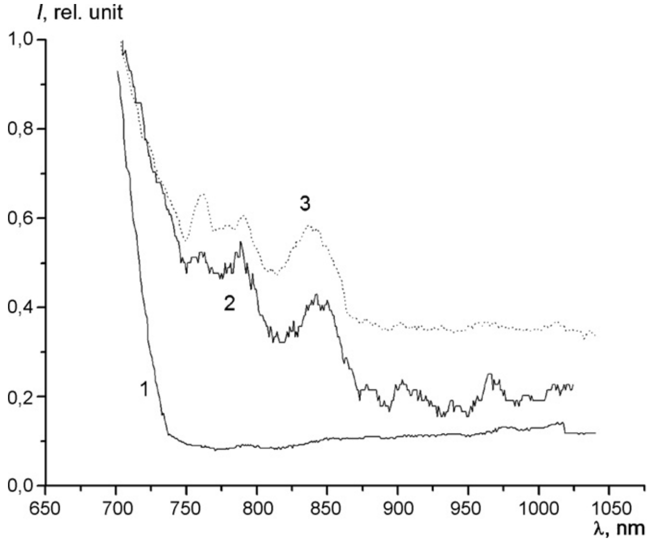

Fig. 3. Luminescence spectra of molecular MgPc (1) and nanocrystals of MgPc (3) adsorbates at surfaces of hydrated SiO_2 and nanocrystals of MgPc (2) adsorbates at surfaces of SiO_2; $\lambda_{exc} = 580$ nm.

excited state lifetimes of these centers do not decrease (as is the case of metal quenching) but, on the contrary, increase. For the non-hydrated samples τ_1 is increased from 1.73 to 2.25 ns and τ_2, from 6.67 to 13.44 ns, and for the hydrated samples τ_1 is increased from 2.32 to 7.51 ns. This shows that the adsorptive properties of these centers are characteristic neither for a surface of platinum nor for a surface of pure SiO_2. As known from the literature, finely dispersed platinum can transform surface centers at the oxide substrate into, for example, specific centers, which are formed on platinized TiO_2 material in the form of the associates of TiO_x groups with the metal particles [12]. The formation of new adsorbate states on the oxide substrates promoted with finely dispersed Pt was also demonstrated in [13,14]. It has been shown that the fluorescence spectra of the molecules adsorbed at different centers of a platinized surface are likely to have slightly shifted maxima and finer vibrational structure. This is in good agreement with our experimental spectra recorded in the presence of the catalyst.

The interaction of MgPc with the new centers formed on the platinized SiO_2 surface results in the activation of the electron-vibrational transitions. This is manifested by the fact that the fluorescence spectrum (Fig. 1) and the spectrum of fluorescence excitation (Fig. 2) have finer resolved structure. Probably, the given fact shows that the strength of the forming centers exceeds that of the adsorption centers on pure SiO_2. The adsorption of a dark $MgPc^{\delta+}\ldots Q^{\delta-}$ charge transfer complex at more powerful centers formed on platinized surface must decrease the energy of its photosplitting to $MgPc^{\bullet+}$ (cation radical) and $Q^{\bullet-}$ (anion radical) in comparison with its adsorption on pure silica. It may be suggested that a decrease in the splitting of H_2O adsorbed on platinized SiO_2 surface in comparison with the case of its adsorption on pure surface is even more considerable.

The luminescence spectrum of the MgPc nanocrystals on SiO_2 has two maxima, at 760 and 787 nm, and broad maximum at 835–840 nm (Fig. 3, curve 2). No shift in the maxima positions was observed in the spectrum of the hydrated sample (Fig. 3, curve 3).

In the spectrum of the platinized sample, the positions of all the maxima are slightly shifted to longer wavelengths (762, 789, and 848 nm, Fig. 4, curve 1). The spectrum of the hydrated sample coated with platinum has maxima at 762, 793–797 and 842–880 nm, i.e., two of them are shifted further to longer wavelengths (Fig. 4, curve 2). As known, the water adsorp-

