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Development of gold nanoparticle-polypyrrole nanocomposites

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Gold nanoparticle and polypyrrole nanocomposites (AuNP/Ppy) were prepared employing in-situ polymerization of pyrrole using tetrachloroauric acid as an oxidant in the presence of gold seeds. The oxidation of pyrrole and the reduction of Au^{3+} ions occurred simultaneously in a single step, which resulted in formation of nanocomposites based on gold nanoparticles entrapped within the polypyrrole layer. UV-Vis absorption spectroscopy, dynamic light scattering, and scanning electron microscopy were used to follow the formation of AuNP/Ppy nanocomposites and to evaluate the size of formed nanocomposites.

Key words: gold nanoparticles, polypyrrole, nanocomposites

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INTRODUCTION

Nanocomposites consisting of conducting polymers and metal nanoparticles have received considerable attention due to the potential possibilities to create suitable materials for electrocatalysis, chemical sensors, and microelectronic devices [1–3]. These nanocomposites were suggested as the possible layers for DNA sensing [4] for the protection and charge transfer in biosensors [5–10], also for immobilization of antibodies [11] or cancer treatment [12]. Conducting polymers are well known for their excellent electronic properties with conductivity covering the whole range from insulator to metal while retaining the lightweight, mechanical properties and processing advantages of polymers [13]. Compared with nanocomposites constructed by insulating polymers, conducting polymers can serve as a novel electroactive relay among metal nanoparticles (NPs) in the nanocomposites matrix [14, 15]. What is more important, such compounds could obtain interesting properties, including thermal energy transfer, which is not common for the bulk materials [16]. Therefore, the fabrication of novel nanocomposites based on metal NPs and conducting polymers would provide various interesting characteristics and new features in nano-technological applications.

Control of morphology is the main objective in the development of advanced nanomaterials [17] and is usually dependent on the synthesis conditions. For the composite of polymer and gold nanoparticles various monomers could be chosen [18]. The synthesis procedure of the AuNP/Ppy composites could be accomplished in different ways: i) by forming the micelles of surfactants where $AuCl_4^-$ and composites from gold atoms are entrapped and later adding the monomer with instantly occurring polymerization [19]; ii) by simultaneously stirring the solution of $AuCl_4^-$ and pyrrole monomer while obtaining gold-polypyrrole core-shell nanoparticles [20, 21]; iii) by forming polypyrrole and then decorating with gold nanoparticles, which are formed in situ in acidic solution by adding hydrochlorauric acid [22]; iv) the opposite order could also be applied firstly producing small gold nanoparticles (in recent publication they are called gold seeds) and later synthesizing polymer shell [16]; v) the electrochemical formation of $AuCl_4^-$ nanocomplexes could also be performed before addition of pyrrole and collection of AuNP/Ppy core-shell nanoparticles [23]. The formation of composite nanomaterials based on the seed-mediated approach recently becomes increasingly popular in the production of ordered morphologies AuNPs in aqueous solutions [24]. In a seed-mediated method, firstly small metal NPs are prepared and later they are used as seeds (nucleation centers) for a systematic growth of larger NPs. However, difficulties arising in order to determine the appropriate growth conditions, which inhibit additional nucleation, generally limit the application of here mentioned methods [25]. Weak reducing conditions are required for a systematic growth of AuNPs [26]. The formation of gold nanoparticles might be controlled by the overall molecular weight and relative block length of the block copolymer if the polymer is used in the reaction solution as a stabilizer [27–30]. Also the stability of the gold nanoparticles was greater when the block copolymer was used instead of the homopolymer. The size and shape of NPs are generally controlled by external factors such as reaction duration, temperature, and precursor or surfactant concentration. Lack of external influence may eventually lead to unregulated growth of NPs and possibly to the loss of their unique properties. On the other hand, polypyrrole offers excellent biocompatibility [31, 32] and could be doped by various biologically active compounds. The release of such compounds in a controlled manner could be induced by infrared irradiation based heating of trapped metal nanoparticles [33]. Therefore, the development of metal nanoparticles and polypyrrole composites could be an important strategy in creation of new targeted drug delivery systems.

The aim of this work was to develop a single-step surfactant free synthesis of AuNPs/Ppy nanocomposite using tetrachlorauric acid as a gold source in the formation of AuNPs and as an oxidant capable to initiate pyrrole polymerization reaction at room temperature.

