Functionalization of organically modified silica with gold nanoparticles in the presence of lignosulfonate

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ABSTRACT

It is shown that lignosulfonate (LS) can be used as an effective reducing agent for gold ions and simultaneously as a stabilizing agent for gold nanoparticles (AuNPs). When organically modified silica is introduced to the reaction mixture, most of the AuNPs grow on the surface of the silica due to hydrophobic interactions between LS and organic layers covering the solid particles. It was also found that the structure of the organic layer is crucial for the effective deposition of gold nanoparticles onto silica spheres in terms of particle size and gold content in the final SiO_2-LS-AuNPs composites. Due to the hydrophobicity of the modified silica it was necessary to carry out the modification in mixed organic/aqueous solvent. The polarity of the organic co-solvent was found to have an effect on the size of the deposited Au-NPs and their quantity. The physical appearance of the obtained hybrids was analyzed by colorimetry, and their structure and composition were evaluated using transmission electron microscopy (TEM). Additionally dispersive and thermal properties were examined by dynamic light scattering (DLS) and thermogravimetry (TG), respectively. The obtained multifunctional hybrid materials exhibits remarkable catalytic activity for the reduction of C.I. Basic Blue 9 (Methylene Blue) by borohydride.

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1. Introduction

Gold nanoparticles are widely used in many fields of science due to their increased surface areas and high density of edge and corner atoms [1]. However, nanostructures of gold or other metals easily undergo aggregation, so that their properties, e.g. the catalytic ability, become progressively worse. To prevent this phenomenon, inorganic carrier materials are used [1]. Silica is a porous material, and its surface can be modified quite easily. Moreover, it is non-toxic, biocompatibility and its low production costs [2]. The combination of gold with an inorganic oxide carrier provides the possibility of creating new materials that combine the advantages of gold and silica nanostructures.

Xu and Perry [3] have synthesized core–shell spheres of Au–SiO_2 using commercial gold colloid and tetraethyl orthosil-

icate as precursors. In turn, Westcott et al. [4] obtained gold nanoparticle aggregates using nanosilica functionalized with 3-aminopropyltrimethoxysilane and *n*-propyltrimethoxysilane and 4-aminobenzene thiol as aggregating agent. Ren et al. [2] synthesized Au nanodots in silica core–shell nanoparticles by reverse microemulsion. The porous structure of the silica and the unique properties of nano-structured gold give the AuNPs–SiO_2 hybrids good catalytic properties, e.g. Tao et al. [5] developed AuNPs supported by bifunctionalized (amino and carboxyl groups) mesoporous silica, which acts as peroxidase and oxidase. Guo et al. [6] synthesized AuNPs embedded in hollow silica nanospheres, which showed high activity in selective oxidation of ethylbenzene and epoxidation of styrene. Peng et al. [1] demonstrated the catalytic activity of gold nanoparticles immobilized on mesoporous silica/graphene oxide in the reactions of reduction of 4-nitrophenol and epoxidation of styrene. Lin et al. [7] prepared a more complicated system consisting of hemin and gold nanoparticles in graphene-mesoporous silica, which acts as an oxidase-peroxidase enzyme system. da Silva et al. [8] demonstrated that mesoporous silica containing Au, Pd and Au–Pd nanoparticles catalyzes

processes of steam reformation of ethanol and oxidation of hydrocarbons.

There are also reports concerning the use of hybrid SiO_2–AuNPs as signal amplifiers for the SERS technique [9,10] and in medical applications in drug delivery systems [11] and photothermolysis [12].

There is a lot of information in the literature of the past few years about methods how to obtain noble metal nanostructures. The most commonly used method for preparing Au-NPs is the reduction of tetrachloroauric acid (Methylene Blue) using sodium citrate. This reaction proceeds at a temperature of $100\,^\circ C$ with rapid stirring. In this reaction, sodium citrate serves both as regulator and as stabilizer [13–15]. Chauhan et al. [16] proposed a reduction of gold using $NaBH_4$. Hussain et al. [17] carried out a similar reaction with L-cysteine as stabilizer. In turn, Guo et al. [18] stabilized the system using 11-mercaptoundecanoic acid. Sugunan et al. [19] obtained gold nanostructures using chitosan as stabilizer. The reducer in this reaction was sodium glutamate.

Luo and Sun [20,21] reported that dendrimers may also be used as stabilizer and reducing agent in the reaction of formation of Au-NPs. Pandey and Chauhan [22] conducted an investigation of gold nanostructures using APTMS (3-aminopropyltriethoxysilane) as a reducer and GPTMS ((3-glycidoxypropyl) methyl-diethoxysilane) as a stabilizer. Milczarek and Ciszewski [23] showed that eugenol can be simultaneously a good stabilizer and regulator in a reaction of Au-NPs formation. Increasingly popular are "green" methods of producing precious metal nanostructures with the use of extracts from various plants, such as coriander leaves [24], *Stachys lavandulifolia* [25], or microorganisms such as *Aspergillus flavus* [26], *Rhodopseudomonas capsulate* [27].

