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THE DEPOSITION OF GOLD NANOPARTICLES ONTO ACTIVATED CARBON

OSADZANIE NANOCZĄSTEK ZŁOTA NA WĘGLU AKTYWNYM

This work reports the results of spectrophotometric, dynamic light scattering (DLS) and microscopic (SEM) studies of the gold nanoparticles (AuNPs) deposition on activated carbon (AC) surface modified with primary (ethanolamine) and secondary (diethylenetriamine and triethylenetetramine) amines. It was found that this method is efficient for deposition of AuNPs from aqueous solution. However, nanoparticles change their morphology depending on the kind of amine used in experiments. On the AC surface modified with ethanolamine, the uniform spherical AuNPs were formed. In case of diethylenetriamine and triethylenetetramine application, the agglomerates of AuNPs are present. The diameter of individual AuNPs did not exceed 15 nm and was bigger as compared with the diameter of particles present in precursor solution (ca. 10 nm).

Keywords: Gold nanoparticles, Activated carbon, Functionalization, Amines

W pracy przedstawiono wyniki badań spektrofotometrycznych, metodą dynamicznego rozpraszania światła (DLS) oraz mikroskopowe (SEM) dotyczące osadzania nanocząstek złota na węglu aktywnym, modyfikowanym aminami: pierwszorzędową (etanoloamina) i drugorzędowymi (dietylenotriamina i trietylenotetraamina). Wykazano, że ten sposób modyfikacji umożliwia osadzanie nanocząstek złota z roztworu wodnego na powierzchni węgla. W zależności od rodzaju używanej aminy ulega jednak zmianie morfologia osadów nanocząstek. Na powierzchni węgla aktywnego, modyfikowanego etanoloaminą, tworzą się jednorodne cząstki złota o kształcie sferycznym. W przypadku zastosowania dietylenotriaminy oraz trietylenotetraaminy obserwowano powstawanie agregatów nanocząstek. Średnica pojedynczych nanocząstek nie przekraczała 15 nm i była większa od średnicy nanocząstek obecnych w roztworze prekursora (ok. 10 nm).

1. Introduction

Noble metals nanoparticles, characterized by the high surface to volume ratio, consist of relatively large number of atoms located on their surface. This fact, in combination with their unique properties, makes them to be used as an efficient catalysts in various chemical synthesis and processes [1-4]. The catalytic properties of these nanoparticles depends on their size, morphology and surface structure as well as their interactions with supports [5]. However, direct use of metal nanoparticles as catalysts is difficult because of their small size and their tendency to aggregation (the presence of attractive Van der Waals forces and coordinative unsaturation of surface atoms). For this reason, they are deposited on the appropriately selected supports, such as polymers [6], metal oxides, [7-9], mesoporous silica [10] or carbon [11, 12]. Usage of the proper support for particles reduces the problem of nanoparticle aggregation and thus, may also improve catalytic activity of resulting material. The support characteristics such as thickness, morphology, chemical structure affect efficiency of the catalyst. For example, gold particles deposited on a support composed of metal oxides exhibit high catalytic activity

for carbon monoxide oxidation at temperatures of 200 K [13]. Among different materials, the carbon is promising one as a support material for catalysts e.g. due to the high chemical resistance, the ability of forming in different shapes and relatively low cost of production [5]. Furthermore, due to the π stacking interactions carbon is well suited for catalytic processes involving aromatic substrates. However, experiments performed with gold(III) chloride complex ions sorption on the surface of activated carbon lead to the formation of sub-micron sized gold particles [14]. The main reason is referred to the type of gold(III) complex used in experiments [15-17]. Downard *et al.* [18, 19] showed that it is possible to deposit nano-sized gold particles when the surface of the activated carbon is modified with the appropriately selected amines. The process of functionalization involved electrochemical oxidation of aliphatic amines on the surface of carbon electrodes. However this method, very efficient at conducting surfaces, cannot be used for non-conducting powder carbon supports. This paper presents simple approach towards functionalization of carbon surfaces with gold nanoparticles via molecular-level modulation of ζ potential. Two stage method involving oxidation and subsequent covalent binding modification with pri-

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mary and secondary aliphatic amines results in carbon materials which spontaneously self-assembles gold nanoparticles on their surfaces.