EXPERIMENTAL

Chemicals

Chemicals of analytical grade and triply distilled water were used, if not otherwise stated. Tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$) and tannic acid were obtained from Carl Roth GmbH & Co (Karlsruhe, Germany), tri-sodium citrate dihydrate was recieved from Scharlau Chemie S. A. (Barcelona, Spain), hydrogen peroxide from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and pyrrole from Alfa Aesar GmbH & Co (Karlsruhe, Germany).

Synthesis of polypyrrole

The polymerization of pyrrole was performed in a mixture of 0.05 M sodium phosphate and 0.05 M sodium acetate buffer pH 1.0 in 1 ml reaction solution, which consisted of 200 mM hydrogen peroxide and 200 mM pyrrole. In the buffer solution firstly the monomer was added and stirred using an ultrasonic bath for 5 min, then followed by the addition of the hydrogen peroxide. The solution was stirred with a shaker for a minute and was kept at room temperature in the dark for 18 h.

Synthesis of gold seeds

Gold seeds of 13 nm were synthesized by reducing $HAuCl_4 \cdot 3H_2O$ with sodium citrate in the presence of tannic acid according to the earlier reported procedure [7]. An aqueous solution of tetrachloroauric acid (80 mL of 0.0125% (w/w) $HAuCl_4$) was heated until 60 °C in an Erlenmeyer flask using a magnetic stirrer with an electric hot plate. The second solution consisting of sodium citrate (4 mL of 1% (w/w)), tannic acid (0.025 mL of 1% (w/w)) and 15.975 mL deionized water was also heated until 60 °C. Both solutions were mixed, heated until 95 °C and kept at this temperature for 10 min to yield colloidal gold nanoparticles. Before the use colloidal gold suspension was stored in dark at +4 °C.

Synthesis of gold nanoparticles using gold seeds

The experiment of AuNP synthesis using gold seeds enlargement strategy was carried out in water. Synthesis solution consisting of 100 μL of gold seeds, prepared as described previously, 5 μL of 25 mmol $HAuCl_4$ solution, and 895 μL of deionized water was mixed and kept at room temperature.

Synthesis of gold nanoparticles and polypyrrole nanocomposites (AuNP/Ppy)

Pyrrole solution in distilled water was stirred in an ultrasonic bath for 5 min in order to dissolve pyrrole in water. Aditionally 100 μL of the prepared gold seed solution and 5 μL of 25 mmol $HAuCl_4$ solution were gently mixed. Then the prepared pyrrole solution and water were added at such amounts that the final volume of the prepared polymerization solutions was 1 mL. Final concentrations of pyrrole in the prepared polymerization solutions were 50, 100, 200 or 400 mmol. All reactions occurring in the synthesis solution are depicted in the Scheme. The reaction procedure consists of two main steps. Firstly, the gold seeds were obtained using tetrachloroauric and citric acids in the presence of tannic acid. Then only tetrachloroauric acid or pyrrole monomers together with tetrachloroauric acid were added to the gold seeds solution. Tetrachloroauric acid acts as an oxidizing agent in the polymerization of pyrrole.

Characterization of gold nanoparticles and nanocomposites

UV-Vis absorption spectroscopy was performed with a double-beam spectrophotometer Lambda 25, PerkinElmer (Shelton, USA). The samples for UV-Vis measurement were dispersed in an aqueous solution and the spectrum was acquired from 330 to 800 nm.

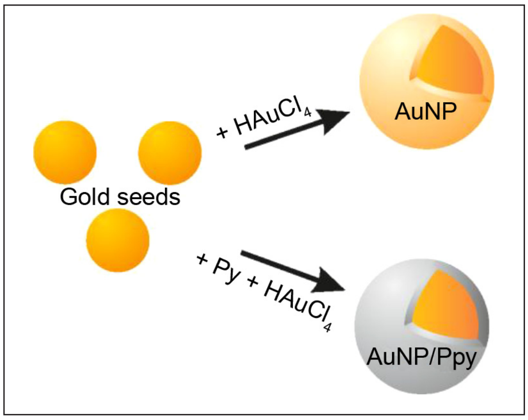
Dynamic light scattering (DLS) measurements were performed with a Malvern Zetasizer Nano ZS (Malvern, Herrenberg, Germany) equipped with a 633-nm He-Ne laser operating at an angle of 173°. The data were collected and analyzed by the Dispersion Technology Software version 6.01 from Malvern. All measurements were performed at a position of 4.65 mm from the cuvette wall with an automatic attenuator and at a controlled temperature of 25 °C.

The size of the synthesized structures was also evaluated by a high resolution field emission scanning electron microscope SU-70 (Hitachi, Japan). Accelerating voltage for the electron beam was set to 5 keV. Samples for the measurement were prepared by depositing a drop of 2 μL of the solution on the fragment of silicon wafer.

