

## TEM analysis of gold nanoparticles attached on the surface of organoclay and obtained by two different methods

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This article studies two different methods for synthesis of gold nanoparticles over organoclay. The preparation of the organoclay suspension is done with two different solvents – i-propanol and distilled water. The study is focused on the determination of the size of gold nanoparticles synthesized with the two different methods, using TEM and corresponding computer software. The results from the TEM analysis show that the sample prepared with the solvent distilled water provides better control over the size of the Au nanoparticles.

**Keywords:** synthesis, gold nanoparticles, organoclay, TEM.

### 1. INTRODUCTION

Typical gold nanoparticles synthesis involves the chemical reduction of gold chloride using sodium borohydride and sodium citrate, producing particles with size of 2–10 and 12–100 nm, respectively [1].

To support gold nanoparticles on a stable inorganic or organic matrix is a prime requirement in applications such as catalysis. Varieties of supports such as SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, carbon, clay and polymer for stabilizing gold nanoparticles have been reported [2–5].

The decoration of gold nanoparticles on layered silicates has been reported in the scientific literature by Zhang et al. [6]. They suggested a simple wet chemical method to synthesize clay-APTES-Au nanocomposites. APTES (3-aminopropyltriethoxysilane) acts as the linkage. The silane terminal of APTES formed bonds with the clay surface, while the other –NH<sub>2</sub> terminal bonds to gold nanoparticles.

Another approach was suggested by Belova et al. [7] in which a sonochemical method for intercalation of Au nanoparticles into multilayered Na<sup>+</sup> montmorillonite clays had been used.

Zhu et al. [8] prepared supported gold nanoparticles on clay minerals (particularly montmorillonite

and sepiolite) by cation adsorption from cationic gold precursor Au(en)<sub>2</sub>Cl<sub>3</sub> (en=ethylenediamine). They reported that the increase of the amount of the gold precursor had resulted in agglomeration of gold nanoparticles.

Chen et al. [9] used polyethylenimine (PEI) to prepare Au nanoparticles on polyethylenimine modified montmorillonite. PEI has been used as both a stabilizer and a reducing agent for preparation of Au nanoparticles.

Patel et al. [10] suggested a method for preparation of gold nanoparticles anchored on surfactant intercalated montmorillonite (MMT). They have used two approaches for synthesis of gold nanoparticles. In the first approach the gold nanoparticles have been synthesized by reduction of gold salt in hexadecyltrimethylammonium bromide (HDTA) and dioctadecyldimethylammonium chloride (DODA), followed by exchange of HDTA and DODA solution containing gold nanoparticles into MMT. In the second approach, HDTA and DODA with gold salt has been exchanged with MMT, and next reduced to obtain gold nanoparticles.

Tamoto et al. [11] described new methods to prepare gold nanoparticle/silica nanohelix hybrid nanostructures which form a 3D network in the aqueous phase. Nanometric silica helices and tubules have been obtained by a sol-gel polycondensation on organic templates of self-assembled amphiphilic molecules, further functionalized with (3-aminopropyl)-triethoxysilane (APTES) or (3-mercaptopropyl)-triethoxysilane (MPTES).

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Si et al. [12] described a one-step, surfactant-assisted, seed-mediated method for growth of short gold nanorods with reasonable yield by modifying an established synthesis protocol. Among the various parameters that influence nanorod growth, the impact of the bromide counterion has been closely scrutinized.

Turkevich method [13, 14] of synthesis of gold nanoparticles involves the reaction of small amounts of hot chloroauric acid with small amounts of sodium citrate solution. In general, the method of Turkevich is used to produce modestly monodisperse spherical gold nanoparticles, suspended in water, with diameter of around 10–20 nm. The formation of colloidal gold is a result of citrate ions acting as both a reducing agent and a capping agent. The capping agent is used in the gold nanoparticle synthesis to stop the particles growth and aggregation. Larger gold nanoparticles can be produced if less sodium citrate is added. S. Nasir et al. [15] present in their study the approximate amount of sodium citrate and the corresponding sizes of the prepared gold nanoparticles.

The aim in the present study is to obtain organoclay decorated with high number of gold nanoparticles, eventually leading to electrical conductivity in nanocomposites based on the decorated organoclay. The gold nanoparticles have been synthesized using Turkevich method, without any modifications. The novelty in the present study is the use of two different solvents (i-propanol and distilled water) for dispersion of the organoclay during the process of decoration of the organoclay with the gold nanoparticles.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Clay Cloisite 30B (Southern Clay Products, Inc.), organically modified with methyltallow bis-2-hydroxyethyl quaternary ammonium chloride (MT2EtOH) was used as a substrate for the gold nanoparticle synthesis. Tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) from Sigma-Aldrich was the precursor for the synthesis of the gold nanoparticles. Trisodium citrate dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) from Merck was used as a reducing agent for the synthesis of the gold nanoparticles. Isopropanol from Sigma-Aldrich was used as solvent.

