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Optical properties of aluminum nanostructures modified by polymer coatings

D.E. Kostina [1] ✉, D. Malo [1, 2], A.A. Lizunova [1], E.I. Kameneva [1]

[1] Moscow Institute of Physics and Technology (National Research University),
Dolgoprudny, Russia;
[2] Damascus University, Damascus, Syria
✉ frolova.de@mipt.ru

Abstract. In this research, optical properties of Al films based on Al nanoparticles (Al NPs) with a particle size of 55 nm were studied by analyzing the absorption spectra before and after deposition of polymer coatings. Plasmonic Al nanostructures films were fabricated using spin-coating on quartz substrates, followed by sequential deposition of polymer using poly-L-lysine (PLL) and dextran. The obtained results showed that dextran coating did not induce significant spectral changes, whereas PLL provided a shift in the absorption resonance peak of Al films from 230 nm to 300 nm. Additionally, at an excitation wavelength of 325 nm, the photoluminescence enhancement of ZnO nanocrystals with 27 nm in particle size was investigated in the presence of Al nanostructures with and without PLL film as intermediate film. The results demonstrated that the increase in photoluminescence enhancement factor at an emission wavelength of 377 nm in the presence of PLL film between ZnO and Al films up to 68%. These findings proved that polymer coatings have a significant impact on the optical response of aluminum nanostructures. The obtained results provide a promising methodology for tuning their optical properties and plasmon-enhanced photoluminescence factor for many plasmonic and biosensing applications in the ultraviolet region.

Keywords: aluminum nanoparticles, poly-L-lysine, dextran, zinc oxide nanoparticles, plasmon resonance, plasmon-enhanced photoluminescence, ultraviolet, spin-coating

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Оптические свойства алюминиевых наноструктур, модифицированных полимерными покрытиями

Д.Е. Костина [1] ✉, Д. Мало [1, 2], А.А. Лизунова [1], Е.И. Каменева [1]

[1] Московский физико-технический институт (национальный
исследовательский университет), г. Долгопрудный, Россия;
[2] Дамасский университет, Дамаск, Сирия
✉ frolova.de@mipt.ru

Аннотация. Проведено исследование влияния полимерных покрытий, нанесенных методом спинкоатинга, на оптические свойства алюминиевых наноструктур. Показано, что использование поли-L-лизина (PLL) приводит к сдвигу пика поглощения с 230 до 300 нм, тогда как декстран не вызывает значимых спектральных изменений. Аналогичный эффект смещения пика поглощения наблюдается и в спектрах поглощения для тонкой пленки из платиновой наноструктуры, что подтверждает универсальность метода. Установлено, что внедрение PLL в структуру ZnO/Al для получения ZnO/PLL/Al структуры обеспечивает увеличение интенсивности фотолюминесценции на длине волны 377 нм до 68% по сравнению с двухслойной системой ZnO/Al без полимерной прослойки при длине волны возбуждения 325 нм. Результаты демонстрируют потенциал полимерной модификации для управления оптическим откликом наноструктур в задачах создания ультрафиолетовых биосенсоров и металл-усиленной фотолюминесценции.

Ключевые слова: наночастицы алюминия, поли-L-лизин (PLL), декстран, наночастицы оксида цинка, плазмонный резонанс, плазмон-усиленная фотолюминесценция, ультрафиолет (UV), спин-коатинг

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Introduction

In recent decades, there has been an increasing interest in Al NPs and the methods of their synthesis, as well as film creation and characterization due to their promising properties in the UV region of spectrum especially their role in plasmon-enhanced photoluminescence for several applications in biosensing [1–3]. One of the approaches to altering the optical response of nanostructures is surface modification with polymer coatings [4]. Polymers such as poly-L-lysine (PLL) and dextran can interact with metal nanoparticles differently, affecting their spectral characteristics. PLL, a positively charged polymer, is known to induce electronic and dielectric modifications at the nanoparticle interface, while neutral polymers like dextran primarily act as passive stabilizers. These interactions are crucial for understanding the plasmonic nanomaterials and optimizing their behaviors [5]. For instance, polymeric coatings on thin films of gold nanoparticles (Au NPs) have been shown to induce a redshift in the localized surface plasmon resonance (LSPR) peak due to changes in the surrounding dielectric permittivity [6]. Moreover, the localized surface plasmon resonance of silver nanoparticles (Ag NPs) had shown to red-shift in response to increasing polymer such as PS-b-PBD-b-PS, PS-co-PMMA and PS-b-PI-b-PS layer thickness and refractive index, as both experimental data and numerical simulations revealed a strong dependence of the plasmonic behavior on the dielectric properties of the surrounding polymer matrix [7]. These results confirm that surface polymer modification enables precise control over the plasmonic response of metal nanostructures. In this work, we investigated the influence of PLL and dextran coatings on the optical properties of Al NPs films by analyzing changes in the absorption in the UV region and the plasmon-enhanced photoluminescence of ZnO NPs in the presence of Al NPs, providing insights into potential applications in plasmonic sensing and material design.

