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The size-controllable, one-step synthesis and characterization of gold nanoparticles protected by synthetic humic substances

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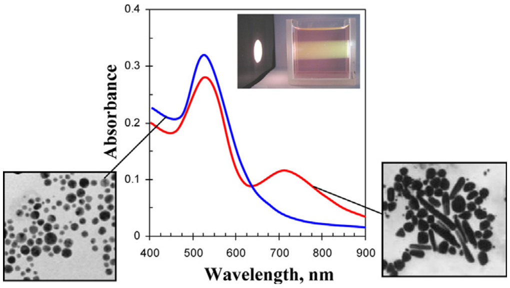
HIGHLIGHTS

- The gold nanoparticles are obtained using different types of synthetic humic substances.
- Synthetic humic substances act as a reducing and stabilizing agents.
- The advantage of synthetic humic substances consists in their reproduced properties.
- The experimental conditions were optimized to attain better yield, controlled size, form and high stability.
- The possible formation mechanism of primary gold nanoclusters is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we demonstrate the use of synthetic humic substances (HSs) in the synthesis of gold nanoparticles in which the unprecedented control of particle size and shape is achieved by varying the experimental conditions. In this reaction, the synthetic HSs are used as a reductive and protective reagent. A number synthetic HSs from different fenol precursors are tested. The nanoparticles formation processes were monitored by UV–visible spectroscopy, and the results were analyzed by transmission electron microscopy and X-ray diffraction. The preference of synthetic HSs over natural HSs is determined by a standardization problem resolution due to the strict control of the HSs formation conditions that expand the areas of application of the gold nanoparticles fabricated with such technique. These nanodispersions are aggregately stable for more than one year. The possible formation mechanism of primary gold nanoclusters is proposed.

1. Introduction

The synthesis of gold nanoparticles (AuNPs) is a growing area of research in materials science because they exhibit the unique properties, different from those of the bulk metal due to their particular size and shape dependent characteristics [1,2]. Because of stability, oxidation resistance, and biocompatibility, AuNPs find a wide application in modern electronics and photonics, catalysis, information storage technology, chemical sensing and imaging, drug delivery and biological labeling methods [3–6]. Unfortunately, high reactionary ability of nanomaterials causes their instability, therefore the important problem is synthesis of nanomaterials of the preset size which throughout enough long period time keep the high chemical and biological activity. In this context the humic substances represent special interest in view of their unique physicochemical and therapeutic properties [7,8]. Humic substances (HSs)

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are highly-abundant organic compounds formed in soils and sediments by the decay of dead plants, microbes and animals [9]. HSs are amorphous, hydrophilic, acidic, polydispersed substances of molecular weight from several hundred to tens of thousands. These macromolecules are operationally classified, according to pH dependent aqueous solubility, into three subcategories: humic acids, which are insoluble at low pH; fulvic acid, lower molecular weight members soluble at all pH; and humin, insoluble at all pH [9]. The combination in one object of the biologically active HSs matrix and of the nanosize gold core opens a perspective of creation of new class of multifunctional drugs with the synergetic enhance of various therapeutic properties for medical application. However the use of natural HSs in synthesis of noble metals nanoparticles is limited by a small amount of studied examples [10–15] that is caused by dependence of the HSs properties on a source and a way of their extraction from natural materials. For example, Baigorri et al. [11] have shown, that the pH change of solution from 9 to 3 is accompanied by increase in the size of AuNPs, using HSs extracted from a chernozem soil at North Bohemia (Czech Republic). Absolutely opposite dependence of the AuNPs size on pH is characteristic for soils, received from a Brazilian peat: with the pH increase the size of nanoparticles increases [14]. The form of AuNPs as a function of pH also depends on a source of HSs used [11,14,15]. Thus the mechanism of metal ions reduction by natural HSs strongly depends on the extraction source. This obstacle hinders development of universal scientific bases for directional preparation of nanomaterials with the desirable properties. Such problem can be practically resolved by implementations of synthetic HSs during AuNPs synthesis, which are characterized by a controllable and reproducible properties [16].

We donot know any reports about use of synthetic substances with the properties which simulate the natural HSs in the synthesis of AuNPs. The main advantage of the synthetic HSs usage as a reducer and stabilizer in the synthesis of AuNPs in comparison with HSs from natural sources is their controllable and reproducable properties that allows to obtain nanoparticles with the standardised properties. This is of great importance for their future application.

