STUDIA UBB PHYSICA, Vol. 62 (LXII), 1-2, 2017, pp. 23-31
(RECOMMENDED CITATION)
doi:10.24193/subbphys.2017.03

SYNTHESIS AND CHARACTERIZATION OF POLYDOPAMINE-COATED GOLD NANORODS

L.C. ŞUŞU[1], A.M. CRĂCIUN[2] and S. AŞTILEAN[1,2*]

ABSTRACT. Biologically inspired polydopamine (Pd) has served as a universal coating of nanoparticles for various applications in nanobiotechnology research fields. In this study, we report the encapsulation of gold nanorods in Pd through the self-polymerization of dopamine molecules under alkaline conditions. The obtained core/shell nanoparticles were optically and morphologically characterized using UV-vis absorption spectroscopy, transmission electronic microscopy, dynamic light scattering and Zeta Potential measurements.

Keywords: *gold nanorods; polydopamine coating; surface plasmon resonance; transmission electronic microscopy; dynamic light scattering; Zeta Potential*

[1] *Babeş-Bolyai University, Faculty of Physics, Biomolecular Physics Department, 1 M. Kogălniceanu str., 400084 Cluj-Napoca, Romania*

[2] *Babes-Bolyai University, Interdisciplinary Research Institute in Bio-Nano-Sciences, Nano-biophotonics and Laser Microscopy Center, 42 T. Laurian str., 400271, Cluj-Napoca, Romania*

** Corresponding author: simion.astilean@phys.ubbcluj.ro*

INTRODUCTION

In the last decade, nanoscience and biotechnology have shown great potential in developing nanoinstruments for use in biological applications such as biosensing, bioimaging and drug delivery. There has been a great appeal in gold nanoparticles (GNPs) over the last years because of their unique shape and size-dependent optical properties originating from their surface plasmon resonances (SPR), arising from the collective oscillations of free electrons at the nanoparticle surface upon interaction with light. The increasing interest in rod-shaped GNPs, also known as gold nanorods (GNRs), is due to the split of the SPR band into two modes: one longitudinal mode (LSPR), parallel to the long axis of the rod, and one transversal mode, perpendicular to the first. As a result of this split, GNRs can absorb light from the visible to the near-IR region of the electromagnetic spectrum by altering their aspect ratio. The biological tissues are transparent in the near-IR region, enabling the use of GNRs in a wide variety of applications such as biological imaging, drug delivery, therapy of cancerous cells, etc. [1].

A new challenge nowadays in bionanotechnology is the fabrication of nanoscale plasmonic devices with high stability, low cytotoxicity and good biocompatibility to be used in practical applications as in-vivo or in-vitro assays. Because of its ease to use and fascinating properties, polydopamine (Pd) has attracted considerable interest in this matter [2]. Dopamine, a well-known neurotransmitter, can undergo self-polymerization onto many solid surfaces at alkaline pH conditions forming robust adherent Pd films [3,4]. The surface of Pd contains amino and cathecol groups, allowing for further conjugation with bio-molecules [5]. More interestingly, Pd coating has been reported to be very biocompatible and stable for in vitro and biomedical applications [6]. Recently, Pd-coated NP have shown great attraction in biological applications, like bioimaging, biosensing, and photothermal therapy, due to their ease of formation, good stability and special molecular absorption [7]. For example, Ju and co-workers designed a dual-mode nanocomplex for magnetic resonance and Raman imaging based on Pd-capped hollow GNPs

conjugated with bio-molecules [8]. On the other hand, Pd-coated GNRs were demonstrated to be efficient in targeted photothermal therapy of breast and oral cancer cells [9]. More recently, Wang et *al*. synthesized Pd-capped GNRs loaded with methylene blue and doxorubicin, for multifunctional drug delivery and multimodal light-mediated therapy [10].

In this paper, we successfully enveloped GNRs in a Pd shell by using dopamine as precursor and adjusting the pH of GNRs's solution to an appropriate alkaline value to ensure polymerization. The coating of GNRs in Pd was experimentally confirmed by UV-vis absorption spectroscopy, transmission electron microscopy (TEM), dynamic light scattering (DLS) and Zeta Potential measurements.

