Singlet oxygen production by a pH-responsive photosensitizer based on porphyrin and hydroxyapatite nanoparticles

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The rapid development of nanotechnology has stimulated the use of nanoparticles in biology and medicine. One of the promising directions in this area is the development of systems for the delivery of photosensitizers into tumor cells. Unlike other inorganic nanoparticles, hydroxyapatite nanoparticles (HAP), as the main inorganic component of bones and teeth, are highly biocompatible and biodegradable materials. In addition, HAP have pH-dependent solubility providing advantages in delivery and release of photosensitizers in tumor tissues. In the present work, we investigated photophysical properties and photosensitized singlet oxygen ($^1O_2$) production by a pH-responsive photosensitizer based on porphyrin and hydroxyapatite nanoparticles. Cationic porphyrin such as 5,10,15,20-tetrakis (4-N-methylpyridyl) porphyrin, TMPyP, was used as photosensitizer. Hydroxyapatite nanoparticles (oval shape) with a particle length <75 nm and a specific volume (29.7- 33.5 ml/g) were synthesized at the Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus.

It was shown that interaction of the porphyrin with HAP in water solution at pH 7.6 leads to a red shift and broadening of the absorption bands of the porphyrin and to a transformation of its fluorescence spectra. It was observed that the pH decreasing less than pH 5.0 causes a reverse shift of the absorption bands of the porphyrin, indicating the destruction of the porphyrin-HAP complexes. The $^1O_2$ luminescence photosensitized by the porphyrin-HAP complexes in the water solutions was investigated. It was found that the efficiency of $^1O_2$ production is decreased up to 10 times upon the complex formation. But the drop of pH to 5.0 leads to increasing in $^1O_2$ luminescence, being slightly below the value for free porphyrin. Such changes in $^1O_2$ luminescence are in good correlation with the transformation of absorption properties of the porphyrin. Therefore, it can be concluded that at low pH value the porphyrin is released from the complex and its photodynamic activity is restored.

This work was supported by the Foundation of Basic Research of the Republic of Belarus (Grant № F22TURTS-008).