A one-pot synthesis of colloidal Ag–Au nanoparticles with controlled composition

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Abstract

We report a one-pot synthesis method for a production of a stable Ag–Au bimetal colloidal solutions (Ag–Au hydrosols) by simply mixing disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) with AgNO_3 and HAuCl_4 in aqueous alkaline medium at 80 °C. We found that Na_2EDTA act not only as a reductant of metal ions and a potent stabilizer of metal nanoparticle size, but also as an effective agent for controlling the composition of the formed nanoparticles, owing to the high complexing affinity of Na_2EDTA to silver ions. It was found that by controlling Na_2EDTA concentration in the reaction mixture it is possible to control not only size and size distribution of a synthesized colloidal bimetallic Ag–Au nanoparticles, but bimetallic Ag–Au nanoparticles composition (Ag/Au ratio) as well.

Graphic abstract

Keywords Bimetal Ag–Au synthesis · Nanoparticles · Ag · Au · Hydrosols · Na_2EDTA

1 Introduction

Currently, systems consisting of precious metal-based nanoparticles with intensive absorption bands in the visible optical region are widely employed in a vast variety of

practical applications. Gold and silver nanoparticles exhibiting surface plasmon resonance (SPR) are of practical interest due to the possibility to tune the spectral position and SPR amplitude by changing composition, size, shape, structure and dielectric surrounding of the nanoparticles

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[1–5]. From the practical standpoint, aside from the morphology and size of such nanoparticle their composition is also a crucial parameter. Composition control opens an additional way for controlling optoelectronic properties and also may enhance the practically important nanoparticle characteristics. For example, it was demonstrated in Ref. [6] that the composition of bimetallic nanoparticles plays an essential role in nonenzymatic detection.

Methods for the preparation of bimetallic Ag–Au nanoparticles using various reducing agents are the subject of a numerous papers [7–12]. For example, in Ref. [13] authors used trimethylamine borane (a reducing agent with relatively low activity) for the preparation of bimetallic nanoparticles with controlled size distribution by exploiting the different reduction rates of silver and gold. In Ref. [14] authors reported the preparation of Ag–Au nanoparticles with controlled composition by the reduction of precursors with oleylamine in the organic medium at different temperatures. In most cases composition control is achieved by varying the relative molar concentration of reactants [15–18] and at the same time a linear relationship between this reaction parameter and the Ag/Au ratio in the final bimetallic nanoparticles is noted.

Regardless of the current progress made in developing of the synthetic procedures, the choice of the reported approaches to the preparation of bimetallic nanoparticles still remains somewhat limited and involved protocols are usually relatively sophisticated. Also, in Ref. [19] authors suggest that the synthetic protocols for high-quality bimetallic nanoparticles with controllable size, morphology, composition and structure have not been sufficiently well-developed thus far.

In this paper we report a simple and single-step approach to the preparation of bimetallic Ag–Au colloids that employs Na_2EDTA , which simultaneously acts as a reductant and an effective agent for regulating the composition of obtained nanoparticles. While synthetic protocols for the preparation of nanoparticles consisting of individual gold or silver using Na_2EDTA (or EDTA) are relatively well-known [20–25], Na_2EDTA -based syntheses of bimetallic Ag–Au nanoparticles have not yet been reported in the literature.

2 Experimental part

Colloidal Ag–Au nanoparticles were synthesized using 0.008 M Na_2EDTA , 0.075 M NaOH , 0.01 M AgNO_3 and 0.023 M HAuCl_4 solutions. In the major set of experiments (except specifically noted cases) the molar ratios of $(\text{Ag} + \text{Au})/\text{Na}_2\text{EDTA}$ and Ag/Au were set equal 1. Total metal concentration $(\text{Ag} + \text{Au})$ in all experiment was 5×10^{-4} M.