EXPERIMENTAL DETAILS

Chemicals

Tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$, 99.99%), cetyltrimethyl-ammonium bromide (CTAB), ascorbic acid and dopamine hydrochloride ($(HO)_2C_6H_3CH_2CH_2NH_2 \cdot HCl$, 98%) were purchased from Sigma-Aldrich. Sodium borohydride ($NaBH_4$, 99%), silver nitrate ($AgNO_3$) and sodium nitrate (NaOH) were obtained from Merck. All chemicals were used without further purification. Ultrapure water (resistivity ~ 18.2 MΩ) was used as the solvent throughout the experiments.

Synthesis of CTAB - stabilized GNRs

A seed-mediated approach was used in this study for the synthesis of GNRs with different aspect ratios. First, gold seeds were prepared by mixing 1.25 ml of 0.2 M CTAB with 1.25 ml of 5mM $HAuCl_4$. Next, 0.9ml of freshly prepared ice cold 1 mM NaBH4 solution was added all at once, resulting in a brownish-yellow seed solution [11].

In order to obtain the growth solution, a total of 10ml of 0.2 M CTAB was first gently mixed with 10ml of 1mM $HAuCl_4$ and various amounts of 4mM $AgNO_3$, adjusted in order to tune the aspect ratio of GNRs. Ascorbic acid was then added to the solution as a mild reductant agent (78.8 mM, 0.15 ml) changing the color of the growth solution from dark yellow to colorless, followed by the addition of 0.024 ml of the seed solution. The color of the solution changed in the first 20-30 min until final stabilization.

The obtained probes were centrifuged at 14000 rpm for 10 min to remove the excess CTAB surfactant and the obtained GNRs were resuspended in ultrapure water for further use [12].

Preparation of Pd-coated GNRs

The pH of 1 ml CTAB-stabilized GNRs was altered from 5 to 8.5 through the addition of 100 mM NaOH solution. Next, we added into the solution 0.516 mM dopamine hydrochloride buffered to pH 8 using NaOH. The sample was allowed to react for 30 min and the GNRs suspension was sonicated for 15 min.

Experimental measurements

The extinction spectra were recorded on a Jasco V-670 UV-Vis-NIR spectrophotometer with 1 nm spectral resolution. The morphology of the obtained GNRs was examined using a FEI Tecnai F20 field emission, high resolution TEM (TEM/HRTEM) operating at an accelerating voltage of 200 kV and equipped with Eagle 4k CCD camera. Dynamic light scattering (DLS) and Zeta Potential measurements were performed using a Zetasizer Nano ZS 90 from Malvern Instruments.

RESULTS AND DISCUSSION

Fig. 1 displays the normalized extinction spectra of CTAB – stabilized GNRs with varying aspect ratio obtained in aqueous solution by varying the concentration of silver ions in the growing solution. As shown in the plot, all recorded spectra exhibit two localized surface plasmonic resonances (LSPR) corresponding to the light-induced electron oscillations perpendicular and parallel to the nanorod length direction.

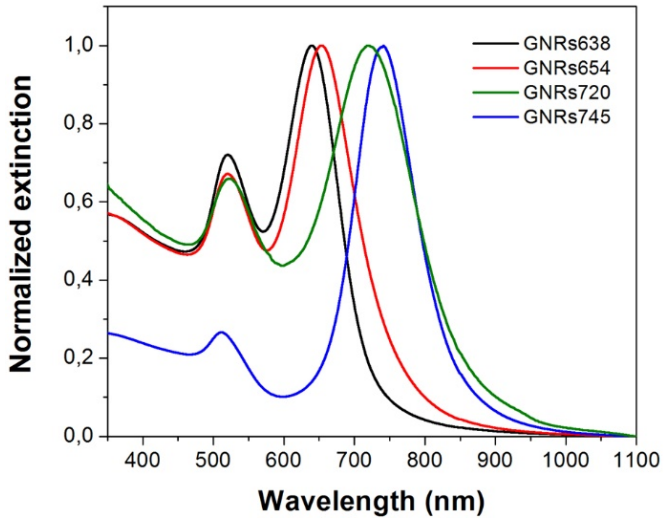

Fig. 1. Normalized extinction spectra of CTAB-stabilized GNRs with different aspect ratio.