Materials and Methods

Poly-L-lysine (PLL) (Sigma-Aldrich, USA; 0.1% w/v in H_2O) and Dextran (Sigma-Aldrich, USA; 1 g/L in deionized water) were used as film-forming polymers. Both polymer solutions were pre-diluted by the ratio of 1:3 (v:v) with 2-propanol for HPLC (Hipersolv Chromanorm, VWR BDH Chemicals, Allemagne). Aluminum NPs colloid of 0.18 g/L (54.6 ± 25.1 nm in particle size, synthesized by an electrical wire explosion method) was prepared in chromatographically pure isopropanol containing citric acid (0.05 g/L) as a stabilizer, following the procedure described in [1]. Zinc oxide NPs colloid of 1.1 g/L with an average particle size of 26.6 ± 7.4 nm was prepared from a dispersion of ZnO particles (Sigma-Aldrich, Switzerland; 40 wt.%) by the steps described in [1]. Suspensions were spin-coated onto quartz substrates (1.2 × 4) cm^2 using a spin coater (EZ4, Schwan technology) with the following coating parameters: 15 μL of suspension, 1000 rpm for 30 s, and acceleration 500 rpm/s (Fig. 1).

The changes of absorption spectra were analyzed for two Al films with different optical densities, resulting in 12 and 27 layers of Al NPs (AlI and AlII), coated with 5 sequential polymer layers, separately.

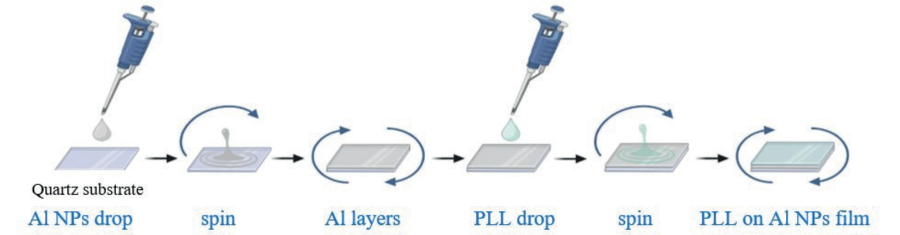

Fig. 1. Spin-coating process for Al NPs with sequential PLL layering

For photoluminescence enhancement investigation, three layers of ZnO NPs were spin-coated and studied in presence of PLL film (5 layers of PLL) and Al NPs film (12 layers of Al). Where seven samples were prepared with various structures: pure film of PLL (PLL), pure film of Al NPs (Al), pure film of ZnO NPs (ZnO), ZnO film applied on PLL film (ZnO/PLL), ZnO film on Al film (ZnO/Al), PLL film on Al film (PLL/Al), and PLL film deposited between ZnO and Al films (ZnO/PLL/Al).

The size and crystal structure of primary NPs were received by transmission electron microscopy (TEM) JEOL JEM 2100 (200 kV). UV-vis-NIR spectra and luminescence emission were obtained using JASCO V-770 and JASCO FP-8300 spectrometers, correspondingly. Surface morphology of the obtained nanostructures films was analyzed by scanning electron microscopy (SEM) JEOL JSM 7001F.

Results and Discussion

TEM analysis showed spherical shape and core-shell structure for Al nanoparticles with metal crystal core and oxide shell (Fig. 2, *a*). The average primary particle size of Al NPs, which formed large agglomerates, was 54.6 ± 25.1 nm including the shell thickness of 3 nm.

According to the obtained spectra of Al NPs films (AlI and AlII) with different initial optical densities before and after coating with PLL layers (Fig. 2, *b*), the absorption peak of Al NPs films, initially observed at approximately 230 nm, shifts towards longer wavelengths after the deposition of PLL layers, reaching approximately 300 nm.

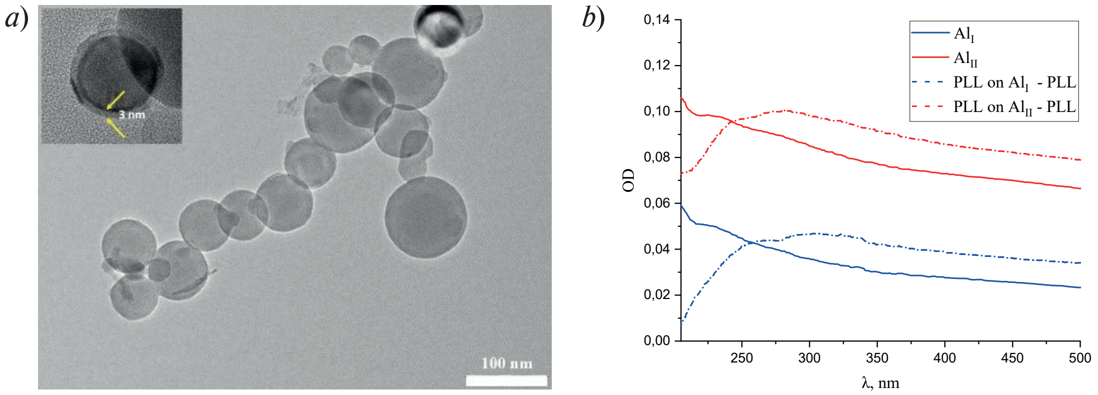

Fig. 2. TEM analysis of aluminum nanoparticles, synthesized by an electrical wire explosion method (*a*); Optical density spectra of Al NPs films before (solid lines) and after PLL modification (dashed lines) (*b*)