2. Experimental

2.1. Materials

Tetrachloroauric acid was obtained by dissolving of gold with a purity of 99.99% in aqua regia, evaporation to dryness and three times dissolution of the deposit in 0.1 M hydrochloric acid. Activated carbon Organosorb 10-CO (Desotec, Poland) (the properties are described in Tab. 1), sodium citrate (p.a., Polskie Odczyniki Chemiczne, Poland), 98% nitric acid (p.a., Polskie Odczyniki Chemiczne, Poland), N-(2-aminoethyl) ethane-1,2-diamine, N,N'-bis(2-aminoethyl)ethane-1,2-diamine (p.a., Sigma Aldrich, Germany), 2-aminoethanol, methanol (p.a., Lachner, Czech Republic), were used as received.

TABLE 1
Specification of activated carbon, Organosorb 10-CO, used in experiments [20]

Type	Coconut shell-based activated carbon – granulated	
	guaranteed	typical
Total BET surface, m ² /g	min. 1000	1100
Iodine number, mg/g	min. 1000	1100
CTC, %	min. 55	60
Moisture, %	max. 5	4.2
Hardness, %	min. 98	99
Density, kg/m ³	500±30	
Particle size, mesh	8*30 (2.36 – 0.6 mm)	

2.2. Methods

UV/Vis absorption spectra were recorded using spectrophotometer (Shimadzu U-2501 PC, Japan) worked in the range of 190-900 nm. Dynamic Light Scattering (DLS) and zeta potential (?) measurements were performed using nanoparticle size analyzer (Zetasizer Nano-S, Malvern, United Kingdom) in aqueous solutions at pH = 6. Electron micrographs were taken using a scanning electron microscope SU-70 (Hitachi, Japan) and a transmission electron microscope JEM-2010ARP JOEL (Philips, The Netherlands).

2.3. Experimental procedure

2.3.1. Functionalization of activated carbon

The activated carbon was pulverized in a mortar. Next, it has been oxidized in the hot nitric acid. Prepared sample was rinsed with deionized water and dried at 50°C for 12 h. After drying, the samples of activated carbon were further functionalized via reaction with anhydrous amines at room temperature for 30 minutes. The excess of amines was washed

out with methyl alcohol. After this, functionalized activated carbon was dried again at 50°C for 12 h.

2.3.2. Gold nanoparticles deposition onto activated carbon

The 1.25 mM sodium citrate aqueous solution was mixed with 0.25 mM HAuCl₄ and then boiled and stirred for 10 min. After completion of synthesis, localized surface plasmon resonance (LSPR) bands (using UV-Vis spectrophotometry), the size (using DLS method) and the morphology (SEM method) of nanoparticles, were determined. Obtained colloid of gold was injected into the reactor containing functionalized activated carbon and was boiled again. All the samples were filtered and dried at 50°C for 12 h. The microscopic analysis of the carbon powders was carried out. The remaining filtrate was analyzed spectrophotometrically to determine the amount of gold colloid residuals.

3. Results and discussion

3.1. Gold nanoparticles characterization

After addition of sodium citrate to the solution containing gold(III) ions, the sample was decolorized (due to the reduction of gold(III) chloride complexes to gold(I)) and after a few minutes changed to the violet (AuNPs appearance in the system) and further to the red color (dispersion of AuNPs). Therefore, it can be inferred, that chemical reaction between gold(III) ions and sodium citrate took place leading to the formation of colloidal gold. The presence of AuNPs in the system was confirmed by the appearance of LSPR band in the visible range of wavelength (maximum of absorbance was detected at $\lambda_{max} = 522$ nm). Registered intensity of scattered light in DLS measurements allowed determination of the hydrodynamic radii of synthesized AuNPs. The distribution of AuNPs hydrodynamic diameter is shown in the Fig. 1.

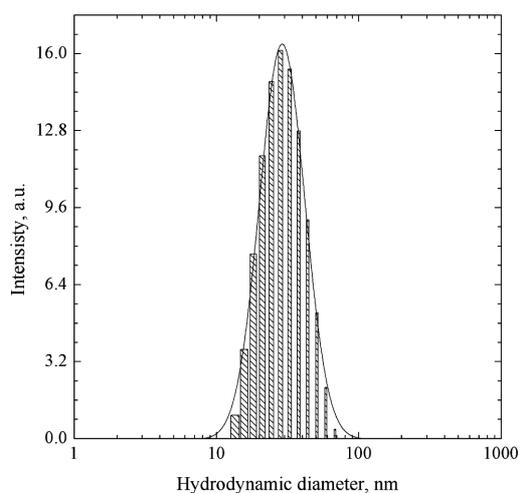


Fig. 1. The size distribution of AuNPs synthesized by reduction of gold(III) complex ions using sodium citrate. Conditions: $C_{0,Au(III)} = 0.25$ mM, $C_{NaCit} = 1.25$ mM, Temperature ca. 100°C

DLS analysis indicated that the mean hydrodynamic diameter of AuNPs has the value $D_H = 29.5 \pm 12.6$ nm. The high negative value of the zeta potential ($\zeta = -46.11$ mV) suggests

the high stability of the synthesized particles (due to the charge stability). In the next stage of our studies microscopic images of synthesized AuNPs have been taken. The example of TEM analysis is shown in Fig. 2. It can be observed that obtained particles have a spherical shapes and narrow size distribution. Size of about 90% of the particles did not exceed 15 nm.

