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THE SYNTHESIS OF STABLE PLATINUM NANOPARTICLES IN THE MICROREACTOR

SYNTEZA STABILNYCH NANOCZĄSTEK PLATYNY W MIKROREAKTORZE

In this work, the synthesis of the spherical clusters containing 3-4 nm platinum nanoparticles enclosed in a polymer capsule is described. The process of nanoparticles formation was intensified by using a microreactor. The application of microreactor enabled us to shorten the time of redox reaction and nucleation stage up to 6 seconds at 105°C in comparison with the process carried out in a batch reactor at 40°C. Using Vitamin C as a bio-reducer of platinum(IV) complexes and biocompatible polymers, the products non-toxic and environmentally friendly, stable for at least 9 months, were obtained. Presented procedure for nanoparticles synthesis seems to be an alternative method for platinum recovery from solutions containing platinum(IV) chloride complex ions.

Keywords: platinum nanoparticle, microreactor, Vitamin C, steric stabilization

W pracy, przedstawiono syntezę sferycznych klastrów zawierających 3-4 nm nanocząstki platyny zamknięte w polimerowej otoczce. Proces formowania nanocząstek platyny został zintensyfikowany poprzez użycie mikroreaktora. Użycie mikroreaktora skróciło czas reakcji redukcji oraz etapu zarodkowania do 6 s w temperaturze 105°C w porównaniu do procesu przeprowadzonego w reaktorze okresowym w temperaturze 40°C. Użycie witaminy C jako bioreduktora chlorkowych kompleksów platyny(IV) oraz biokompatybilnego polimeru pozwala na uzyskanie nietoksycznych oraz stabilnych przez co najmniej 9 miesięcy produktów. Przedstawiona metoda syntezy nanocząstek może stanowić alternatywny sposób odzysku platyny z roztworów zawierających jej chlorkowy kompleks.

1. Introduction

The recovery of noble metals ions such as platinum, palladium and gold from waste is still one of the most important investigated issue, due to their decreasing natural sources. There are many methods used for noble metal recovery from their chloride complex ions e.g. chemical reduction [1, 2], photoreduction [3] and adsorption [4, 5]. Among them, chemical reduction is one of the most often applied method. In this method, as a results of chemical reaction, noble metal ions are reduced to metallic form and reductant is oxidized. In particular cases, metal nanoparticles can be obtained. The process of metallic nanoparticles formation includes several steps such as reduction of metal ions to metal on zero oxidation stage, nucleation and growth of obtained particles, and their possible further coarsening. The synthesis of nanoparticles can be carried out either in a batch reactor or in a microreactor. The microreactor, as opposed to batch reactor, allows for separation of consecutive stages of the process (i.e. reduction, nucleation, growth etc.). This feature can play a crucial role in synthesizing particles with well-defined shape and size, due to a better mixing and better mass and heat transfer of reagents caused by reduction of the diffusion path. Moreover, the microreactor systems allow to conduct the synthesis process continuously and under extreme conditions (high temperature, high pressure, etc.). Wagner et al. [6] applied the system, which consists of several microreactors connected with one another, to synthesized 4 nm gold nanoparticles (AuNPs). Such a system allowed them to control the synthesis parameters (concentration of reagents) and to introduce reagents stream in due time of the process. In the other work, Wagner et al. [7] obtained AuNPs with the size of about 11-23 nm and with narrow size distribution, using a seed-mediated growth method. Weng et al. [8] shortened time of reduction reaction of Au(III) complex ions with sodium citrate from 30 (in batch reactor) to 5 min. (in a microchip). The use of a microchip made it possible to heat reagents up to 115°C. Well-defined ~10 nm platinum nanoparticles (PtNPs) were synthesized by Niesz et al. [9] within a few seconds. These PtNPs were used as nuclei for larger nanoparticles synthesis (seed-mediated growth method) deposited on SiO_2 (support of catalyst) in the same continuous flow.

The first stage of metal nanoparticles (MNPs) formation is the reduction reaction of metal (e.g. Au, Pt) ions by a chosen reducer [10-16]. Depending on the nature of the reductant ("weak" or "strong") and the type of used stabilization

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(electrostatic, steric), it is possible to produce stable MNPs of different size. The reduction of metal ions with strong reducing agent such as hydrogen [17-20], sodium borohydride [21, 22], hydrazine [23], ethanol [24], etc. is usually carried out at room temperature and does not require special conditions. In the case of "weak" reducing agents as Vitamin C, depending on the experimental conditions the reaction reduction of metal ions can be slow or fast. The reduction of Au(III) to Au(I) with Vitamin C is very fast but formation of colloidal gold in the batch takes about half an hour. The same process takes a few seconds in a micromixer [21]. However, the reduction reaction of Pt(IV) ions to Pt(0) with Vitamin C is very slow. Mehrotra et al. [25], Hindmarsh et al. [26] and Elding et al. [27] reported that at room temperature Pt(IV) ions can be reduced in the batch by Vitamin C only to Pt(II) ions. Therefore, taking into account the literature data, we chose Vitamin C as a "weak" reductant, and carried out experiments in a flow microreactor at the temperature of 105°C (i.e. at the temperature and pressure not available in the batch reactor).

