FLUORESCENCE PROPERTIES OF SILVER NANOCLUSTERS SYNTHESIZED IN SURFACE-GRAFTED POLYMER TEMPLATE

A.A. Gorbachev, O.N. Tretinnikov
B.I. Stepanov Institute of Physics, NASB, 68 Nezavisimosti Ave., 220072 Minsk, Belarus
a.gorbachev@ifanbel.bas-net.by, o.tretinnikov@ifanbel.bas-net.by

Fluorescent silver nanoclusters were obtained and fixed in a nanolayer of poly(acrylic acid) grafted to the surface of polypropylene films via template-based photochemical synthesis. Fluorescence spectra study shows dependence of fluorescence intensity on the graft density of poly(acrylic acid). Obtained nanoclusters show high sensitivity to Hg^{2+} ions unlike other heavy metal ions, which makes them promising selective mercury sensors. Long-time storage at room conditions study shows that higher graft density provides better protection for clusters (up to 80 days).

Keywords: fluorescence; nanoclusters; silver; template synthesis; surface immobilization; mercury; sensors.

Introduction

Noble-metal (Ag, Au, Cu) nanoparticles smaller than 2 nm in size exhibit fluorescence in the visible and near-IR regions [1]. These particles are usually called "nanoclusters" (NCs) to distinguish them from metal nanoparticles that have larger sizes and do not fluoresce. Metal NCs are synthesized in aqueous solutions of corresponding metal ions and template molecules represented by some synthetic and natural polyelectrolytes [2]. Polyelectrolyte macromolecules immobilize metal ions, restrict the size of growing NCs, and protect them from aggregation and sedimentation. In recent years, thus-obtained aqueous solutions of silver and gold NCs have been the objects of numerous studies as a nontoxic and efficient alternative of fluorescent semiconductor nanocrystals (quantum dots) for biomedical markers, visualizers, and test systems [3].

Immobilization of fluorescent NCs on solid substrates opens new possibilities in the field of materials for chemical and biological sensors, optical information recording, and electroluminescent devices [4]. Recently we have proposed a method of irreversible immobilization of fluorescent silver NCs on a solid substrate by their synthesis in a template polymer, poly(acrylic acid) (PAA) obtained by surface grafting polymerization, as a result of which each polymer chain is chemically bound by one of its ends to the substrate [5]. An important specific feature of surface-grafted polymers is the dependence of their structure and properties on the grafting density. Taking the aforesaid into account, we cannot exclude that the optical properties of NCs synthesized at different PAA grafting densities may be different. The present work is devoted to the study of this question. Also, possible effects of heavy metal ions on the fluorescence of NCs are investigated.

Experimental section

We used acrylic acid (AA) and benzophenone (BP) from Sigma-Aldrich (Germany) with a purity of no less than 95%. The silver nitrate purity was 99.9%. All reagents were used without additional purification. A polypropylene (PP) film that was 40 μm thick was purified by extraction with acetone in a Soxhlet apparatus.

To obtain surface-grafted PAA, a photoinitiator (BP) was first deposited on the surface of the PP film from a 5% solution in acetone; then, the film's surface was coated by a thin layer of 20% AA aqueous solution, covered by a quartz plate, and irradiated for a particular time by UV light with a wavelength of 365 nm and a power density of 70 mW/cm^2 from a homemade source based on light-emitting diodes. Then, the film was washed in distilled water for 5 h with continuous stirring and dried in air. Graft densities (G) were obtained from FTIR spectra [6].

Conversion of PAA into sodium acrylate were held by dipping grafted films into 0,1 M NaOH for 20 min with continuous stirring.

To obtain silver NCs, we fixed the PP film, one side of which was preliminarily modified by surface-grafted PAA, on the bottom of a Petri dish so that the modified surface faced up, poured a silver nitrate solution in deionized water (0.1 mol/L) in the dish, covered the dish with a lid, and then kept the dish in the dark for 20 min and exposed to UV radiation with a wavelength of 365 nm and a power density of 50 mW/cm^2 for 8 min. After this, the film was washed in distilled water for 1 min with continuous shaking, rinsed in a new portion of water, and dried in air.

In the study of the heavy metal ions influence on Ag NCs fluorescence, 0.02 ml solutions of mercury (II) acetate and chromium (III), cadmium (II) and nickel (II) nitrates (C=10^{-5} M) were dripped and dried on the grafted films with Ag NCs.

Fluorescence spectra were measured with a SDL-2 (graft density dependence) and Fluorolog-3 (heavy ion influence study) spectrofluorimeters. The excitation and recording axes were oriented at 90° to each other; the angle between the studied film surface and the recording axis was 30°. Excitation wavelength (λ_{ex}) was 485 nm.