Fig. 1 Normalised absorption spectra of colloidal solutions of silver (1), gold (3) and bimetallic (2) nanoparticles prepared at the molar ratios $\text{Me}/\text{Na}_2\text{EDTA} = 1$, $\text{Ag}/\text{Au} = 1$ at 80 °C. Reaction time is 20 min

The synthesis was carried according to the following protocol. Under the intensive stirring, in a 100 ml reaction flask 39.1 ml of distilled water was mixed with 6 ml of NaOH solution and with 3.1 ml of Na_2EDTA solution; then this solution with pH 12.0 alkalinity was heated to 80 °C. The sequence of the further addition of reagents is of principal importance, since it is known that when both silver nitrate and hydrogen tetrachloroaurate are simultaneously present in the solution, insoluble silver chloride may form [8]. In order to avoid this adverse side reaction, 1.25 ml of AgNO_3 solution was added first to the hot pH 12.0 alkaline Na_2EDTA basic solution to produce a clear solution of the strong silver complex with EDTA. Almost immediately after that, 0.55 ml of HAuCl_4 solution was added under vigorous stirring and after 5–10 s the reaction mixture changed colour, so that the final volume of the reaction mixture was 50 ml. For comparison, colloidal solutions of individual silver and gold nanoparticles were prepared under identical conditions.

Samples of colloidal nanoparticles were characterized using optical spectroscopy, transmission electron microscopy (TEM). Optical absorption spectra in 200–800 nm wavelength range were acquired using Cary 500 double-beam spectrophotometer. The composition of nanoparticles was determined by inductively coupled plasma optical emission spectrometry using Prodigy Plus analyser.

3 Results and discussion

Figure 1 shows optical absorption spectra of bimetallic (line 2) and individual (lines 1 and 3) metal nanoparticles. The appearance of only one absorption band in the

spectrum of the colloidal solution of bimetallic nanoparticles ($\lambda_{\max}=472$ nm) positioned practically in the middle relative to the absorption band of silver ($\lambda_{\max}=418$ nm) and gold ($\lambda_{\max}=520$ nm) nanoparticles, indicates of the formation bimetallic alloy.

The presence of only one absorption band (Fig. 1, curve c) in the spectrum of the bimetallic sol ($\lambda_{\max}=472$ nm), located almost in the middle relative to the absorption bands of silver ($\lambda_{\max}=418$ nm) and gold ($\lambda_{\max}=520$ nm), indicates that alloy particles of two metals are formed.

Figure 2 shows TEM-images and particles size distribution of the obtained colloidal nanoparticles. As one can see, Ag–Au bimetallic nanoparticles have spherical shape, narrow size distribution and the mean size of approximately 10 nm, while the nanoparticles of individual metals prepared under the same conditions are larger and less uniform in size.

In further work, the influence of the concentration of Na_2EDTA on the formation of bimetallic sols was studied in

more details. Figure 3 shows the $\lambda_{\max}$ of the colloidal solutions of the obtained Ag–Au nanoparticles as a function of the Ag/Au molar ratio in the starting reaction mixture at different Na_2EDTA concentrations. Similar studies with various reducing agents (but not Na_2EDTA) were conducted earlier [15–18], where a linear dependence was observed. However, our results demonstrate that the investigated dependence is more complex and is altered considerably by the changes in the Na_2EDTA concentration in the reaction mixture (Fig. 3a–c).

Figure 4 shows the $\lambda_{\max}$ position in the optical absorption spectra of the colloidal solution of Ag–Au nanoparticles as a function of the reaction time at different Na_2EDTA concentrations. When there is “insufficient” Na_2EDTA , i.e. molar concentration of Na_2EDTA is lower than the sum of molar concentrations of starting metals (Fig. 4, line 3), the reaction is inhibited and starts approximately after 5 min after the injection of all reagents. Then a slight redshift of the absorption spectrum is observed and $\lambda_{\max}$ changes

Fig. 2 TEM-images and particle size distribution of colloidal metallic nanoparticles prepared in identical conditions: **a**—Ag, **b**—Au, **c**—Ag–Au bimetal

Fig. 3 The influence of Ag/Au molar ratio in the starting reaction mixture on the $\lambda_{\max}$ position in the optical absorption spectra at different Na_2EDTA concentrations: **a**— 1.25×10^{-4} M; **b**— 5×10^{-4} M; **c**— 2×10^{-3} M; reaction time is 20 min