In this paper we demonstrate the use of synthetic HSs in the synthesis of AuNPs, where unprecedented control of particle size and shape is achieved by varying the experimental conditions. Our results suggest that the pH value (e.g., addition of NaOH) in the reaction system provides a great influence on the yield of generated AuNPs and on their size. The ratio Au/HSs influences the shape of AuNPs. It is found, that the basic mechanisms of the sizes, forms and stability change of AuNPs prepared with synthetic HSs produced from various phenolic precursors are similar. It allows to use the studied approaches to synthesis of the AuNPs with the use of synthetic substances from other possible phenolic precursors. The size, crystallinity, and morphology of the fabricated AuNPs were determined by UV–vis spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD).

2. Experimental

2.1. Materials

All reagents (analytical-grade) were used as received from Sigma–Aldrich. The deionized water (18 MΩ cm^{-1}) employed for preparation of the studied solution was obtained from a Millipore Milli-Q water purification system.

2.2. Preparation of the synthetic humic substances

A substance with characteristics similar to those of natural fulvic acids was obtained by the method described in Ref. [17]. Generally, the synthetic fulvic acids were prepared by oxidative polymerization reaction in an alkaline medium using pyrocatechol or hematoxylin as precursors. After the reaction time of about 2 h a brown mixture was obtained, which we call as the synthetic fulvic acids from pyrocatechol (FAP) and synthetic fulvic acids from hematoxylin (FAH), respectively. The concentration of synthetic fulvic acids in solution was determined gravimetrically.

The synthesis of synthetic humic acid was described previously [16]. In general, the synthesis was performed during two stages: (i) production of the nitrogen-containg oligomer in the condensation reaction between urotropin and pyrocatechol; (ii) oxidation of the oligomer by molecular oxygen in the alkaline medium.

2.3. Preparation of gold nanoparticles using synthetic humic substances

For finding the optimum conditions of AuNPs formation using synthetic HSs the two sets of experiments were performed. The parameters of these sets are summarized in Table 1. In a typical experiment, in a conical flask of 100 ml we injected 18.5 ml of distilled water, then we added a solution containing 2 mg of synthetic FA (FAC or FAH) and 1.2 ml of 0.1 M solution of NaOH. The prepared solution pH ∼ 11.0. The flask was placed in a water bath at a temperature of 30 °C. Then 0.3 ml of $HAuCl_4$ (0.1 M) were added while stirring vigorously. Reduction of the $[AuCl_4]^-$ ions was controlled by the spectrophotometric technique based on the absorption band intensity measurements at $\lambda = 520$ nm. A constant value of the optical density indicates the final point of the process. The peculiarity of the synthesis of AuNPs using synthetic HA is the need for prolonged refluxing of the reaction mixture (∼2.5 h).

2.4. Characterization

The UV–visible absorbtion spectra of the synthesized AuNPs were recorded with a Lambda 35 Perkin Elmer UV–visible spectrophotometer in the range of 400–700 nm. The 1.5 ml aliquots of gold colloid were diluted to 25 ml in the UV–visible experiments.

The X-ray powder diffraction (XRD) analyses were performed with a DRON-2 X-ray diffractometer (LOMO, Russia) using Fe Kα radiation ($\lambda = 1.9360$ Å) at a scanning rate of 0.01°/s over the 2θ range of 20–120°. The average size of the AuNPs was estimated from the width of reflection in the X-ray diffraction pattern according to the Scherrer's equation [18]:

$$D = \frac{0.89 \cdot \lambda}{\beta_{1/2} \cdot \cos\theta} \tag{1}$$

where $D$is the mean size of the metal nanoparticles (Å), λ is the wavelength of X-ray radiation (Å), $\beta_{1/2}$ – full width at the half-maximum height of the peak (in radians) and θ is the angle of diffraction (in degrees).

The solid samples for XRD analysis were prepared using the AuNPs which were recovered several times from the aqueous

Table 1
Different sets of group experiments for the preparation of AuNPs.

Variables	Parameters of group experiments
Concentration of NaOH	HS (0.1 g l^{-1}), $HAuCl_4$ (1.5 mM), NaOH (0–7 mM), $T = 30$ C (at use of synthetic FAP and FAH) and 100 °C (at use of synthetic HA), $t = 5$ h
Concentration of $HAuCl_4$	HS (0.1 g l^{-1}), NaOH[a] (1.5–8 mM), $HAuCl_4$ (0–3.5 mM), $T = 30$ °C (at use of synthetic FAP and FAH) and 100 C (at use of synthetic HA), $t = 2$–2.5 h

[a] Concentration of NaOH in each case picked up thus that pH of solution in the end of synthesis was within 9–10.5.