

# PREPARATION OF METALLIC NANORODS FOR PLASMONIC APPLICATIONS BY CHEMICAL WAY

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## 1. Introduction

Preparation of metal nanoparticles such as gold or silver of various shape is very attractive for applications in plasmonics and sensorics. Plasmonic photovoltaics uses plasmonic effects inherent to metallic nanostructures to enhance the power conversion efficiency of photovoltaic devices. In particular, gold and silver nanoparticles (NPs) strongly absorb light in the visible region as a result of the surface plasmon resonance. The resonance wavelength depends on the nanoparticle size and shape, aggregation state as well as the dielectric constant of the surrounding medium. The optical properties are related to the interaction between the metal conduction electrons and the electric field component of the incident electromagnetic radiation, which in the case of a few metals, such as gold and silver, leads to strong, characteristic absorption bands in the visible and near-infrared region of the spectrum, not observed in the bulk material [1,2,3]. The best way to achieve monodisperse stable metallic nanoparticles in solution is the formation of these particles by chemical methods. This work will focus on two very simple and rapid preparation methods of stable gold and silver nanorods in colloidal solution. The first one is thermal decomposition and reduction of metallic precursor and steric stabilization of nanorods by polymer. The second one is seed-mediated growth where nanorods are stabilized in an aqueous medium by ionic surfactant.

## 2. Experimental part

### 2.1. Chemicals

Ethylene glycol (99.8%), gold(III) chloride hydrate (52%) Au basis, poly(N-vinylpyrrolidone) (PVP; mol wt 40 000), silver nitrate (99%), hexadecyltrimethylammonium bromide (CTAB, 98%), sodium borohydride (98%) were obtained from Sigma-Aldrich (Slovakia); ethanol for UV spectroscopy (99%), sodium citrate (99%), L-ascorbic acid (99%) were obtained from mikrochem (Slovakia); and 1,5-pentanediol (97%) was purchased from Fluka.

### 2.2. Synthesis of gold nanorods in organic solvent

The mixtures of 3 ml HAuCl<sub>4</sub> (0.05 M) in 1,5- pentanediol , and 3 ml PVP (0.01 M) in 1,5- pentanediol were injected alternatively and very slowly into a flask with a boiling mixture of AgNO<sub>3</sub> (different ratio Ag/Au), and 1,5- pentanediol (5 ml). The reaction took place in the

boiling flask for 60 min. at 170 °C. The mixture was stirred with a magnetic stirrer. During the refluxing, the colour of the reaction mixture changed from brown to red.

In the next step, the Au nanorods were precipitated several times with ethanol, centrifuged to remove the solvent and redispersed in ethanol [4].

### 2.3. Synthesis of gold nanorods in water

Preparation of the seed solution: chloroauric acid (1 mM) was reduced in water environment under ambient atmosphere at room temperature with a sodium borohydride (0.1M) to achieve 5 nm seed particles electrostatically stabilized by sodium citrate ( $2.6 \times 10^{-4}$  M).

Preparation of the growth solution: HAuCl<sub>4</sub> (0.24 mM) and CTAB (0.5 M) were mixed at room temperature with an ascorbic acid to reduce the gold ions [3,5].

Step 1: The seed solution (1 ml) was added to the growth solution (9 ml) which contained a weak reducing agent, namely ascorbic acid, which is an ideal secondary reducing agent; it reduces the gold precursor Au<sup>3+</sup> to Au<sup>0</sup> in the growth step and CTAB which supports the controlled growth of the final nanorod shape.

Step 2: The solution from step 1 (1 ml) was added to the growth solution (9 ml).

Step 3: The solution from step 2 (10 ml) is added to the growth solution (90 ml).

### 2.4. Synthesis of silver nanorods in organic solvent

The mixtures of 0.05 g PVP in 5ml EG and 0.5 g AgNO<sub>3</sub> in 5 ml were injected alternatively and very slowly into a flask with 40 ml EG at 175 °C. The mixture was stirred with a magnetic stirrer.

In the next step, the Ag nanorods were precipitated several times with ethanol, centrifuged to remove the solvent and abundant PVP surfactant and redispersed in ethanol.