RESULTS AND DISCUSSION

Gold seeds of 13 nm were synthesized according to the protocol presented in the Experimental part and were used for two main purposes: for the synthesis of larger gold nanoparticles and for the synthesis of gold nanoparticles and polypyrrole composites (Scheme). After adding tetrachloroauric acid to the gold seeds solution some enlargement of gold seeds was observed possibly due to decomposition of $HAuCl_4$ and reduction of Au^{3+} to Au^0. This system was monitored by a UV-Vis spectrophotometer (Fig. 1). Initially, the increase of the absorbance intensity and not very significant red shift were observed from 527 to 544 nm during the first 2 h. Later a small blue shift was registered. After 7 h the peak reached 531 nm and became stable at this wavelength range as it is seen to form the spectra monitored after 26 h (Fig. 1A). These shifts are related to the growth of gold seeds and formation of larger AuNPs. Moreover, some changes on the right slope of the spectra were observed. Firstly, it was growing together with the peak, but after 7 h small and after 22 h significant decrease were registered. This could be explained by the stabilization of the colloidal solution and the increase of monodispersity of the particles. During the growth process gold nanoparticles assumed different crystal forms and, therefore, the absorption peak became broader. In time the equilibrium of the growth was reached and the plasmonic peak of the particles became sharper. Spectra were stable up to 117 h what indicates the stability of the AuNP in the solution (Fig. 1B). After 117 h the decrease of the intensity was observed without shifting the peak indicating the start of aggregation and precipitation processes. The aggregation process was also confirmed by the appearance of the second peak at about 700 nm wavelength. After 142 h most of the particles were aggregated and dispersed at the bottom of the cuvette. After mixing of the solution, the acquired spectrum is more influenced by scattering processes than by optical light absorption of the particles.

For better understanding and comparison of the obtained results the control solution of gold seeds dissolved in distilled



Scheme. Principle of gold nanoparticles enlargement (AuNP) using gold seeds and synthesis of gold nanoparticle- polypyrrole nanocomposites (AuNP/Ppy)

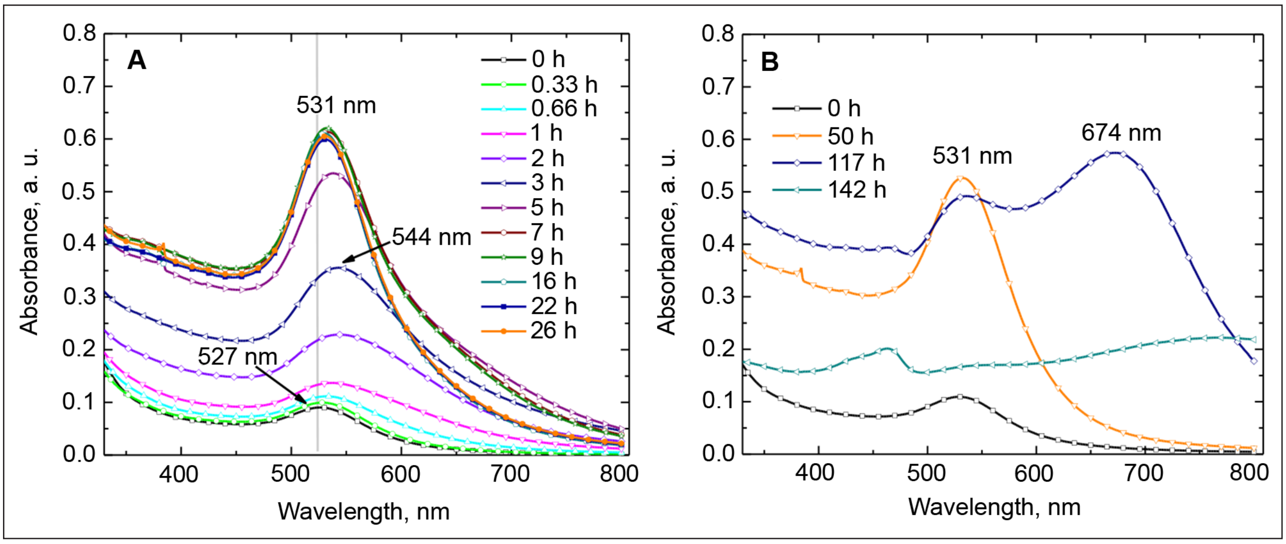


Fig. 1. Time dependent UV-Vis spectra of colloidal gold nanoparticles in the gold seeds solution after the addition of tetrachloroauric acid; A – Spectra registered from the initial mixture formation (0 h) until 26 h. A vertical grey line indicates the shift of the peak; B – Comparison of spectra registered after 0, 50, 117 and 142 h

water up to the same concentration as it was in the previously presented experiment was prepared. The absorption curves are presented in Fig. 2A. The colloidal solution of gold seeds was stable until 50 h and later the absorption intensity started to decrease most likely due to the aggregation, precipitation, and sedimentation of gold seeds on the bottom of the cuvette. However, no shift of the absorbance peak was observed.