Fig. 4 Variation of $\lambda_{\max}$ in the absorption spectra of Ag–Au colloidal solutions in time at different concentration of Na_2EDTA : 1— 2×10^{-3} M; 2— 5×10^{-4} M; 3— 1.25×10^{-4} M; Ag/Au molar ratio = 1, $[\text{Ag} + \text{Au}] = 5 \times 10^{-4}$ M

from 460 to 467 nm (until 20 min); after that the position of $\lambda_{\max}$ remains unchanged until the end of the reaction (40 min). Moreover, judging by the value of $\lambda_{\max} = 460$ nm, bimetal nanoparticles with a predominance of silver are formed from the very beginning of the reaction.

At the high excess of Na_2EDTA , i.e. when the molar concentration of Na_2EDTA is 4 times higher than the sum of molar concentrations of starting metals (Fig. 4, line 1), a completely different behaviour is observed. As indicated by the visually noticeable colour change, the reaction starts several seconds after the injection of all reagents.

Judging by value of $\lambda_{\max} = 517$ nm, from the very beginning of the reaction, almost pure gold nanoparticles are formed. But over time scene changes rapidly, position of

$\lambda_{\max}$ shifts into the short wavelength region and stabilizes approximately after 20 min. Further increase of the reaction time (>20 min) does not result in significant changes of the $\lambda_{\max}$ at all investigated Na_2EDTA concentrations (Fig. 4, lines 1–3).

TEM-studies (Fig. 5) of the prepared colloids show that Na_2EDTA concentration also considerably alters the average size and size distribution of the Ag–Au nanoparticles.

At lower Na_2EDTA concentration the average size of Ag–Au nanoparticles increases and the size distribution becomes broader. It is worth pointing out that the stability of the prepared colloidal solutions also depends on the Na_2EDTA concentration: at $[\text{Na}_2\text{EDTA}] \geq 5 \times 10^{-4}$ M solutions remain stable for more than 1 year, while at lower concentration ($[\text{Na}_2\text{EDTA}] = 1.25 \times 10^{-4}$ M) solutions are stable only for several weeks.

Considerable difference of $\lambda_{\max}$ in the absorption spectra of the colloidal solutions prepared using different Na_2EDTA concentrations suggests that nanoparticles in these solutions have different composition. To test this assumption a series of analyses were conducted using inductively coupled plasma optical emission spectrometry. Measurement results are provided in the following Table 1 along with the data obtained using optical spectroscopy and TEM.

As one can see from the table, at the same molar ratio of the starting reagents (Ag/Au = 1) as the Na_2EDTA concentration decreases, the nanoparticles become enriched in silver and at the same time their size increases. It is interesting to note that such a trend, i.e. the simultaneous increase in the silver content and nanoparticle size is similar to the one reported in Ref. [13], although the synthetic protocol for bimetallic nanoparticles employed in that paper is completely different (reduction with oleylamine in organic medium).

Fig. 5 TEM-images of Ag–Au nanoparticles prepared at different Na_2EDTA concentrations in the reaction mixture (Ag/Au = 1, time—20 min): **a**— 2×10^{-3} M; **b**— 5×10^{-4} M; **c**— 1.25×10^{-4} M

Table 1 Characteristics of the colloidal solutions of Ag–Au bimetallic nanoparticles as a function of Na₂EDTA concentration (Ag/Au molar ratio = 1, reaction time—20 min)

Na ₂ EDTA concentration in the reaction mixture (M)	Position of $\lambda_{\max}$ (nm)	Ag/Au molar ratio in the bimetal (%)	Average diameter of the bimetallic nanoparticles (nm)
2×10^{-3}	483	25/75	7.4
5×10^{-4}	472	40/60	10.4
1.25×10^{-4}	466	45/55	12.5

4 Discussion

Obtained experimental results demonstrate that the composition of bimetallic nanoparticles, their size and size distribution is determined by the concentration of Na₂EDTA. Theoretical modelling [26] shows that the $\lambda_{\max}$ in the absorption spectra of the Ag–Au spherical nanoparticles is almost linearly dependent on their composition, i.e. the molar ratio of metals in the particle. It should be emphasized that in the majority of works reporting the synthesis of Ag–Au nanoparticles using a range of different reducing agents [15–18] a good correlation with theoretical calculations was observed. However, our results differ noticeably from the data mentioned above.