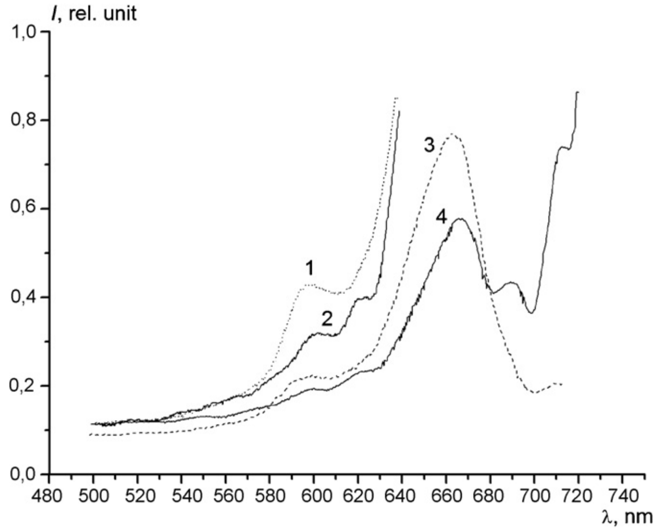

Fig. 2. Excitation spectra of MgPc adsorbates at surfaces of SiO_2 (1 and 3) and Pt/SiO_2 (2 and 4); $\lambda_{rec} = 665$ nm (1 and 2) and 740 nm (3 and 4).

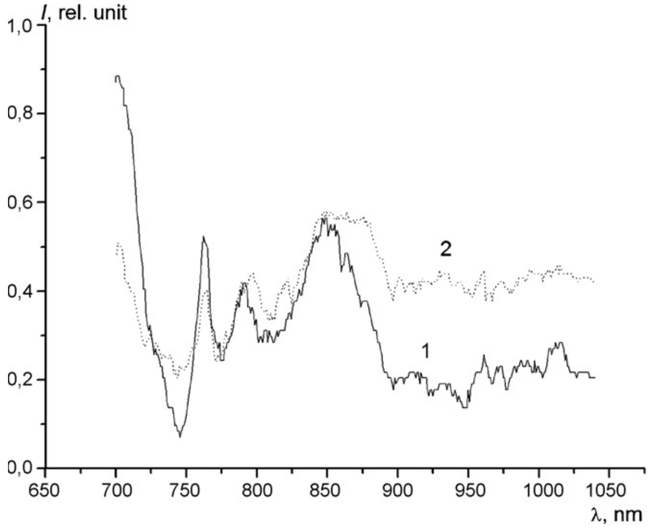

Fig. 4. . Luminescence spectra of nanocrystals of MgPc adsorbates at surfaces of Pt/SiO_2 (1) and hydrated Pt/SiO_2 (2); $\lambda_{exc} = 580$ nm.

tion causes single molecules absorbed on a hydroxyl cover of the SiO_2 surface to approach the state of molecules in a solution. This phenomenon consisting in a 3-nm long-wave shift of the luminescence maximum has been observed previously for magnesium phthalocyanine adsorbates in [4].

On feeding water vapor, the luminescence maxima in the spectrum of the adsorbates of MgPc nanocrystals retain their positions, whereas in the case of platinized surface, two maxima are shifted to longer wavelengths. The maximum at 789 nm is shifted to 795 nm and that at 748 nm is shifted by 5–10 nm and its width is considerably increased.

3.2. Water splitting photosensitized by MgPc nanocrystals

The use of MgPc nanocrystals as sensitizer instead of MgPc molecules increases the efficiency of the water splitting by a factor of 3. In the case of MgPc molecules, molecular hydrogen was liberated at simultaneous irradiation of the system within two spectral regions, 300–400 nm and 600–700 nm. In the system containing MgPc nanocrystals the hydrogen was also recorded at the simultaneous irradiation within two regions, with the second region however broader, 650–830 nm. Presence of two exciting wavelengths implies that water photodestruction occurs in a multistage process.

3.3. Scheme of reactions

Reactions order in the case of molecular MgPc has been established in the previous study [5]. MgPc and *p*-benzoquinone adsorption leads to the formation of the "dark"/$MgPc^{\delta+}\ldots Q^{\delta-}$/charge transfer complex (1). Absorption of a photon with wavelength 600–700 nm by this complex leads to charge separation (2). The anion radical of $Q^{\bullet-}$ interacts with the water molecule with formation of the semiquinone $QH^{\bullet}$ and the hydroxyl ion OH^- (3). At the next stage two $QH^{\bullet}$ molecules give *p*-benzoquinone Q and hydroquinone QH_2 (4) which on absorption of a photon with wavelength 300–400 nm dissociates into $QH^{\bullet}$ and $H^{\bullet}$ (5):