The nanorods were characterized by scanning electron microscopy SEM (JEOL7500F) and by UV/VIS/ NIR spectrophotometry (SolidSpec 3700 Shimadzu).

## 3. Results and discussion

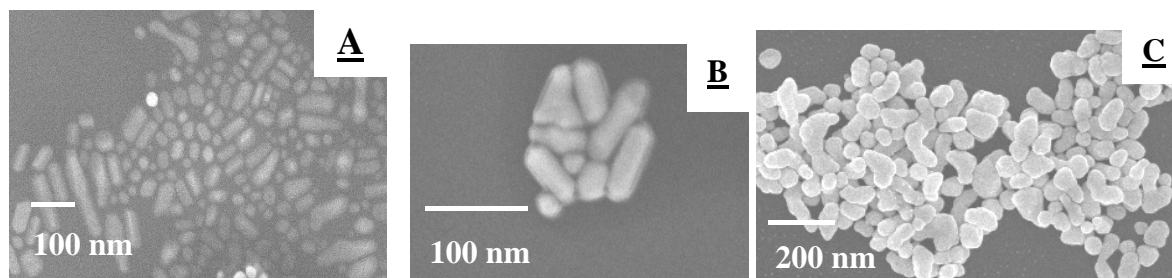


Fig.1: SEM pictures of metallic nanorods deposited on silicon substrate: A) Au nanorods prepared in organic solution with molar ratio Ag/Au 1/7; B) Au nanorods prepared in water; C) Ag nanorods prepared in organic solvent. Nanorods were deposited by spontaneous solvent evaporation in a colloid drop on a silicon substrate.

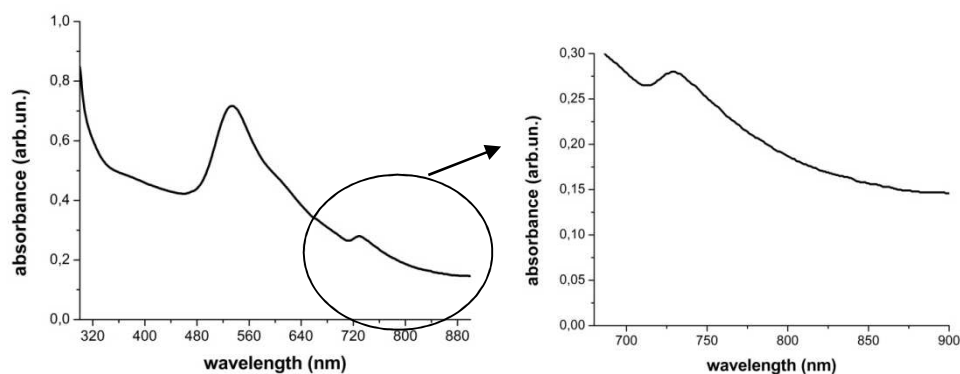


Fig.2: *The UV/VIS spectrum of Au nanorods in water with aspect ratio ~3 measured in colloidal solution. The first peak (530 nm) and second peak (730 nm) show the presence of nanorods in a colloidal solution.*

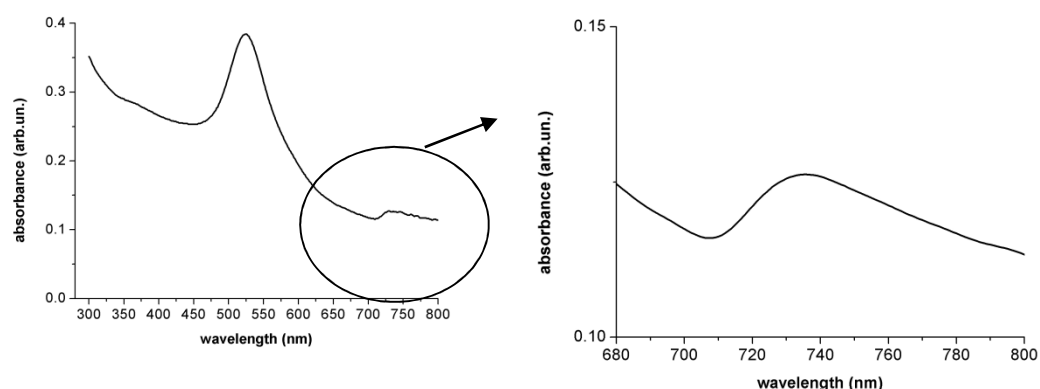


Fig.3: *The UV/VIS spectrum of Au nanorods in organic solvent with aspect ratio ~9 measured in colloidal solution. The first peak (520 nm) and second peak (735 nm) show the presence of nanorods in a colloidal solution.*