Such a discrepancy from the existing data may be explained in the following manner. In our case Na₂EDTA plays several different roles. Firstly, it is a reducing agent ensuring the formation of metallic nanoparticles. Secondly, it acts as a stabilizing agent providing small size of the prepared particles (bimetallic nanoparticles are known to reach 100 nm and more in size in the absence of stabilizing agents [6]). Thirdly, Na₂EDTA forms complex compounds with metal ions, and especially strong ones with Ag⁺ ($pK_1 = 7.31$, $pK_2 = 11.31$ [27]). In addition to that Na₂EDTA is known to act as a reducing agent for Au³⁺ ions in the broad range of Au/Na₂EDTA ratios from 1/0.3 to 1/100 [18, 28]. As we have demonstrated earlier [29], silver colloids are formed at Ag/Na₂EDTA = (1/1 ÷ 2/1), that is, when the concentration of Na₂EDTA is less than the concentration of Ag⁺. While at higher Na₂EDTA concentrations (Ag/Na₂EDTA < 1), that is, when the concentration of Na₂EDTA is higher than the concentration of Ag⁺, no reaction occurs. Taking into account all the presented above considerations, the observed peculiar effect of the Na₂EDTA concentration on the $\lambda_{\max}$ dependence of the metals Ag/Au molar ratio is related to Na₂EDTA silver chelating ability. As a result, silver complex compounds of different composition are formed, and a change in the composition of these complexes occurs during the reaction. Thereby silver complex compounds of different composition are forming and transforming over the course of the reaction.

At low concentrations (1.25×10^{-4} M, ratio Ag/Na₂EDTA = 2/1) complexing ability of Na₂EDTA is not too

significant and thus the relationship between $\lambda_{\max}$ position of Ag–Au colloids and the Ag/Au molar ratio is almost linear, except for the low silver concentration region (Fig. 3a). On the contrary, at significant Na₂EDTA concentrations (2×10^{-3} M, ratio Ag/Na₂EDTA = 1/8) complexing ability of Na₂EDTA is significant and therefore Na₂EDTA almost entirely hinder silver nanoparticles formation and as a result at first primarily gold nanoparticles are formed (Fig. 4, initial area of line 1). In this case, the absence of the zero point on the line (Fig. 3c) is very significant and indicates that at high Na₂EDTA concentrations (2×10^{-3} M), in the absence of Au, the synthesis reaction does not occur. In the case of high Na₂EDTA concentrations (2×10^{-3} M) we assume, that gold nanoparticles are formed on early stages of the reaction and then serve as a catalyst for the reduction of silver ions and thus as a result final bimetallic nanoparticles are “enriched” with gold (see Table 1). To test this assumption, we conducted the following experiment. We added 2% molar mass (to the molar mass of silver) of pre-synthesized gold nanoparticles to the reaction medium with high concentration of Na₂EDTA (2×10^{-3} M) and obtained a silver colloid with a pronounced plasmon peak at $\lambda_{\max} = 418$ nm, which, in our opinion, indicates the formation of silver nanoparticles. As we established earlier [29], under such conditions (in the presence of high concentration of Na₂EDTA) without gold nanoparticles the synthesis reaction of silver nanoparticles does not occur.

5 Conclusions

This paper for the first time demonstrates a method of one-pot preparation of stable colloids of bimetallic Ag–Au nanoparticles using Na₂EDTA without any polymeric stabilizing agents. Na₂EDTA was found to act not only as a reductant of metal ions but also as an effective agent for controlling the composition of the formed nanoparticles, which may be explained by the high complexing ability of Na₂EDTA to silver ions. It was found that by controlling Na₂EDTA concentration in the reaction mixture when other reaction parameters are fixed (most importantly the concentration of Ag and Au salts) it is possible to control composition (Ag/Au ratio), size and size distribution of a synthesized colloidal bimetallic Ag–Au nanoparticles.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

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