

SILVER BASED NANOMATERIALS - FLUORESCENCE ENHANCEMENT IN SILVER DOPED SILICA BASED NANOBIMATERIALS

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Abstract

The sol-gel derived silica spheres with surfaces modified by silver nanoparticles were used to enhance the emission efficiency of PDT photosensitizer Photolon. Two various materials with different Ag concentrations were prepared by exploiting the Tollen's method. The silica nanoparticles were prepared by modified Stöber synthesis. The diameter of obtained silica spheres was ca. 100nm. These silica spheres we used as a carrier for noble nanoparticles, since they can be easily doped by various substances that can change their physical and chemical properties. The colloidal water solutions of Ag-doped SiO₂ particles have been prepared. It was demonstrated that the fluorescence intensity of Photolon is influenced by silver nanoparticles concentration, however it is not proportional to the silver concentration. The fluorescence intensity of Photolon with silver doped silica nanoparticles is much higher than fluorescence intensity of Photolon in water solution. This result is very promising and may be used to enhance the photodynamic effect.

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Introduction

Recently, there is a big interest in nanomaterials and nanobiotechnologies. The preparation procedures and characterization of various nanopowders are extensively discussed. Silica particles may be easily doped by various substances that can change their properties and they may be used in many applications, including optics, catalysis or biotechnology. For instance, nanosized metallic silver or silver-gold has been known to have powerful antibacterial activity [1] but may also allow to enhance singlet oxygen generation, what may be used for sterilization. In this work, the sol-gel derived silica spheres with surface-modified by silver nanoparticles were used to enhance the emission efficiency of Photolon photosensitizer.

Materials

The silica nanoparticles were prepared by modified Stöber synthesis [2]. The silica nanoparticles were prepared

by the successive addition of ethyl alcohol (95%, Polish Chemicals), ammonium water (25%, Polish Chemicals), hydrofluoric acid (35%, Polish Chemicals) and tetraethyl-ortosilane (TEOS from Aldrich) at room temperature. Next, silica nanoparticles sediment was rinsed in methyl alcohol, and after that dried 24 hours in 70°C. Tollen's method for silica silver doped nanospheres production was exploited [3]. Silica spheres were dispersed in water solution and silver ammonia complex $\text{Ag}(\text{NH}_3)_2^+$ [0.4mol] was added. Glucose solution at room temperature was used as the reducing agent. When the so-called first reduction reaction had started, a progression of color changes were observed.

The materials after first reduction reaction were used to second reduction reaction. To the Ag-SiO₂ (after first reduction reaction), the silver nitrate [0.5mol], ammonium water (25%) and solutions of glucose were added. After 24 hours of incubation at 70°C temperature silica spheres with silver nanoparticles were prepared.

The colloidal water solutions of Ag-doped SiO₂ particles with different dispersed phase concentration have been prepared. The concentration of metals in supernatant liquid compound of Ag-SiO₂ was determined by means of Atomic Absorption. Total concentration a silver nanoparticles in supernatant liquid Ag-SiO₂ after I reduction reaction was 5.3 [mg/dm³], and after II reduction reaction was 2.6 [mg/dm³].

The photosensitive agents Photolon (18-carboxy-20-(carboxymethyl)-8-ethenyl-13-ethyl-2,3-dihydro-3, 7, 12, 17 – tetramethyl - 21H, 23H – porphin–2-propionic acid) from Haemato, Poland) was used as dopant. Stock solutions 0.01% of Photolon were prepared by dissolving the photosensitizer in distilled water. 1ml photosensitive dye was added to the fresh prepared silica spheres with Ag-doped nanoparticles. The concentration of metallic silver was changed (TABLE 1). Emission spectra under 404nm laser excitation have been measured and the Metal-Enhanced Fluorescence was observed.

TABLE 1. Samples specification.

I reduction reaction		II reduction reaction	
Sample	Ag [µg/ml]	Sample	Ag [µg/ml]
A	21.2	G	10.4
B	31.8	H	15.6
C	42.4	I	20.8
D	53.0	J	26.0
E	79.5	K	39.0
F	106.0	L	52.0

Results

The absorption spectra of Photolon solutions were obtained by means of Lambda 2 (Perkin Elmer, UK) spectrophotometer. UV-VIS absorption spectra of Photolon with Ag-doped nanospheres are shown on FIG. 1. The Soret band and additional absorption bands in the wavelengths range 500–700nm (Q-bands) were observed. Two prominent absorptions, at 403nm (Soret band) and at 655nm (chlorine-type band), are visible. The others peaks at 536 and at 601nm are observed, as well.

Fluorescence spectra were obtained by means of a fluorescence spectrometer LS-50B (Perkin Elmer/UK). Fluorescence of Photolon (concentration 0.01%) spectra with Ag-doped silica nanoparticles are depicted on FIG. 2.

Analysis of the recorded spectra revealed the fact that the fluorescence intensity strongly depends on the concentration of Ag nanoparticles, however it is not linear.