$$MgPc + Q \rightarrow /MgPc^{\delta+}\ldots Q^{\delta-}/ \tag{1}$$

$$/MgPc^{\delta+}\ldots Q^{\delta-}/ \xrightarrow{h\nu_1} MgPc^{\bullet+}\ldots Q^{\bullet-}, \quad \lambda_1 = 600\text{–}700\,\text{nm} \tag{2}$$

$$Q^{\bullet-} + H_2O_{(ad.)} \rightarrow QH^{\bullet} + OH^- \tag{3}$$

$$2QH^{\bullet} \rightarrow Q + QH_2 \tag{4}$$

$$QH_2 \xrightarrow{h\nu_2} QH^{\bullet} + H^{\bullet}, \quad \lambda_2 = 300\text{–}400\,\text{nm} \tag{5}$$

$$2H^{\bullet} \rightarrow H_2\uparrow \tag{6}$$

$$MgPc^{\bullet+} + OH^- \rightarrow MgPc + OH^{\bullet} \tag{7}$$

$$2OH^{\bullet} \rightarrow H_2O_2 \tag{8}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow \tag{9}$$

Photosensitizer returns at the initial state after reaction (7). When MgPc nanocrystals are photosensitizes first active wavelength λ_1 moves to long wave—650–830 nm. This shift correlates with longer wavelength absorbance of MgPc nanocrystals in comparison with absorbance of MgPc molecule.

3.4. Platinum effect

With finely dispersed platinum in the system, the quantum efficiency by the hydrogen formation in the presence of molecules and nanocrystals of the MgPc sensitizer increased by an order of magnitude. Alongside with this, the luminescence spectra of the adsorbed MgPc molecules demonstrate quenching of the excited states of the sensitizer. This means that platinum plays the ambiguous role in the system studied. On the one side, platinum deactivates the excited electronic states of the adsorbed MgPc molecules (metal quenching). The metal quenching of singlet states, associated with the radiationless dipole–dipole energy transfer to the metal, is especially efficient [15]. On the other side, platinum catalyses the transfer of an H atom or electron. The adsorption of water dissociates on platinum may also contribute into the increase in the quantum efficiency of water splitting [16–18].

Let us consider manifestation of the known properties of a platinum catalyst in the described heterogeneous system at single stages of the water splitting (scheme of reactions). Ability of Pt to catalyze liberation of molecular hydrogen must be realized at the stage of its formation [reaction (6)]. Also, platinum is known as promoter of hydrogen peroxide decomposition [3], which proceeds in our system at the stage (9). Platinum may facilitate the H_2 liberation in the course of the disproportionation reaction (4). According to [19], adsorption of semiquinone radical $QH^{\bullet}$ on platinum catalyst involves its dissociation with following formation of bond between fragments and surface. This reaction is reverse. Therefore, presence of a large amount of adsorbed hydrogen atoms on the surface makes complete hydrogenation of quinone Q probable. Participation of Pt also makes it possible to avoid difficulties associated with the spin-forbidden disproportionation of semiquinone radicals $QH^{\bullet}$ in the stage (4).

In hydrogenation of semiquinone anion radical $Q^{\bullet-}$ by adsorbed water, which splits on Pt surface to $H^{\bullet}$ and $OH^{\bullet}$ radicals, platinum catalyst can also produce the same effect [17]. In this case, hydroquinone can be formed directly in the stage (3).

The dependence of the catalytic activity of metallic and plated platinum on the H_2 pressure over the catalyst is known from the literature [18,14]. This dependence was also determined in our experiments. Two regimes of water splitting were realized: accumulation of the separated products over the sample and a continuous pumping with a rate larger than the rate of H_2 formation (dynamic regime). At large concentration of H_2 over the sample (in the accumulation regime) the relative increase in the amount of formed molecular hydrogen was considerably larger than in the dynamic regime. So, in the given case, the catalytic efficiency of the platinized carrier correlates with the pressure of the gaseous products over it. The given results can be accounted for by the effect exerted by Pt on the products of reaction (5) and course of reaction (8). In our experiments, the

SiO_2 surface was completely hydrogenated. Therefore, owing to its mobility, the atomic hydrogen liberating in the course of the reaction (5) can recombine with hydroxyl radicals to yield water molecules. This reaction is reverse. Water molecules formed via recombination in the dynamic regime are pumped and frozen in a trap, which shifts the equilibrium between $H^{\bullet}$ and H_2O to water formation. In the accumulation regime, platinum catalyses conversion of hydrogen atoms into the H_2 molecule, thus impeding recombination of the products of water decomposition into initial molecule.