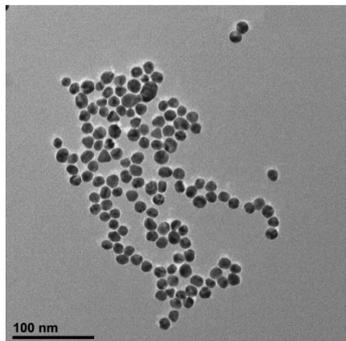


Fig. 2. TEM images of the AuNPs synthesized by the reduction of gold(III) complex ions with sodium citrate. Conditions: $C_{0,Au(III)} = 0.25$ mM, $C_{NaCit} = 1.25$ mM, Temperature ca. 100°C

3.2. Functionalization of carbon surfaces

From ζ potential analysis (at pH = 6) it was found that particles of unmodified activated carbon were negatively charged ($\zeta = -12.6$ mV). This renders direct interaction with negatively charged gold nanoparticles impossible. After modification of the AC surface with aliphatic amines, positive charging of the carbon surface can be observed at pH = 6. For ethanolamine the ζ potential increased to ca. +15.6 mV, while for secondary amines (diethylene triatramine and triethylene tetra mine) smaller, but still essential changes of ζ (+2.1 and +4.9 mV, respectively) have been registered.

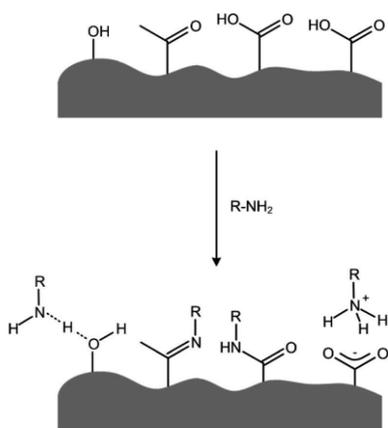


Fig. 3. The scheme of the reaction of primary, aliphatic amines with oxidized carbon surface. Secondary amines should interact primarily on electrostatic pathway

Oxidative treatment of various carbon samples results in functionalization of their surface with hydroxylic and carboxylic groups. Also, the formation of aldehyde functionalities cannot be excluded, especially for the samples of organic origin that contain residual hydrogenated fragments [21]. These groups can further react with primary and secondary amines yielding the whole range of products. E.g., the primary amines can interact with carboxylic groups and aldehyde

giving amides and Schiff bases, respectively (Fig. 3). The secondary amines interact mainly electrostatically forming ionic bonds with different functionalities present at the carbon surface.

Despite strong covalent interactions of primary and electrostatic ones of secondary amines with carbon surfaces, multilayer adsorption is very probable because aliphatic amines tend to form strong hydrogen bonds. This multilayers explains well the observed attraction of gold nanoparticles at carbon surfaces (*vide infra*)

3.3. Deposition of gold nanoparticles

After addition of 10 mL of colloidal gold solution to the samples containing 0.2 g of amine-modified activated carbon, the complete decoloration of samples occurred. Spectrophotometric analysis indicates disappearance of the LSPR band which can be explained by the attraction between AuNPs and amine-functionalized carbon (Fig. 4).

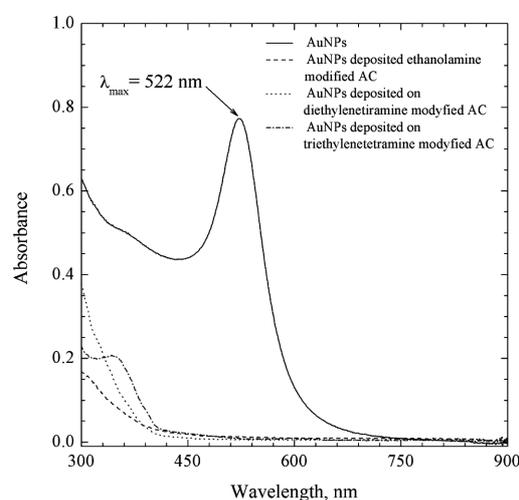


Fig. 4. Plasmon resonance absorption band of AuNPs present in the precursor solution and the spectra of the filtrate after AuNPs deposition on AC functionalized with ethanolamine, diethylenetriamine and triethylenetetramine. Conditions: $C_{0,Au(III)} = 0.25$ mM, $C_{NaCit} = 1.25$ mM, Temperature ca. 100°C