The transversal band is located at around 520 nm for all the probes whereas the longitudinal band is tuned from 638 nm to 745 nm, confirming the successful synthesis of GNRs of increasing aspect ratio.

In view of future applicability in biomedical applications, we have selected for encapsulation in Pd the GNRs displaying longitudinal LSPR band in the biological window, at 745 nm (GNRs745). Fig. 2(a) shows the normalized extinction spectra of GNRs745 before and after coating with Pd

(Pd-GNRs745) together with the spectrum of Pd-coated GNRs recorded after long-time storage (*i.e.* 3 months). As shown, the longitudinal LSPR band undergoes a red shift from 745 nm to 757 nm after the formation of Pd at the surface of GNRs while the position of the transversal band remains almost unchanged. This red shift can be assigned to the increase of refractive index around de GNRs after Pd deposition. After long-time storage, the longitudinal LSPR band displays a slight blue shift, however the spectral shape of the spectrum remains unaltered indicating that the synthesized Pd-coated GNRs745 have good stability in time.

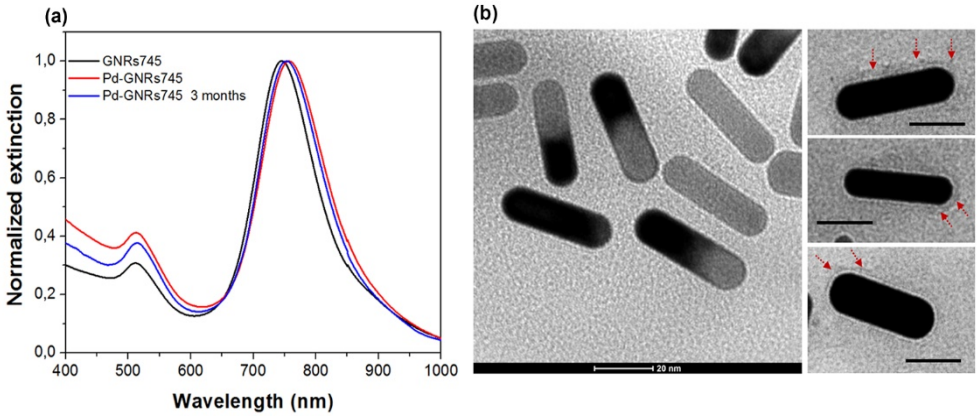

Fig. 2. (a) Normalized extinction spectra of GNRs745 before and after Pd coating and its evolution in time; (b) TEM images illustrating CTAB-stabilized GNRs745 (left) and Pd-coated GNRs745 (right). All scale bars have the same length (20 nm).

Further, we performed TEM measurements in order to evaluate the morphology of our samples. Fig. 2(b) (left), displaying a typical TEM image of CTAB-stabilized GNRs745, confirms the formation of GNRs monodisperse in size and shape with average length × width of 40 × 12 nm and an aspect ratio of 3.3. Moreover, TEM images presented in Figure 2(b) (right), confirm the

deposition of a 2-3 nm thick Pd shell (marked with red arrows) at the surface of GNRs. Future work is in progress in order to optimize the encapsulation procedure and obtain a more uniform Pd shell around the GNRs.

Subsequently, DLS and Zeta Potential measurements were performed in conjunction with absorption spectroscopy and TEM in order to validate the presence of Pd coating. Fig. 3(a) reveals an increase of the hydrodynamic diameter, after Pd coating, indicating the presence of an extra layer at the surface of the nanorods, thus confirming the results obtained from TEM. Zeta Potential measurements (Fig. 3(b)) were performed to analyze the change in surface charge at the surface of GNRs. As displayed, the charge value dropped from +48.7 mV to +31 mV after Pd deposition, which can be attributed to the catechol and -OH groups from the surface of the Pd shell [13]. Moreover, the slightly small change observed after 3 months of storage in the hydrodynamic diameter and Zeta Potential indicate once more the good stability of Pd – GNRs745 in time.

