Characterisation of Porphyrin–TiO$_2$ Complex Using Raman Spectroscopy and Electron Paramagnetic Resonance

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A complex of *meso*-tetrakis (4-sulphonatophenyl) porphyrin covalently linked to titanium dioxide has been studied. Illumination of the complex with visible light was shown to result in formation of cationic radicals of the porphyrin. Shape and kinetics of the electron spin resonance signals were analysed which permitted calculation of spectroscopic parameters characterising the photoinduced process of the radicals formation. The dye–semiconductor complex was thoroughly characterised to indicate its possible applications.

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1. Introduction

Nanotechnology has permitted production of new hybrid materials, including those consisting of porphyrin derivatives conjugated with metallic or semiconductor nanostructures. Various materials based on nanoscale titania can be used for development of solar cells, as carriers in phototerapeutic treatment, or as efficient agents for wastewater purification due to high yield of active oxygen species generation [1, 2].

A *meso*-tetrakis (4-sulphonatophenyl) porphyrin (TSPP) in complex with a semiconductor was obtained by covalent bonding of anionic porphyrin with nanostructural form of TiO$_2$. In a previous work [3] the radiation and thermal deactivation processes of this complex have been studied and as a result a photosensitization mechanism has been proposed [3]. TiO$_2$ colloidal carriers modifying the thermal energy distribution and considerably influencing the photophysical processes were found to induce changes in the depopulation of the porphyrin excited states, resulting in singlet oxygen generation and/or electron transfer [3]. The presence of charge transfer as a competing channel of the excited states quenching has been suggested responsible for the decrease in the efficiency of the photosensitized formation of singlet molecular oxygen from 80% to 13% of TSPP free and coupled with TiO$_2$, respectively [3]. The excitation of porphyrin by visible light can induce electron transfer to TiO$_2$ conduction band. Further interaction of molecular oxygen with electrons in the conduction band of TiO$_2$ can generate free radicals of O$_2$.

In this work, a TSPP dye and its complex with TiO$_2$ were investigated by the Raman spectroscopy and electron paramagnetic resonance (EPR). These measurements provided information about the interaction between TSPP and TiO$_2$ and radical formation due to photoinduced processes. The kinetics and parameters of EPR signals in the dark and under illumination were analysed.

2. Experimental

The complex of anionic porphyrin coupled with TiO$_2$ and TiO$_2$ nanoparticles were kindly presented by Prof. R.M. Ion. The synthesis of a TSPP–TiO$_2$ complex based on covalent bonding of the dye to the semiconductor nanostructure was described earlier [4]. TSPP were purchased from Sigma–Aldrich. To get reliable information four samples were studied; the complex of TSPP with TiO$_2$, a physical mixture of these components and TiO$_2$ as well as TSPP alone.

The Raman spectra of all samples were recorded at room temperature using a Via Renishaw micro-Raman system. Non-polarised Raman scattering spectra were recorded in the range from 100 cm^{-1} to 3200 cm^{-1} (at the resolution of 1 cm^{-1}), using an objective with magnification of $\times 50$ (long working distance – LWD). As an excitation light we used argon-ion laser operating at 488 nm, of the power of about 10 mW. The signal was recorded with the help of a CCD camera RenCam (Renishaw). The measuring system was controlled by Wire 2.0 Renishaw program.

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EPR measurements were performed with a Radiopan SE/X2540 X-band spectrometer (the microwave frequency used was (9.401 ± 0.001) GHz) with an RCX 660A resonator operating in the TM_{110} mode with an 8 mm optical window and with the optical system facilitating illumination of the sample during the experiment [5]. Powder samples were placed into quartz tubes of 2.4 mm in inner diameter. The EPR signals of all samples were recorded in the dark and under illumination with the white light from a halogen lamp (150 W), at a power level of about 40 mW/cm^2. All measurements were performed at room temperature and at liquid nitrogen temperature (77 K). For liquid nitrogen temperature measurements, each sample was frozen in a Dewar flask (Radiopan KP211) inside the resonator. The EPR signals from the samples not illuminated during the experiment or frozen without illumination were referred to as dark. Some other samples were frozen prior to illumination and their signals were then recorded. The absolute magnitude of g-value was calculated using an NMR gaussmeter for obtaining the static magnetic field strength and the g-value was corrected in relation to DPPH standard.