Another direction of our research applying gold seeds was synthesis of gold nanoparticles and polypyrrole nanocomposites (AuNP/Ppy). The reaction mixture consisting of gold seeds, HAuCl$_4$ and pyrrole was prepared, and changes in UV-Vis spectra were recorded within 6 days (Fig. 3). At the initial stage resonance modes of gold [34] at 750 nm were registered after mixing all of reaction components. In addition, the broad absorption band of gold seeds (where Au is in zero valent state) was observed at the interval 500–650 nm with the maximal intensity around 560–570 nm (Fig. 3A). This information suggests reduction of AuCl$_4^-$ ions. In comparison to the growth of AuNP when no monomer was added to the solution, here the peak is red-shifted (final plasmonic peak of AuNP is at 531 nm and that of AuNP/Ppy is at 570 nm) which indicates that the growth of the AuNP is accomplished by the synthesis of Ppy. The peak, which is characteristic for polypyrrole formation (460 nm), was observed only after 7 h, but up to 26 h it was still not well expressed. Also relatively high background absorption was noticed during all the measurements and only after 26 h it started to decrease. This might be explained by the light scattering from the pyrrole monomer micelles. Only after some time, when a significant part of the pyrrole becomes polymerized, the light was more absorbed by Ppy than scattered by micelles of an unpolymerized pyrrole. Therefore, the background was reduced and the Ppy and

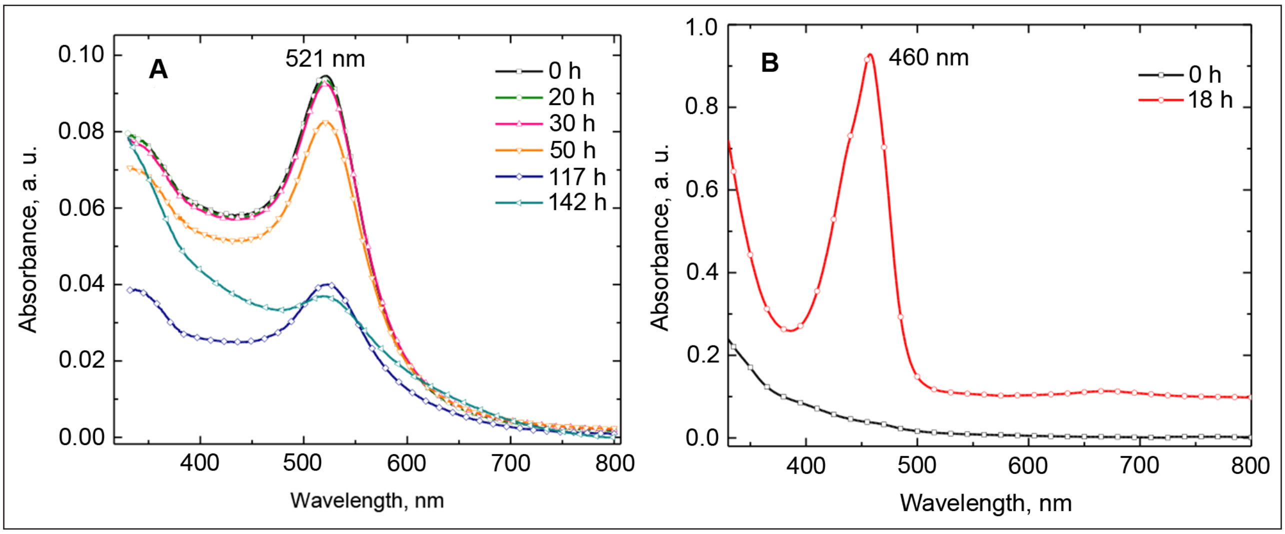


Fig. 2. Absorption spectra of gold seeds (A) diluted in water and polypyrrole (B) in the buffer as a function of time