This attraction, deriving from the opposing electric charges of the reactants, may result in efficient adsorption of AuNPs onto carbon surface. At the beginning, the interaction mostly involves electrostatic interaction. Next, direct contact between gold nanoparticles and amine chains (in the case of multifunctional modifiers) results in the formation of strong gold-nitrogen coordination bonds [22-24]. Microscopic analysis (Fig. 5) of the obtained samples show that in case of all AC surface modifiers, it is possible to deposit gold nanoparticles on such prepared carbons.

However, the size and morphology of AuNPs deposited differs slightly from morphology of initial AuNPs present in solution. It can be seen that in case of ethanolamine application the deposited gold particles doesn't form aggregates and AC surface is covered with AuNPs, uniformly. These nanoparticles did not exceed 15 nm in diameter. In case of AC functionalized by diethylenetriamine (Fig. 6), and triethylenetetramine (Fig. 7) deposited AuNPs indicate the tendency to forming larger agglomerates. However, the size of singular

Au particles, remain the same (ca. 10 nm) as in precursor solution.

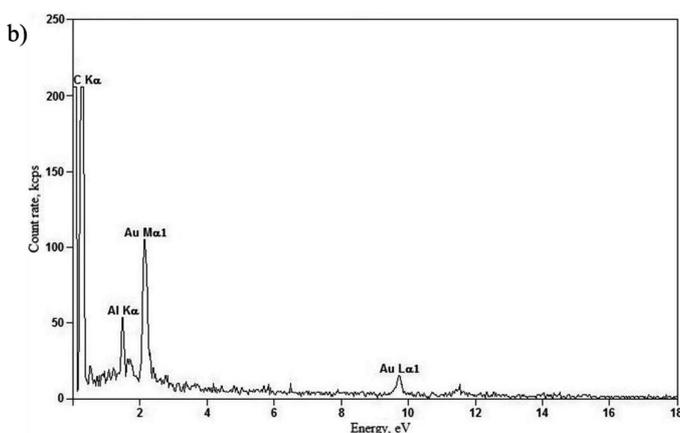
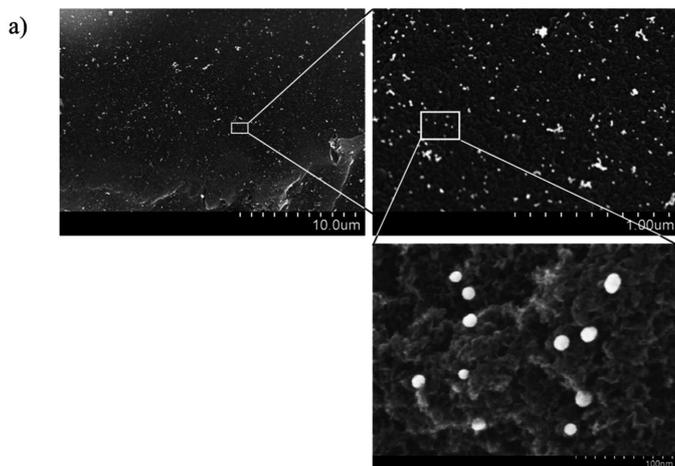


Fig. 5. a) SEM micrographs of AuNPs deposited on 10-CO Organosorb AC modified with ethanolamine molecules; b) EDS analysis of deposits. Conditions: $C_{0,Au(III)} = 0.25$ mM, $C_{NaCitrate} = 1.25$ mM, Temperature ca. 100°C

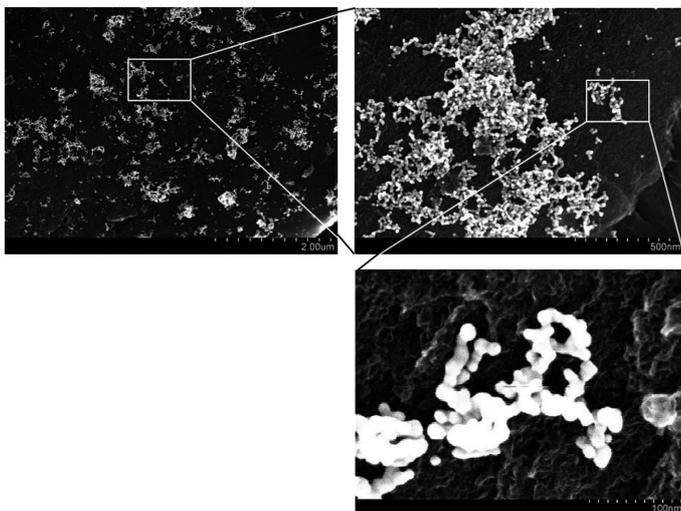


Fig. 6. SEM micrographs of AuNPs deposited on the 10-CO Organosorb AC modified with diethylenetriamine molecules. Conditions: $C_{0,Au(III)} = 0.25$ mM, $C_{NaCitrate} = 1.25$ mM, Temperature ca. 100°C