3. Results and discussion

Figure 1 presents the Raman scattering spectrum of TiO_2 nanoparticles and that of a complex of TiO_2 with TSPP porphyrin. The spectra of TiO_2 and its complex with TSPP porphyrin in the range 250–1000 cm^{-1} are characterized by strong bands and show active modes of B_{1g}, E_g, A_{1g} and B_{2g} symmetry at 143, 448, 609, and 836 cm^{-1} assigned to TiO_2 [6]. The frequencies of the Raman bands assigned to TiO_2 are of the same intensity and at the same positions in the spectra of both TiO_2 and its complex with TSPP, which suggests the lack of possible oscillation changes caused by complex formation. Moreover, the two spectra show the same number of the Raman bands, which means that the symmetry of TiO_2 nanoparticles has not been changed by complex formation. Additionally, for the heterocomplex (TSPP covalently bonded to TiO_2) a luminescence in the spectral range above 1000 cm^{-1} related to the porphyrin presence and the absence of the Raman bands assigned to TSPP is observed. Similarly, it was also observed [7] that the Fourier transform infrared (FTIR) spectrum of pure TSPP sample shows the sulphonato group stretching vibration at 1480 cm^{-1} which is absent in the spectrum of TSPP chemically bonded to TiO_2.

Figure 2 presents the Raman spectra of a physical mixture of TiO_2 with TSPP and of TSPP alone. The spectrum of TSPP shows a characteristic band assigned to the pyrole ring at 992 cm^{-1} (N–H vibrations) and a few bands assigned to the stretching C–C vibrations at 1016, 1231, 1537, and 1553 cm^{-1} [8]. The spectrum of a mixture of TiO_2 with TSPP reveals weak bands assigned to the stretching C–C vibrations in TSPP. Because of a large cross-section for light scattering, the intensity of the bands assigned to TiO_2 is much higher than that of
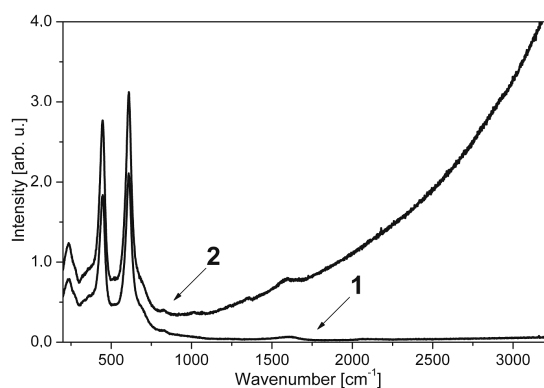

Fig. 1. Raman spectra of TiO_2 (1) and TiO_2–TSPP complex (2).
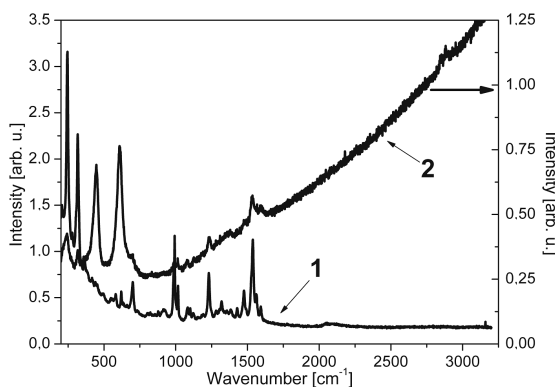

Fig. 2. Raman spectra of TSPP (1) and mixture of TSPP with TiO_2 (2).

the bands assigned to TSPP molecules vibrations. The Raman spectrum of the TiO_2 mixture with TSPP also shows the luminescence background assigned to TSPP which increased above 1000 cm^{-1}.