In addition, hydroxyl radicals entering reaction (8) and hydrogen atoms can recombine with the formation of the initial water molecule. Naturally, the above process decreases the amount of hydroxyl radicals ($OH^{\bullet}$) interacting with each other and may result in the "collapse" of the cyclic process (1)–(9) in the stage (7). In the presence of platinum catalyst, a majority of hydrogen atoms obtained in the system in the accumulation regime enter reaction (6) to yield molecular hydrogen. Therefore, lesser amount of hydrogen atoms participates in the $H^{\bullet} + OH^{\bullet}$ recombination, which ensures recurrence of water splitting.

4. Conclusion

Photocatalytic splitting of water in the heterogeneous system consisting of nanocrystals of Mg phthalocyanine (photosensitizer), *p*-benzoquinone (intermediate electron carrier) was carried out using vacuum reactor.

The use of MgPc nanocrystals as sensitizer instead of MgPc molecules increases the efficiency of the water splitting by a factor of 3.

In the case of MgPc molecules, molecular hydrogen was liberated at simultaneous irradiation of the system within two spectral regions, 300–400 nm and 600–700 nm. In the system containing MgPc nanocrystals the hydrogen was also recorded at the simultaneous irradiation within two regions, with the second region however broader, 650–830 nm.

With finely dispersed platinum in the system, the quantum efficiency by the hydrogen formation in the presence of molecules and nanocrystals of the MgPc sensitizer increased by an order of magnitude.

A new adsorption centers were detected on the platinum-modified surface of silica. Adsorption of the Mg phthalocyanine molecules on them increases the lifetime of the excited states of the adsorbates.

The luminescence spectra of the adsorbates of Mg phthalocyanine nanocrystals on SiO_2 demonstrated negligible changes in comparison with spectra of individual nanocrystals.

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References

[1] Y. Liu, L. Guo, W. Yan, H. Liu, J. Power Sources 159 (2006) 1300–1304.

[2] H. Jeong, T. Kim, D. Kim, K. Kim, Int. J. Hydrogen Energy 31 (2006) 1142–1146.

[3] S.O. Vysotskaya, V.I. Korotkov, Khimicheskaya fizika 9 (2003) 55–58.

[4] S.O. Vysotskaya, V.I. Korotkov, Optics Spectr. 89 (2000) 944–948.

[5] A.V. Barmasov, V.I. Korotkov, V. Ye Kholmogorov, Biofizika 39 (1994) 263–266.

[6] O.V. Krylov, V.F. Kiselev, Adsorption and Catalysis by Transition Metals and its Oxides, Chemistry, Moscow, 1981.

[7] G.G. Bond, Disc. Faraday Soc. 41 (1966) 200–205.

[8] I.Yu. Denisyuk, Sci.D. thesis, S.I. Vavilov State Optical Institute, St. Petersburg, Russia, 2001.

[9] V.I. Korotkov, L.L. Basov, V. Ye Kholmogorov, Dokl. Acad. Nauk USSR 209 (1973) 392–395.

[10] V.L. Rapoport, N.N. Zgadin, Dokl. Acad. Nauk USSR 212 (1973) 1155–1158.

[11] I.A. Akimov, I.Yu. Denisyuk, A.M. Meshkov, Optics Spectr. 77 (1994) 954–958.

[12] D.D. Beck, J.M. White, J. Phys. Chem 88 (1984) 2764–2771.

[13] F. Boccuzzi, A. Chiorino, E. Guglielminotti, Surf. Sci. 368 (1996) 264–269.

[14] G. Shahid, N. Sheppard, J. Chem. Soc. Faraday Trans. 90 (1994) 513–516.

[15] V.M. Agranovich, M.D. Galanin, Transfer of Electronic Excitation Energy in Condensed Media, Science, Moscow, 1978.

[16] A. Anderson, Surf. Sci. 105 (1981) 159–165.

[17] G. Gilarowski, W. Erley, H. Ibach, Surf. Sci. 351 (1996) 156–168.

[18] E. Fridell, A.-P. Elg, A. Rosen, J. Chem. Phys. 102 (1995) 5827–5839.

[19] J. Halpern, Adv. Catal. 11 (1959) 301–309.