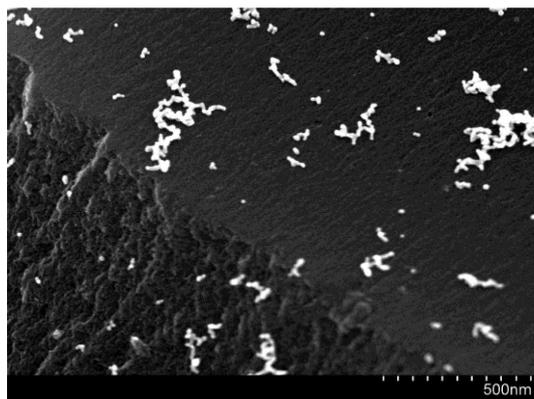


Fig. 7. SEM micrographs of AuNPs deposited on the 10-CO Organosorb AC modified with triethylenetetramine molecules. Conditions: $C_{0,Au(III)} = 0.25$ mM, $C_{NaCitrate} = 1.25$ mM, Temperature ca. 100°C

Formation of AuNPs aggregates is most likely related to the structure of amines used. Longer aliphatic chains may facilitate aggregation of gold nanoparticles due to the presence of coordination between nitrogen and gold atoms. Furthermore, individual amine chains can interact via hydrogen bonding (*vide supra*). Therefore some of the amine molecules are covalently attached to the surface, while other molecules can be adsorbed at the point of covalent modification due to hydrogen bonding. These molecules, facilitate attraction of individual gold nanoparticles and probably yields their aggregation. Thus, covalent modification of carbon surfaces creates a kind of receptor site which scavenges multiple gold nanoparticles and aggregates them with long pendant amine chains. As a result, formed surface aggregates can be stabilized simultaneously by covalent, coordination and hydrogen bonds. The mechanism suggested above is schematically shown in Fig. 8.

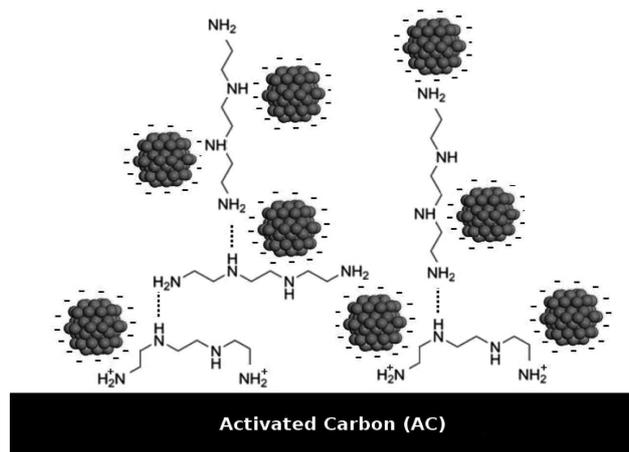


Fig. 8. The suggested mechanism for bridging of the amine and adsorption of AuNPs on the AC surface modified with triethylenetetramine molecules

4. Conclusions

After functionalization of activated carbon (AC) with amines, gold nanoparticles are electrostatically attracted by the carbon surfaces. This attraction initializes the adsorption process.

The functionalization of AC surface modulates the efficiency of electrostatic interactions between AuNPs and carbon surfaces and influence morphology of AuNPs. Functionalization of activated carbon with short-chained aliphatic amines allows for deposition of uniform AuNPs and prevents against their aggregation. In case of unfunctionalized AC, the deposited AuNPs have submicron sizes.

The application of long-chained oligoamines results in formation of gold aggregates on the carbon surface due to the combined effect of covalent amine grafting, hydrogen bonding and coordination between nitrogen and gold atoms.

Acknowledgements

This work was supported by the European Regional Development Fund under the Innovative Economy Operational Program (Grant No.01.01.02-00-015/09-00) and by National Science Centre (grant No DEC-2011/03/B/ST5/01495).

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