EPR signals of TSPP in the form of powder recorded at room temperature, testify to the existence of an unpaired spin state (Fig. 3). Upon the sample illumination, the signal intensity increases 2.3 times. Both light-induced and dark signals are symmetrical and reversible, they also have the same spectroscopic parameters (within experimental error), i.e. g-value of about (2.0029 ± 0.0001) and linewidths $\Delta B = (0.51 \pm 0.01)$ mT. After switching off the light, the light-induced signal decays to the level of the dark signal within 2 s. TSPP sample frozen in liquid nitrogen (77 K) in the dark shows no EPR signal within experimental error (not shown), but illumination of the TSPP sample during freezing or its illumination after freezing in the dark, induces at 77 K an EPR signal with the same spectroscopic parameters as those of the signal recorded at room temperature and the signal of TSPP samples is stable in time within 24 h.

Figure 4 presents the EPR signal of TSPP–TiO_2 complex recorded at room temperature. The signal of the complex is observed only under illumination and
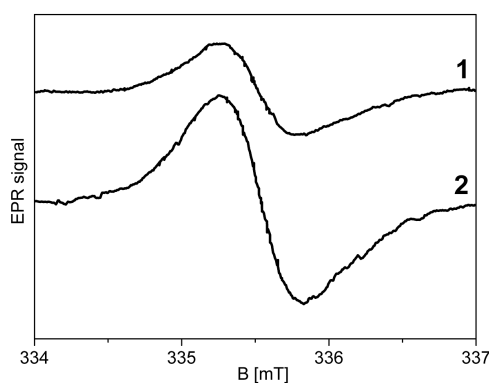
Fig. 3. EPR spectra of TSPP measured at room temperature of the sample in the dark (1) and during illumination (2); modulation amplitude 0.1 mT, microwave power 8 mW, amplification gain 5×10^3, microwave frequency (9.401 ± 0.001) GHz.
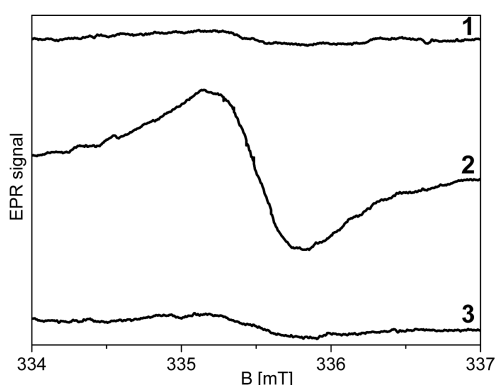

Fig. 4. EPR spectra of TSPP–TiO$_2$ complex measured at room temperature of the sample in the dark (1), during illumination (2) and 60 s after switch off the light (3); the experimental condition as in Fig. 3.

its spectral parameters are similar to those of TSPP alone. Time-dependent investigation shows that the light-induced EPR signals of the complex grow gradually and achieve maximal intensities in about 5 s. After switching off the light the decay to zero of the signal amplitude is observed within 60 s (Fig. 4). At 77 K no dark nor light-induced EPR signals recorded for the complex were observed. The signals of the mixture of TSPP and TiO$_2$ powder behave similarly as those observed for TSPP alone, at both, room temperature and 77 K.