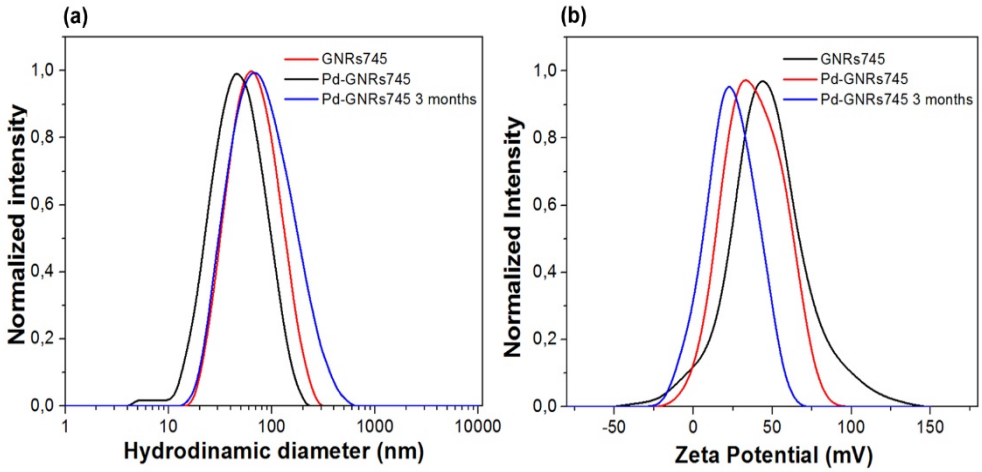

Fig. 3. Hydrodynamic diameter (a) and Zeta Potential (b) of GNRs745 before and after Pd deposition and their evolution in time.

CONCLUSIONS

In conclusion, we have successfully synthesized stable core/shell nanoparticles by coating GNRs with Pd shell. The first evidence of successful coating with Pd is the 12 nm red shift of the longitudinal LSPR peak occurring as a consequence of dielectric constant modification after polymerization of dopamine. The nanocomposites were morphologically characterized using TEM, which further reaveled the presence of a 2-3 nm Pd layer around GNRs. Finally, DLS and Zeta Potential measurements confirmed the presence of the Pd layer at the surface of the nanorods and their good stability in time, even 3 months after the coating procedure. Further improvement of the encapsulation process and adjustment of Pd shell thickness can lead to valuable platforms for various biomedical applications.

ACKNOWLEDGMENTS

This work was supported by CNCS - UEFISCDI, Romania, under the project number PN-III-P4-ID-PCE-2016-0837.

REFERENCES

1. Z.Y. Ma, H.X. Xia, Y.P. Liu, B. Liu, W. Chen, Y.D. Zhao, *Chin Sci Bull,* 58, 2530 (2013).
2. X. Liu, J. Cao, H. Li, J. Li, Q. Jin, K. Ren, J. Ji, *ACS Nano*, 7, 9384 (2013).
3. H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, *Science*, 318, 426 (2007).
4. Y. Liu, K. Ai, L. Lu, *Chem. Rev*., 114, 5057 (2014).
5. W. Tao, X. Zeng, J. Wu, X. Zhu, X. Yu, X. Zhang, J. Zhang, G. Liu, L. Mei, *Theranostics*, 6, 470 (2016).

6. S. Hong, K.Y. Kim, H.J. Wook, S.Y. Park, K.D. Lee, D.Y Lee, H. Lee, *Nanomedicine*, 6, 793 (2011).
7. M.E. Lynge, P. Schattling, B. Stadler, *Nanomedicine*, 10, 2725 (2015).
8. K.-Y Ju, S. Lee, J. Pyo, J. Choo, J.-K. Lee, *Small*, 11, 84 (2015).
9. K. CL Black, J. Yi, J. G. Rivera, D.C. Zelasko-Leon, P.B. Messersmith, *Nanomedicine*, 8, 17 (2013).
10. S. Wang, X. Zhao, S. Wang, J. Qian, S. He, *ACS Appl. Mater. Interfaces*, 8, 24368 (2016).
11. B. Nikoobakht, M.A. El-Sayed, *Chem. Mater.,* 15, 1957 (2003).
12. V. Sharmaa, K. Parka, M. Srinivasarao, *PNAS*, 106, 4981 (2009).
13. D.R Dreyer, D.J. Miller, B.D. Freeman, D.R. Paul, C.W. Bielawski, *Langmuir*, 28, 6428 (2012).