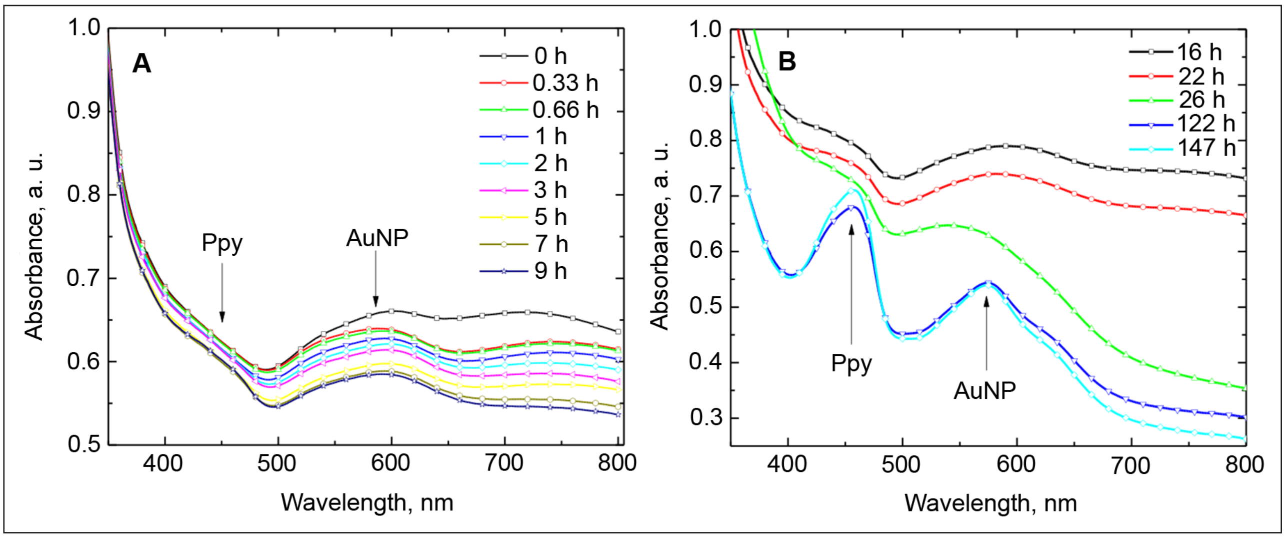


Fig. 3. UV-Vis absorption spectra of AuNP/Ppy composites in time from 0 to 9 hours (A), and from 16 to 147 h (B) during the polymerization procedure. The concentration of the pyrrole in the solution was 200 mmol

Au plasmon peaks become more obvious (after 122 h). The absorption band at 460 nm could be assigned to π-π transition of Ppy, but no absorption band due to charge carriers, i. e. polarons at 685 nm, was present. These observations indicate the formation of AuNP/Ppy nanocomposite with a core-shell structure [35]. For verification of the polypyrrole spectrum the chemical polymerization was initiated with the hydrogen peroxide at pH 1.0 and the absorption spectrum was registered in time. As could be seen in Fig. 2B, the UV-Vis spectrum of polypyrrole at the interval from 330 to 800 nm shows only the peak at 460 nm. Thus during the AuNP/Ppy nanocomposite synthesis (Fig. 3) other observed peak appears only due to the gold nanoparticles.

Different concentrations of the pyrrole were used to evaluate the influence of monomers concentration on the size of the AuNP/Ppy nanocomposites. The solution was kept for 122 h and then spectra were registered. As could be seen from Fig. 4, only the intensity of the absorption of polypyrrole and a gold plasmon band were changed but no shift of peaks was registered. This indicates that the tested concentrations of the monomer do not affect the size of the particles using 100 µL of the prepared gold seed solution after 122 h of reaction. Selvan et al. also confirmed that mixing different concentrations of pyrrole with tetrachloroauric acid AuNP/Ppy composites of a uniform 24 nm size are always obtained [21].

The size distribution of gold seeds, AuNPs in the $HAuCl_4$ solution and AuNP/Ppy nanocomposites formed in the presence of $HAuCl_4$ is presented in the DLS image (Fig. 5). According to DLS data the gold seeds diameter is in the range of 10.45 nm; after the treatment by the $HAuCl_4$ solution and