2. Materials and methods

2.1. Materials

As a precursor of platinum nanoparticles, chloroplatinic acid(IV) was used. Solution of Pt(IV) chloride complex was prepared from metallic platinum (99.99%, provided by Mennica Polska S.A.). The metal was dissolved in aqua regia, and the mixture was evaporated several times to obtain pure solid chloroplatinic acid by removing nitric acid and excess of hydrochloric acid. The acid was dissolved in deionized water to obtain required initial concentrations of platinum(IV) chloride complexes 1.0 mM. An aqueous solution of Vitamin C (Chempur, Poland) was used as the ions reducer. Aqueous solutions of polyvinyl alcohol (PVA, 67000, Sigma Aldrich) or polyvinyl pyrrolidone (PVP, 44000, Sigma Aldrich) were used as the steric stabilizers of platinum nanoparticles. The initial concentration of the reductant was kept at 60 mM, whereas the amount of a polymer was adjusted to keep the weight ratio of polymer to platinum at 50. Please note, that initial concentration of reagents means concentrations of Pt precursor and Vitamin C after mixing in volume ratio 1:1. All reagents used were pure grade.

2.2. Microreactor setup

The microreactor system (Fig. 1) consists of the glass chip (Syrris, UK) of 250 μl volume (mixing channel: 250 μm in depth, 300 μm in width, 532 mm in length; reaction channel: 250 μm in depth, 400 μm in width, 2509 mm in length) with 3 inputs for injecting reagents, 2 syringe pumps assuming the flow rate in the range from 0.001 to 10 mL/min, back pressure regulator and PTFE microcapillary that was used to bring about the reagents to the microreactor and also to let out the synthesized product to a sampler.

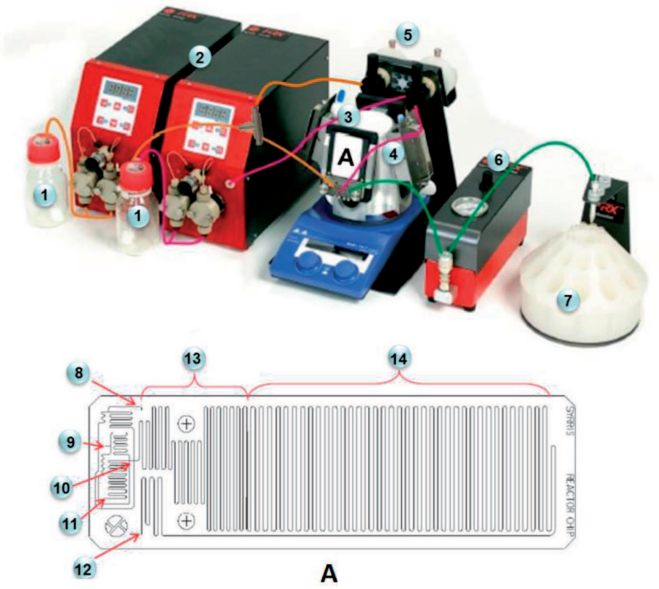

Fig. 1. Scheme of the microreactor set up with chip details (A). 1 – water or polymer; 2 – pumps; 3 – thermostat; 4 – chip holder; 5 – reagents container (aqueous solution of Pt(IV) ions and Vitamin C; 6 – back pressure regulator; 7 – sampler; A – chip details: 8 – first fluid input (polymer); 9 – second fluid input (Vitamin C); 10 – double T mixing junction; 11 – third fluid input (platinum(IV) ions); 12 – fluid output; 13 – mixing channel; 14 – reaction channel. Figures adapted from http://syrris.com/flow-products/frx-flow-chemistry-overview