Results and discussion

Fig. 1 shows the fluorescence spectra (λ_{ex}=485 nm) of Ag NCs synthesized on the surface of PAA-grafted PP films with various graft densities by their UV irradiation in an aqueous AgNO3 solution. Spectral data indicates that the fluorescence intensity monotonically increases with increasing grafting density, while the fluorescence band position and shape almost do not change and its maximum lies at 765 ± 15 nm for all films. The increase in the fluorescence intensity with increasing G can be explained by the fact that, by increasing the grafted polymer amount, we increase the number of carboxyl groups, which are the centres of NCs nucleation and growth. As a result, a larger amount of fluorescent NCs is formed in samples with a higher grafting density. Stable position of the fluorescence band can be considered evidence of the independence of the size of synthesized NCs on the PAA grafting density.

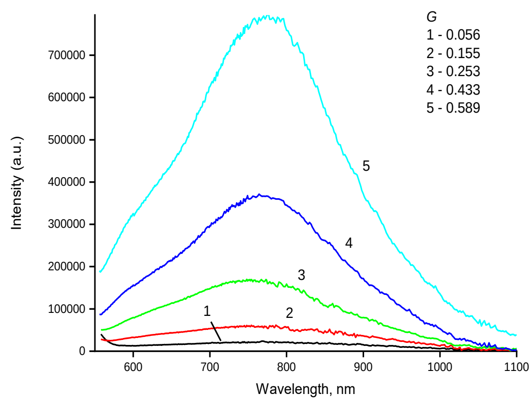

Fig. 1. Fluorescence spectra of Ag NCs synthesized in surface-grafted PAA on PP films with various graft densities (G)

Fig. 2 shows the influence of Cd^{2+}, Ni^{2+}, Cr^{3+} and Hg^{2+} ions on Ag NCs fluorescence. As it is seen from the represented data, application of mercury ions solution with a concentration of 10^{-5} M leads to significant fluorescence quenching, whereas other heavy metal ions with the same concentration have no effect on the fluorescence.

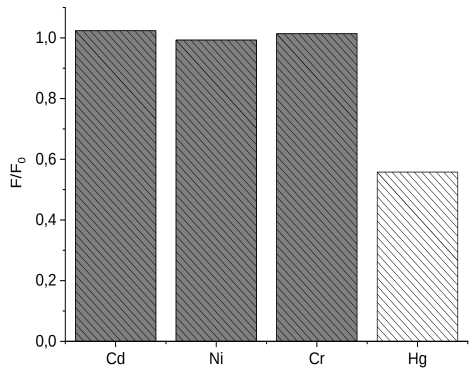

Fig. 2. Effect of different heavy metal ions on the fluorescence emission of Ag NCs. F and F_0 are fluorescence intensities at 750 nm before and after application of 10^{-5} M solutions of the ions

One important factor for practical applications of NCs is stability of their fluorescence properties during long storage. Table 1 presents data on the fluorescence stability of silver NCs synthesized in surface-grafted PAA with intermediate and high graft densities during storage in the dark at room conditions. It is seen that the fluorescence of the sample with an intermediate grafting density decreases more than twofold after 80-day storage, while the intensity of the sample with a high grafting density almost does not change.

Table 1. Fluorescence intensity of silver NCs (I_t) at different storage times (t) normalized to the initial intensity (I_0) for two PAA grafting densities (*G*)

G (a. u.)	*t* (days)		
	2	7	80
	I_t/I_0		
0.38	0.72	0.66	0.38
0.62	0.99	0.98	0.96

Grafted PAA forms dense compact structure due to strong hydrogen bonds between carboxylic groups [7]. NCs, synthesized in PAA appear to be “caged” between polymer chains, which preserve them from degradation, aggregation and oxidation. To prove this assumption, the effect of hydrogen bonds in the grafted template was excluded by synthesis of Ag NCs under the same condition on the films with surface=grafted poly(sodium acrylate). Fig. 3 shows fluorescence spectra of this sample obtained after 1 and 30 day storage under room conditions. After 1 day storage NCs shows bright intensive fluorescence with maximum at 790 nm. After 30 day storage fluorescence vanishes, which indicates NCs degradation.

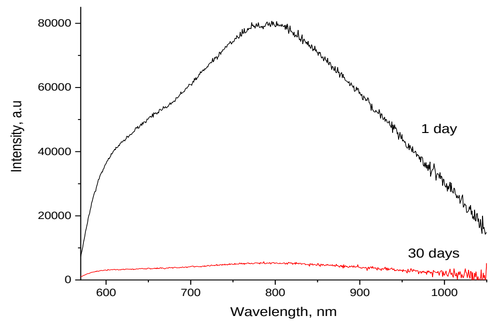

Fig. 1. Fluorescence spectra of Ag NCs synthesized in surface-grafted sodium acrylate on PP films after 1 and 30 days storage

Conclusions

Highly fluorescent Ag NCs irreversibly bound to PAA-grafted plastic substrates have been obtained, and the influence of graft amount on the NCs optical properties were studied. Under identical conditions, a larger number of fluorescent NCs are formed in samples with a higher grafting density. Also high G provides high fluorescence stability up to 80 days. Synthesized Ag NCs show perfect sensibility and selectivity as Hg^{2+} detectors.

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