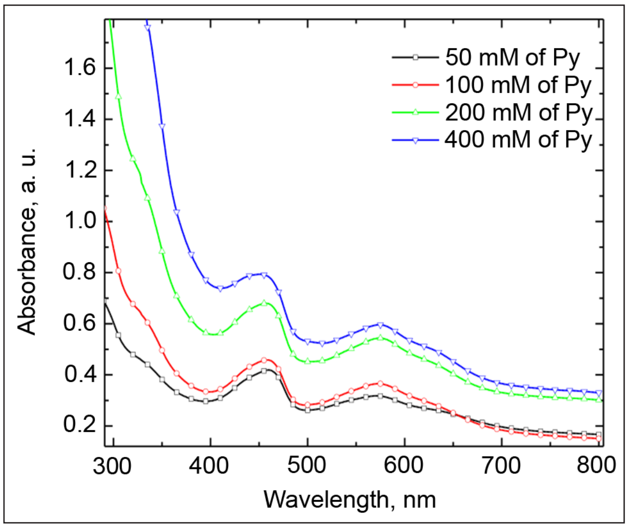


Fig. 4. UV-Vis absorption spectra of AuNP/Ppy composites formed at the 0.125 mM $HAuCl_4$ concentration and different pyrrole concentrations: 50, 100, 200 and 400 mM after 122 h of reaction

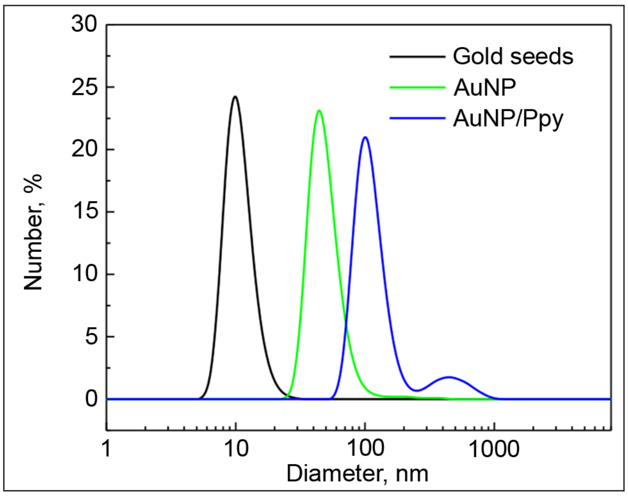


Fig. 5. The distribution of the particle diameter measured by a dynamic light scattering method: gold seeds (black colour), AuNPs after an additional treatment by the $HAuCl_4$ solution (green colour) and after the formation of AuNP/Ppy nanocomposites (blue colour)

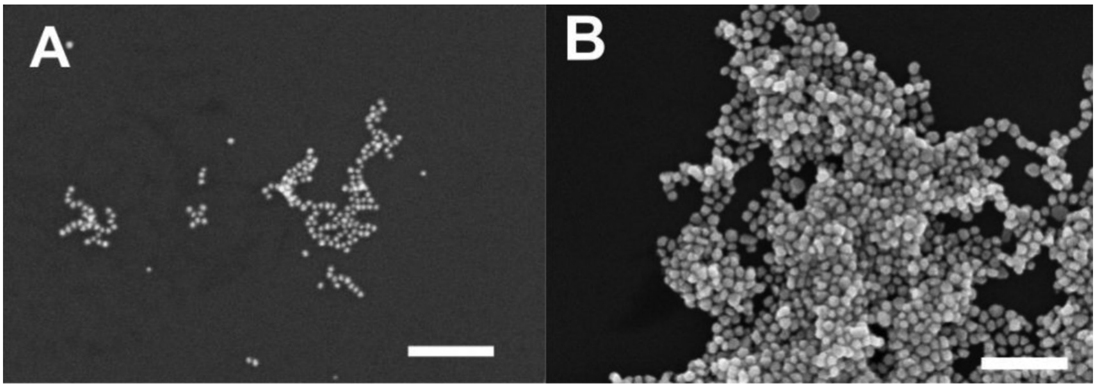


Fig. 6. SEM images of gold seeds (A) and enlarged gold nanoparticles (B) deposited on the silicon wafer. The bar corresponds to 200 nm