2.3. Synthesis of Platinum nanoparticles

In batch reactor, the synthesis of platinum nanoparticles takes about 40 minutes at 40°C. Heating reagents up to boiling point of solvent (water) causes, that after a few minutes the platinum nuclei are formed. However, the use of high temperature (i.e. 100°C) has influence on reaction conditions i.e. initial concentration of reagents which changing with time. Moreover, in case of batch reactor rate of temperature increase is controlled by heat transfer by external surface of reactor. In order to eliminate those adverse effects, the microreactor was used. The nanoparticles synthesis was carried out at 105°C at a back pressure of 2 bar (to eliminate the possibility of reagents boiling in the microreactor). Taking into account that this device has much higher volume to surface ratio, the reagents heating is faster compared to the batch reactor. The total value of the flow rate of the reagents was set experimentally at 2.4 mL/min, where flow rates of particular reagents, i.e. platinum(IV) ions, Vitamin C and polymer equal to 0.6, 0.6 and 1.2 mL/min, respectively. For lower flow rates i.e. 0.8 and 1.6 mL/min deposition of PtNPs inside of microreactor at the $^1/_2$ and $^3/_4$ of the channel length was observed. Here, the prediction of nucleation time in microchanell using a kinetic equation was not possible, due to applied extreme conditions for the aqueous solution.

Next, the colloidal platinum synthesized in microreactor was directed to the microcapillary, where the solution was cooled down to room temperature. The samples containing PtNPs, were analyzed 10 min and 6 days after they were collected from the microcapillary using SEM/HRSTEM, DLS and UV-Vis spectroscopy.

2.4. Analysis

The microstructure observations were performed with the help of High Resolution Scanning Transmission Electron Microscopy (HRSTEM, Hitachi HD-2700, 200 kV, Cs corrected) and Scanning Electron Microscopy working in STEM mode (SEM, Hitachi SU-70, 30 kV, Japan). The samples were prepared by dropping colloidal platinum on the copper grids covered with carbon film. Prepared samples were dried at room temperature. The size of PtNPs was examined with the dynamic light scattering method (DLS, Malvern, UK). The red laser light (Tyndall effect) was used to reveal the presence of solid phase. The UV-Vis spectroscopy was used to register the spectrum after reduction of Pt(IV).

3. Results and discussion

3.1. Synthesis of PtNPs in microreactor

The experiments showed that the products of reduction reaction of chloride complex platinum (IV) ions with Vitamin C conducted in the microreactor under the extreme conditions adopted in this study are the platinum nanoparticles approximately 3 nm in diameter. These nanoparticles are covered by the polymers, such as PVA or PVP, injected after mixing of platinum ions with Vitamin C, as schematically shown in Fig. 1. The fast cooling of colloidal platinum right at the exit from microchannel as well as the addition of a polymer effectively protect synthetized nanoparticles from their further growth. The obtained colloidal solution is almost colorless as opposed to intensively yellow colour of Pt(IV) complexes and it may suggest the presence of platinum nanoparticles. Indeed, the presence of small nanoparticles was confirmed by Tyndall effect, DLS study (Table 1) and HRSTEM micrographs (Fig. 3).

TABLE 1
Results of DLS analysis. R_{IH} and R_{NH} denote a hydrodynamic radius by intensity and number, respectively

Time from the end of synthesis process	Stabilizer	R_{IH}, nm	R_{NH}, nm
10 minutes	PVA	9.8±4.4	4.2±1.3
6 days		43.4±16.1	23.7±6.5
10 minutes	PVP	6.4±3.5	2.6±0.8
6 days		58.7±20.4	34.4±10.8

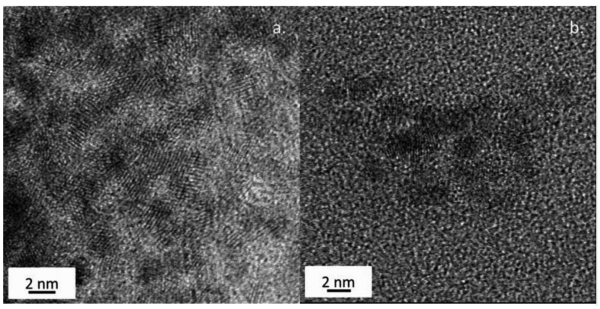

Fig. 2. HRSTEM micrographs of PtNPs stabilized by PVA after the end of synthesis process (a) and PVP (b), after 10 minutes

The change of color of colloidal platinum solutions was monitored by over two weeks. During this period, changes from colorless to grey were observed (after a few hours) and then to intensively black (after 4 days).

The change of the colloid color was not related to the growth of individual nanoparticles. In fact it was the result of clusters formation as schematically shown in Fig. 3. The scanning electron microscopy (SEM) indicates that the diameter of platinum nano-crystals remains equal to 3 nm. In the same time the results obtained by DLS analysis showed the change in the particles size, with average size increasing to 30 nm. Based on STEM observation, this is the size of platinum clusters.