In contrast, no significant peak shift was observed when dextran was used as the polymer coating. This shift is attributed to the changes in the local refractive index and potential electronic interactions at the nanoparticle-polymer interface. Another group [8] presented that the absorption peak of oleate-modified iron oxide magnetite nanoparticles shifted from 255 nm to 267 nm after PLL adsorption onto OL-MNPs. This confirms that PLL coating significantly influences the UV plasmonic behavior of different metal nanoparticles that can be utilized for tuning their optical properties in UV region.

SEM images of the surface morphology for various nanostructures films of pure Al, pure ZnO, and ZnO applied on PLL deposited on Al films (ZnO/PLL/Al), presented in (Fig. 3, *a*). The Al film consists of aggregated nanoparticles forming uneven coverage on the substrate. The ZnO film exhibits large, poorly distributed clusters with weak surface adhesion. In contrast, the ZnO/PLL/Al nanostructure demonstrates a more uniform and continuous layer, indicating improved adhesion and surface compatibility using polymer PLL between ZnO and Al films.

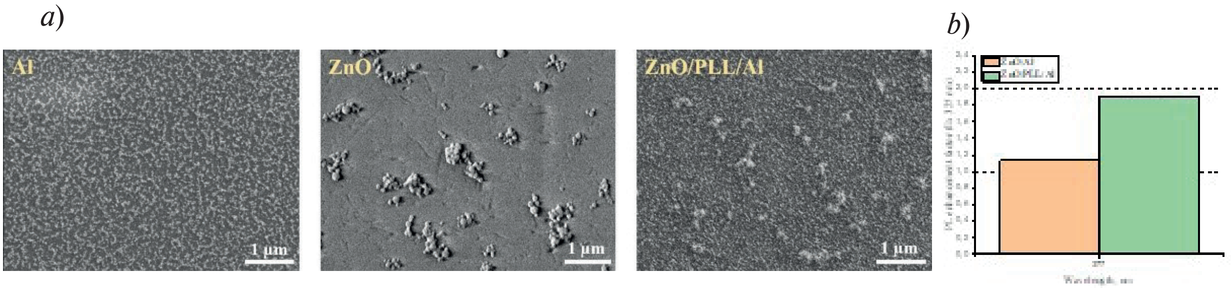

Fig. 3. SEM images of nanostructures films: pure Al, pure ZnO, and ZnO/PLL/Al (*a*); Photoluminescence enhancement factor of ZnO film in the presence of Al nanostructure with and without PLL film between them at an excitation wavelength of 325 nm (*b*)

The optical properties of various structures, including (PLL, Al, ZnO, ZnO/PLL, ZnO/Al, PLL/Al, and ZnO/PLL/Al), were examined to determine the effect of PLL film on PL enhancement of ZnO NPs emission in the presence of Al NPs. As shown in (Fig. 3, *b*), the ZnO film deposited on Al film (ZnO/Al) has provided PL enhancement factor of 1.13-fold at an emission wavelength of 377 nm, whereas applying PLL film between ZnO and Al films (ZnO/PLL/Al) increased the PL enhancement factor up to 1.9-fold. In another study [9], the researchers used PLL coating to achieve yield percentage of Au nanoplates up to 59%.

In summary, the obtained results indicate a positive role of polymer not only to modify the optical behaviors of metal nanoparticles but also to enhance the fluorescence and the electromagnetic interaction between fluorophore and metal nanoparticles to reach higher amplification of PL emission.

Conclusion

The influence of polymer coatings on the optical properties of Al nanostructures films in UV region was investigated. The obtained results showed that while dextran did not induce any noticeable spectral shifts, PLL caused a significant shift in the absorption peak of Al NPs films from 230 nm to 300 nm. Moreover, the ZnO/PLL/Al nanostructure demonstrated PL enhancement amplification up to 68% at an emission wavelength of 377 nm compared to ZnO/Al sample without PLL, at an excitation wavelength of 325 nm. These outcomes confirm the promising potential of polymer-modified aluminum nanostructures for plasmon-enhanced photoluminescence. Thus, polymer modification on plasmonic behavior of Al NPs will be a promising field to tune and achieve new properties of Al nanostructures for many metal-enhanced fluorescence applications and biosensing in the UV region.

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THE AUTHORS

KOSTINA Dina E.
frolova.de@mipt.ru
ORCID: 0009-0000-7489-4391

MALO Dana
malo.d@mipt.ru
ORCID: 0000-0001-6310-9183

LIZUNOVA Anna A.
lizunova.aa@mipt.ru

KAMENEVA Ekaterina I.
katerinakamenev@yandex.ru
ORCID: 0009-0001-7234-8730

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