Lignin is an abundant biopolymer, present in wood. The derivatives of lignin called lignosulfonates have hydrophilic sulfonic acid groups and are redox-active. They are a waste product in the manufacture of cellulose from wood (effluent lignosulfonates). We have recently shown that lignosulfonates can be effective "green" reducers of gold ions and simultaneously stabilizers of Au-NPs [28]. Besides, lignosulfonates have been proved to promote the grafting of silver nanoparticles on surface-functionalized silica [29]. For this reason it is important to enable the use of this material and to identify potential applications, which will undoubtedly lead to the development of new technologies for its utilization [30]. Constant technological progress means that more and more new solutions are coming to light in the world of science which make use of lignin and its derivatives [30–33]. Suitably modified, lignin serves as a polarographically active material [34] with the possibility of undergoing a variety of electrochemical reactions, involving both oxidation and reduction, and for that reason it has found interesting applications in recent years in electrochemistry.

The aim of this study was to develop a method for producing new systems consisting of silica-lignosulfonate-gold nanoparticles, wherein the lignin derivative is a reducer and stabilizer of gold nanoparticles. It is expected that SiO_2-LS-AuNPs biocomposites will find applications as functionalized fillers of biologically active polymer composites, catalysts and other nanostructured materials.

2. Experimental

2.1. Materials

Four silicas were used in this study: unmodified silica (Syloid 244, denoted hereinafter as (A), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (B), phenyltrimethoxy silane (C) and octadecylsilane (D), and three kinds of organic solvents: dioxane (1), acetone (2) and DMF (3)). The silane compounds were purchased from Sigma–Aldrich (Germany) and applied as received.

Potassium gold(III) chloride, sodium salt of lignosulfonic acid and C.I. Basic Blue 9 (methylthioninium chloride, Methylene Blue) were purchased from Sigma–Aldrich (Germany). The organic solvents 1,4-dioxane and acetone were produced by POCh (Poland). *N,N*-dimethylformamide was purchased from Fluka (Germany). All used reagents were of analytical grade and were used without further purification.

The unmodified silica Syloid 244 (A) was subjected to preliminary modification with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (B), phenyltrimethoxy silane (C) and octadecylsilane (D) in order to activate the material (5 parts by weight of silane per 100 parts silica). The hydrolyzed modifier dissolved in a mixture of water/methanol in a ratio of 1:4 (v/v) was applied to the silica surface with the use of an atomizer; then the solvent was distilled off by vapor distillation (Büchi Labortechnik, Switzerland) and the modified precipitate was dried in a dryer (Memmert) at $105\,^\circ C$ for about 12 h. A detailed description of the modification process is contained in our previous publications [35–37].

2.2. Synthesis of the SiO_2-LS-AuNPs biocomposites

For the synthesis of the SiO_2-LS-AuNPs biocomposites, 0.2 g of silica was weighed and taken up in 1.5 mL of organic solvent. Then 1 mL of an aqueous solution of lignosulfonate (LS) at a concentration of $12.5\,g\,L^{-1}$ and 2.5 mL of aqueous solution of gold salt at a concentration of $1\,g\,L^{-1}$ were added. The mixture was stirred for 20 min and allowed to stand for sedimentation of the solid. Then the sample was decanted and the precipitate was repeatedly washed with a mixture of water and organic solvent in a ratio of 2:3. The final step was convection drying of the sample to remove residual solvent.

2.3. Evaluation of physicochemical properties

The particle size distribution was determined by an Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK) using the NIBS method.

Colorimetric analysis based on the *CIE L*a*b** color space system was carried out using a spectrophotometer Specbos 4000 (JETI Technische Instrumente GmbH, Germany).

Thermogravimetric analysis was conducted using a TG Jupiter STA449F3 (Netzsch, Germany). Samples having the weight of approximately 10.0 mg were placed in an aluminum oxide crucible and heated from $30\,^\circ C$ to $1100\,^\circ C$ in a nitrogen atmosphere at a rate of $10\,K\,min^{-1}$.

Optical absorption spectra were determined with an Ocean Optics (USA) UV–vis spectrophotometer, model USB4000.

Various microstructure parameters of the gold particles deposited on the surface of silica spheres, e.g. their crystallinity and shape, the size of gold crystallites and the kind of the microstructure defects were obtained from TEM investigations. The TEM sample was prepared by placing a drop of the water suspension with SiO_2-LS-AuNPs on the carbon hole film of a TEM grid (Plano GmbH, Wetzlar, Germany), which was subsequently dried in air. For the microstructure study using TEM, selected area electron diffraction (SAED), high resolution TEM (HRTEM) and energy dispersive X-ray spectroscopy (EDX) were utilized. The TEM experiments were carried out in a JEM2200FS transmission electron microscope (JEOL, Japan), which was equipped with a C_s-corrected illumination system, ultra-high resolution (UHR) objective lens ($C_s = 0.5$) and in-column filter. The acceleration voltage was 200 kV. The corresponding TEM micrographs and SAED patterns were collected with a STEM bright field detector and a $2\,K \times 2\,K$ CCD camera (Gatan Inc., USA). The elemental mapping was performed by using a JED-2200 energy dispersive X-ray analyzer (JEOL, Japan). To determine the mutual orientation of the particles of the AuNPs, evaluation