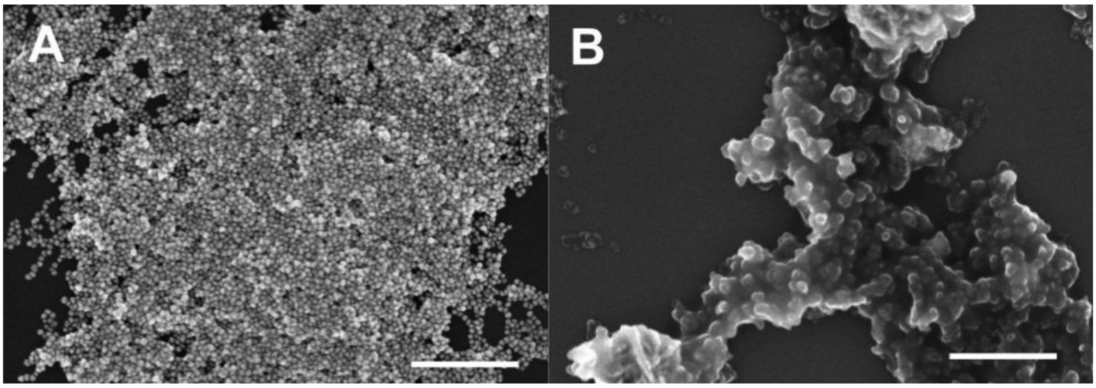


Fig. 7. SEM images of AuNPs (A) and AuNP/Ppy (B) nanocomposites deposited on the silicon wafer. The bar corresponds to 500 nm

keeping for 147 h, the size of AuNPs increased almost by 5 times and was in the range of 51.48 nm. Bimodal distribution of the particle size was registered after gold seeds treatment by $HAuCl_4$ and the pyrrole mixture after 147 h. For AuNP/Ppy composites one higher peak indicating the average 111 nm diameter of particles and another smaller one indicating the average 479 nm diameter of formed particles were observed.

The SEM measurements of gold seeds, AuNP and AuNP/Ppy nanocomposites were performed in order to evaluate the morphology of the particles and to compare the results obtained with the DLS method.

The obtained results correlated with the dynamic light scattering measurements. The gold seeds were about 10 nm in diameter (Fig. 6A). Enlarged gold nanoparticles were of 30–40 nm in diameter, although during the enlargement the round shape of the nanoparticles was lost and high heterogeneity was observed (Fig. 6B). The results of AuNP/Ppy nanocomposites obtained by DLS and SEM were more difficult to compare (Fig. 7). Due to the absence of a detergent during the drying procedure the particles were agglomerated and it was not possible to distinguish a single particle and to evaluate the actual size. It is also possible that the aggregation started before the drying in the solution of the polypyrrole. However, no separate gold nanoparticles on the top of the polymer were distinguished that was recently done by Haghighi et al. [9].

The obtained results indicated that the gold nanoparticles were entrapped within the polymer layer during the polymerization procedure. Using this AuNP/Ppy nanocomposite synthesis protocol no separate core shell nanoparticles were observed by SEM. Also it was found out that all gold nanoparticles were entrapped within the polymer layer. Other scientists used some detergents for the separation of the particles, however, these detergents are not biocompatible, and possible application of particles for the following experiments with the living cells becomes complicated. For this reason some new approaches of separation of the particles should be elaborated.

CONCLUSIONS

This work has shown that by adding tetrachloroauric acid to the solution of gold seeds without and with pyrrole the increase of gold nanoparticles or gold nanoparticles and polypyrrole nanocomposites in size was observed. Also it was observed that all gold nanoparticles were entrapped within the polymer layer, however, the composites were stuck together and no separate core-shell nanoparticles were observed. For this reason the separation of the composite to the monomers should be the scope of further investigations.