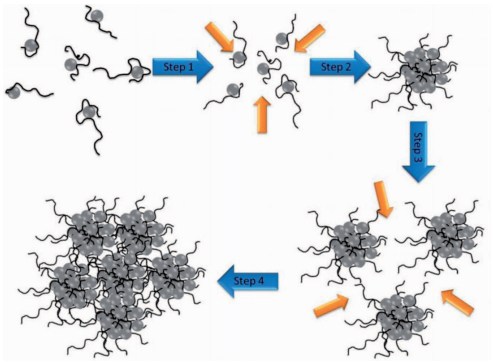

Fig. 3. The PtNPs cluster formation mechanism (Step 1 – interaction between nanoparticles; Step 2 – primary cluster PtNPs-polymer formation; Step 3 – interaction between PtNPs-polymer clusters; Step 4 – secondary cluster of PtNPs – polymer formation)

The mechanism of clusters formation runs through several stages (Fig. 3). Initially synthesized platinum particles, surrounded by single polymer chains, are freely suspended in the solution. Next (step 1), the particles intersperse because of Brownian motion, increasing the probability of catching a "tail" of polymer chain that surrounds one particle with another "tail" of a polymer chain surrounding another particle. As a results of a formation of such polymer bridges, the clusters are generated (step 2). The platinum nanograins, are located in the center of such a cluster. Outside of the cluster there are located the "tails" of the polymer chains (Fig. 3-5). Such a specific architecture can be related to the tendency of the particle-polymer system to decrease the surface energy. The clusters size varies from 10 to 60 nm and seems to be determined by the probability of encountering other particles. Due to this fact during the next stage (step 3) even bigger agglomerates are formed.

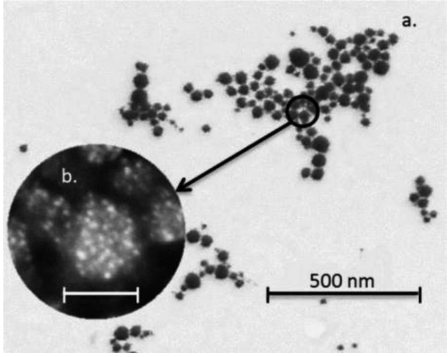

Fig. 4. BF-STEM(a)/DF-STEM(b) micrographs presented spherical cluster of PtNPs-PVA after 6 days. Scale bar 50 nm

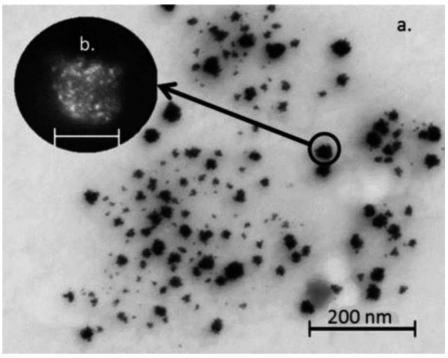

Fig. 5. BF-STEM(a)/DF-STEM(b) micrographs presents spherical cluster of PtNPs-PVP after 6 days. Scale bar 50 nm (b)

The properties of colloidal platinum were monitored spectrophotometrically after sample collecting (10 minutes later) with no change in the level of turbidity. This is an indication of a very small size of platinum particles. After 6 days (black color of the solution), the level of the turbidity changed as demonstrated in Fig. 6.

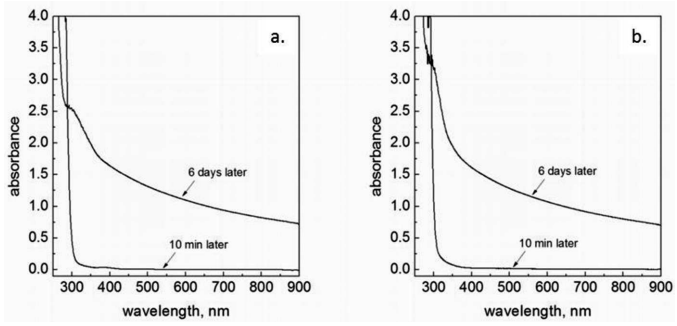

Fig. 6. UV-Vis spectra of colloidal Platinum obtained in microreactor (a) with PVA and (b) with PVP

4. Conclusions

In this paper we demonstrated, that the reduction of Pt(IV) ions to metallic platinum with Vitamin C is possible at high temperature of 105°C and at back pressure 2 bar. The application of microreactor was necessary in order to intensify the process of particle formation. This intensification results from an appropriate choice of synthesis conditions (reagents concentrations, temperature) and flow rates. The obtained Pt nanoparticles had diameter of 3 nm if PVP was added as stabilizer, and 4 nm for PVA. It was observed that colloidal platinum remains in the form of singular nanoparticles for a few days. Formation of platinum agglomerates (10-60 nm in diameter) was observed later, while the size of PtNPs was still of 3 or 4 nm (diameter). The obtained particles have been stable for at least 9 months.

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