The synthesis of gold and silver nanorods in organic solvent was based on thermal decomposition and reduction of chloroauric acid ( $\text{HAuCl}_4$ ) and silver nitrate ( $\text{AgNO}_3$ ) in the presence of stabilizing agents. The thermal decomposition and reduction of metallic precursors were realized in two steps. First, the degradation of the Au and Ag precursor was initiated by its injection into a hot solvent with a high boiling point to achieve temporally separated homogeneous nucleation. Second, the controlled nanorod growth from nuclei formed at nucleation took place. The main preparation step of metallic nanorods is the sequential addition of the precursors to the solvent in which the surfactant is dissolved. This step controls the binding of the surfactant (PVP) to the metallic nanorod core and ensures a low size distribution. The reaction temperature is limited by the boiling point of the solvent.

The colour of the colloidal solution and the nature of metallic nanorods (shape, size, polydispersion) depend on various factors: such as the precursor and stabilizer concentrations, reaction temperature, and reaction time.

A common method to form the shape anisotropy during the nanocrystal growth is addition of the "structure-directing" agent CTAB (cationic surfactant). The main function of CTAB is adsorption on the seed particles to support the nanocrystal growth along specific facets. In the case of preparation of gold nanorods in water, presumably  $\text{AuCl}_4^-$  ions first displace  $\text{Br}^-$  ions and then tightly bind to  $\text{CTA}^+$  micelles. Addition of the reducing agent reduces  $\text{AuCl}_4^-$  to  $\text{AuCl}_2^-$  at the micelle surface. Hence, the growth rate of different nanocrystal facets is determined by the transfer of the micelles and thus gold species toward the facets of the gold seed particles that are also covered with CTAB [6].

For preparation of gold nanorods in organic solutions, low concentration of  $\text{AgNO}_3$  (selective adsorbate) in molar ratios 1/7 Ag/Au to promote nanocrystal growth in a particular direction was used.

The spherical gold nanoparticles absorb light in the visible region around 520/560 nm (depending on their size) and exhibit one peak, while absorption spectrum of gold nanorods exhibits two plasmonic modes and thus two absorption peaks with the positions depending on the aspect ratio of the nanorods. In particular, the UV/VIS spectrum of Au nanorods prepared in water (Fig.2.) exhibits two peaks from transverse absorption band (530 nm) and longitudinal absorption band (730 nm) and absorption spectrum of Au nanorods prepared in organic solution (Fig.3.) exhibits two peaks at 520 nm and 735 nm. The position of the second peak strongly depends on the aspect ratio and shifts towards the near-infrared region (red shift) with increasing aspect ratio while the first peak position is basically determined by the nanorod diameter.

#### 4. Conclusion

Synthesis methods described in this work are suitable for preparation of nanorods with different aspect ratios and hence plasmonic properties in the UV-vis region. In particular, Au nanorods produced in the aqueous medium and in the organic solution exhibit aspect ratios of 3 and 9, respectively. CTAB proved to be very effective as cationic surfactant for production of water-soluble nanorods, because its bromide counterions can chemisorb on metallic surface and its large head-group supports crystal growth in a specific direction. On the other hand, PVP is known as non-ionic surfactant for the synthesis of stable nanorods in organic solution because it creates a strong bond to the surface of the metallic nanostructures.

The proved ability of the presented methods to synthesize Au and Ag nanorods in various solvents with different aspect ratios has direct implications for preparation of tailored plasmonic nanostructures for applications in photovoltaics, optoelectronics, Raman scattering and other fields.

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