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References

1. H. Segawa, T. Shimidzu, K. Honda, *Chem. Commun.*, **(2)**, 132 (1989).
2. A. Sargent, T. Loi, S. Gal, O. A. Sadik, *J. Electroanal. Chem.*, **470(2)**, 144 (1999).
3. J.-M. Kern, J.-P. Sauvage, *Chem. Commun.*, **(10)**, 657 (1989).
4. J. Wilson, S. Radhakrishnan, C. Sumathi, V. Dharuman, *Sens. Actuators, B*, **171**, 216 (2012).
5. J. Njagi, S. Andreescu, *Biosens. Bioelectron.*, **23(2)**, 168 (2007).
6. N. German, J. Voronovic, A. Ramanavicius, A. Ramanaviciene, *Procedia Engineer.*, **47**, 482 (2012).
7. N. German, A. Ramanavicius, J. Voronovic, A. Ramanaviciene, *Colloids Surf., A.*, **413**, 224 (2012).
8. T. G. S. Babu, D. Varadarajan, G. Murugan, T. Ramachandran, B. G. Nair, *J. Appl. Electrochem.*, **42(6)**, 427 (2012).
9. B. Haghighi, M. A. Tabrizi, *Colloids Surf., B*, **103**, 566 (2013).
10. M. Kesik, F. E. Kanik, G. Hizalan, et al., *Polymer*, **54(17)**, 4463 (2013).
11. L. Qu, C. Bian, J. Z. Sun, et al., *Proceedings of the 4th Ieee International Conference on Nano/Micro Engineered and Molecular Systems,* Shenzhen (2009).
12. J. Li, J. S. Han, T. S. Xu, et al., *Langmuir*, **29(23)**, 7102 (2013).
13. T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, *Handbook of Conduction Polymers*, Marcel Dekker (1998).
14. K. Vijaya Sarathy, K. S. Narayan, J. Kim, J. O. White, *Chem. Phys. Lett.*, **318(6)**, 543 (2000).
15. T. Hertel, E. Knoesel, M. Wolf, G. Ertl, *Phys. Rev. Lett.*, **76(3)**, 535 (1996).
16. H. J. Shin, I. W. Hwang, Y. N. Hwang, et al., *J. Phys. Chem. B.*, **107(20)**, 4699 (2003).
17. T. Akagi, M. Kawamura, M. Ueno, et al., *J. Med. Virol.*, **69(2)**, 163 (2003).
18. P. Alexandridis, *Chem. Eng. Technol.*, **34(1)**, 15 (2011).
19. S. T. Selvan, J. P. Spatz, H. A. Klok, M. Moller, *Adv. Mater.*, **10(2)**, 132 (1998).
20. S. H. Han, Y. S. Cho, J. Y. Kim, et al., *Mol. Cryst. Liq. Cryst.*, **371**, 127 (2001).
21. S. T. Selvan, M. Nogami, *J. Mater. Sci. Lett.*, **17(16)**, 1385 (1998).
22. M. C. Henry, C. C. Hsueh, B. P. Timko, M. S. Freund, *J. Electrochem. Soc.*, **148(11)**, D155 (2001).
23. Y. C. Liu, T. C. Chuang, *J. Phys. Chem. B.*, **107(45)**, 12383 (2003).
24. M. S. Bakshi, A. Kaura, G. Kaur, K. Torigoe, K. Esumi, *J. Nanosci. Nanotechnol.*, **6(3)**, 644 (2006).
25. N. R. Jana, *Small*, **1(8–9)**, 875 (2005).
26. N. R. Jana, L. Gearheart, C. J. Murphy, *Small*, **13(7)**, 2313 (2001).
27. T. Sakai, P. Alexandridis, *Langmuir,* **20(20)**, 8426 (2004).
28. T. Sakai, P. Alexandridis, *J. Phys. Chem. B*, **109(16)**, 7766 (2005).
29. T. Sakai, P. Alexandridis, *Langmuir*, **21(17)**, 8019 (2005).
30. D. Ray, V. K. Aswal, *J. Macromol. Sci., Part B: Phys.*, **49(4)**, 810 (2010).
31. A. Vaitkuviene, V. Kaseta, J. Voronovic, et al., *J. Hazard Mater.*, **250**, 167 (2013).
32. A. Ramanaviciene, A. Kausaite, S. Tautkus, A. Ramanavicius, *J. Pharm. Pharmacol.*, **59(2)**, 311 (2007).
33. B. Pelaz, V. Grazu, A. Ibarra, et al., *Langmuir*, **28(24)**, 8965 (2012).
34. J. E. Millstone, S. Park, K. L. Shuford, et al., *J. Am. Chem. Soc.*, **127(15)**, 5312 (2005).
35. J.-E. Park, M. Atobe, T. Fuchigami, *Electrochim. Acta*, **51(5)**, 849 (2005).

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AUKSO NANODALELIŲ IR POLIPIROLO NANODARINIŲ SINTEZĖ IR TYRIMAS

Santrauka

Darbe aprašyta aukso nanodalelių didinimo bei jų padengimo polipirolo sluoksniu metodika. Susidariusios aukso nanodalelės buvo tiriamos spektrofotometriškai, dinaminiu šviesos sklaidos metodu bei skenuojančiu elektroniniu mikroskopu. Pradiniame tirpale aukso nanodalelių dydis buvo 10 nm. Į tirpalą papildomai įdėjus vandenilio tetrachloroauratą (III), po 7 val. buvo stebimas aukso nanodalelių padidėjimas iki 30–40 nm diametro. Aukso nanodalelių augimas tirpale esant vandenilio tetrachloroaurato (III) bei pirolo buvo registruojamas spektrofotometriškai pagal aukso nanodalelėms bei polipiroliui būdingų smailių atsiradimą bei intensyvėjimą. Skenuojančio elektroninio mikroskopo vaizduose matome, kad aukso nanodalelės, padengtos polipirolo sluoksniu, agreguoja ir sudaro vientisą nanokompozitinę struktūrą. Tokių agregatų susidarymą lėmė detergento nebuvimas sintezės tirpale.