Irrespectively of the system investigated, the parameters of EPR signals are characteristic of the porphyrin cation radicals (electron donor) [9]. Recombination of TSPP cation radical is slower in the complex with TiO$_2$ than in TSPP alone at room temperature. At 77 K, TSPP molecules are immobilized, therefore light-induced TSPP radicals are frozen and stable. TSPP and TiO$_2$ in the complex are covalently linked and photoinduced electron transfer is probably also possible at 77 K, but we did not observe it because of the time resolution

of the EPR spectrometer. Time resolution of EPR spectrometer is *ca.* 0.1 s and it is probably insufficient to record short-lived light-induced radicals produced by porphyrin– semiconductor complex but it is enough to observe the kinetics of decay of the slow radical recombination processes (samples at room temperature, Figs. 3 and 4). On the basis of a decrease in the fluorescence yield describing the radiation processes in 10^{-9} s time range [3] and the EPR results presented of the TSPP–TiO$_2$ complex it is possible to describe the processes taking place in ns to ms time range. If charge transfer occurs, EPR studies reveal the signals attributed to cation and anion radicals. Assuming that electron transfer from porphyrin to TiO$_2$ and further to O$_2$ is possible and only EPR signal of electron donor is observed, it means that probably signals assigned to oxygen radicals could not be observed due to their fast recombination (below the time resolution of the apparatus). For metal carboxyl-phenylporphyrins [10] the formation of oxygen reactive species such as superoxide radical (O$_2^{\cdot-}$) as a result of photosensitization of TiO$_2$ with porphyrin dye was confirmed. The time constant for electron transfer obtained from independent measurements was about 8.2×10^8 s^{-1} for the complex and 0.25×10^8 s^{-1} for TSPP adsorbed on TiO$_2$ [3, 11].

The kinetics describing the increase and decrease in the EPR signals upon switching on/off the light could suggest the participation of unpaired electrons in porphyrin triplet states. Indeed the population of TSPP triplet state is quite high (0.78) and its lifetime of the order μs [3, 12]. The nonradiative relaxation processes studied by time-resolved photothermal method for TSPP–TiO$_2$ complex have not indicated, at least up to 5 μs that the dye triplet states may be sources of EPR signals.

It was reported [13] that the binding state between the dye and the semiconductor surface is a very important factor for the performance of the dye-sensitized solar cell. The dye with a chemical linkage to semiconductor electrodes enhances the solar energy conversion efficiency when compared to that for the weak interaction between TSPP and TiO$_2$ surface (related to an electrostatic attraction force) [13]. The chemical bonding is considered to be an important factor because it directly influences the photoinduced transfer (Fig. 4) and finally the electron injection efficiency. The electron from the dye can be transferred to the semiconductor conduction band through space (in the mixture of compounds) and a conjugated linkage (in the complex), the latter route seems to be preferred to that of the former.

On the basis of *in vitro* studies the photodynamic activity of hybrid porphyrin-TiO$_2$ nanostructure complexes has been shown to be higher than that of the original photosensitizer and the above complexes have been suggested as suitable for photodynamic therapy [14–16]. Our results confirmed that the TiO$_2$ carriers chemically bonded to the photosensitizer modify the electron transfer and as a consequence they also influence the radical formation processes. In the complex studied, porphyrin radicals

are generated only under illumination at room temperature (Fig. 4), which means that switching off light can immediately stop the therapeutic photoreaction. Thus, the photosensitized complex applied in dark will be not toxic toward the cells. Because of the close distance between the dye (covalently bonded) and the semiconductor, the decrease in singlet oxygen generation yield and triplet lifetime of the complex with respect to those of TSPP alone reported in [3], could be correlated mainly with the electron transfer processes and a possible complex phototoxicity mediated by superoxide radical anion as proposed earlier [3].

4. Conclusions

The results have provided evidence on the radicals formation by heterogeneous dye–semiconductor nanosized assemblies and have confirmed the earlier proposed [3] photosensitization mechanism of TSPP–TiO$_2$ complex. The Raman spectroscopy results have suggested the formation of a chemical bonding between TiO$_2$ and TSPP but it is impossible to conclude from their analysis on the type of the bond.

It seems that the hybrid complexes consisting of porphyrin derivatives chemically coupled with semiconductor nanostructures are promising materials to use in quite different applications (photovoltaic and photomedicine) but in both types of applications the charge transfer processes over a short distance (*ca.* length of chemical bond) significantly improve the efficiency of the desired photoinduced processes.

Acknowledgments

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