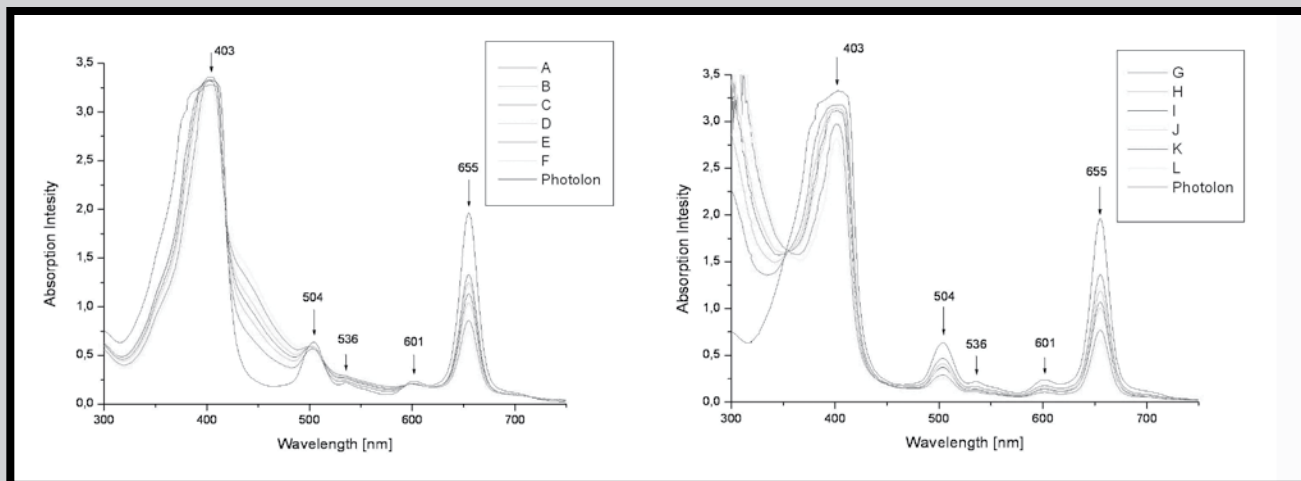


FIG. 1. UV-VIS absorption spectra of Photolon in with of Ag-doped silica nanoparticles. For sample description see TAB. 1.

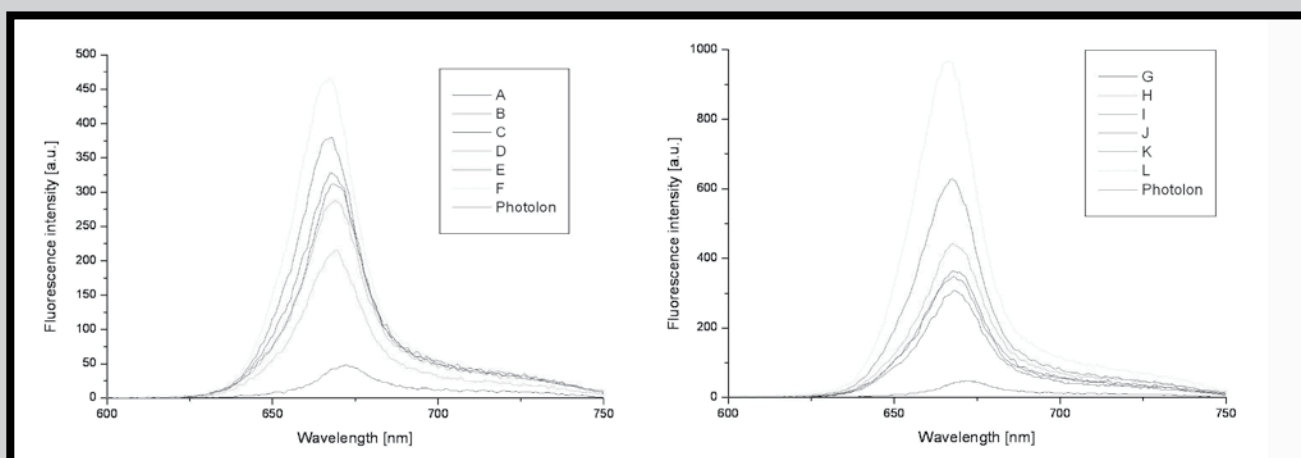


FIG. 2. Emission spectra of Photolon in with of Ag-doped silica nanoparticles.

Conclusions

This work was focused on the measurement of the fluorescence properties of noble metal-doped silica nanoparticles. The emission spectra under 404nm laser excitation have been measured and the metal fluorescence enhancement MEF was observed. The fluorescence intensity of Photolon is influenced by the silver concentration.

MEF is believed to occur due to a coupling of the fluorophore with the plasmon resonance from a metal particle, and the enhancement scale depends on the particle size and shape [4]. The plasmon resonance of a metal particle represents the existence of an electromagnetic field near the metal particle. MEF is caused by increasing the excitation and emission rate of the fluorophore in a localized electromagnetic field [5,6]. When the metal particles are in close proximity to each other, the localized electromagnetic fields from individual particles are expected to overlap and result in a denser overlapped field. Fluorescence is enhanced more efficiently when the fluorophore is localized in such an overlapped field [7,8].

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