### 2.2. Preparation protocols

#### 2.2.1. First preparation method (i-propanol as solvent)

The Turkevich method [13] was applied for the synthesis of gold nanoparticles using triso-

dium citrate as a chemical reducing agent. 10 ml of 2.05 wt%  $\text{HAuCl}_4$  solution is added to 60 ml of boiling distilled water, and the mixture was heated at 100 °C, and then 5 ml of 18.06 wt% sodium citrate was added. The citrate was selected with the appropriate concentration in order to get the following mole ratio:

$$\begin{aligned} [\text{Au}^{3+}]/[\text{citrate}] &= 0.0006 \text{ mol}/0.0035 \text{ mol} \\ &= 0.17. \end{aligned}$$

After the citrate had been added to the gold salt solution, the mixture was stirred for 5–10 min. The color of the mixture started to change first to blue and then to dark red. After the last color change, the heating was stopped and the mixture was left to cool to room temperature. The size of the gold nanoparticles synthesized using the above  $[\text{Au}^{3+}]/[\text{citrate}]$  mole ratio was expected to be around 10 nm.

Further on, a suspension of 1 g of clay in 30 ml of isopropanol was prepared by ultrasonic treatment for 15 min at 250 W and then poured into the water solution containing the gold nanoparticles. The clay/gold suspension was again submitted to an ultrasonic treatment for 15 min. The mixture was then filtrated and the gold nanoparticles decorated clay (AuNPs/clay) is dried in oven for 16 h at 80 °C.

#### 2.2.2. Second preparation method (distilled water as solvent)

In the first part of the synthesis, 9 ml of 0.1 wt%  $\text{HAuCl}_4$  solution was added to 40 ml of boiling distilled water. The mixture was heated at 100 °C, until it starts boiling again. After that 5 ml of 0.9 wt% sodium citrate was added to the mixture. The citrate was selected with the appropriate concentration in order to perform the following mole ratio:

$$\begin{aligned} [\text{Au}^{3+}]/[\text{citrate}] \text{ ratio} &= 0.0000265 \text{ mol}/ \\ &0.00017 \text{ mol} = 0.16 \end{aligned}$$

After the citrate had been added to the gold salt solution, the mixture was stirred for 5–10 min. The color of the mixture started to change first to blue and then to dark red. After the last color change, the heating was stopped and the mixture was left to cool to room temperature. The size of the gold nanoparticles synthesized using the above  $[\text{Au}^{3+}]/[\text{citrate}]$  mole ratio was expected to be around 10 nm.

Suspension of 1,03 g organoclay in 50 ml distilled water was prepared and then is mechanically mixed for 15 minutes and dispersed with ultrasonic treatment for 15 minutes at 250 W. In the prepared suspension of organoclay in water, 5 ml of 0.9 wt% sodium citrate was added. Sodium citrate has been added to the suspension for two reasons: first, it ensures the completion of the reduction process of the gold cations and second, the sodium citrate acts as a stabilization agent, which prevents the agglomeration of gold nanoparticles. The pre-

pared suspension was poured to the previously prepared solution of gold nanoparticles. After that the mixture was filtrated and the produced organoclay with gold nanoparticles was dried in oven for 16 h at 80 °C.

### 2.3. Characterization methods

#### 2.3.1. TEM

Transmission electron microscope JEOL JEM 2100 with selected area electron diffraction (SAED) was used for characterization of the morphology and element analysis (in a local place) of the sample. Powder samples were deposited on the TEM holders. High magnification TEM was performed with magnification from 50 to 1 500 000 times.

## 3. RESULTS AND DISCUSSIONS

### 3.1. TEM characterization of gold nanoparticles over organoclay using the first method.

TEM method has been used for characterization of the gold nanoparticles size, shape and distribu-

tion over the surface of organoclay. Figure 1 shows the TEM images of the powder sample of 10.6 wt% Au/organoclay synthesized using i-propanol as solvent of organoclay. The TEM analysis of the powder sample prepared using the first method shows formations of big agglomerates of gold nanoparticles (the mean size is around 537 nm). The agglomerates exhibit high variance in terms of both shape and size. There are two reasons for the formation of larger agglomerates of gold particles. The first reason is that the solutions of  $\text{HAuCl}_4$  and sodium citrate have been with 20 times higher concentration than in the second method. The intention of using higher concentrations has been to produce higher number of gold nanoparticles, eventually leading to electrical conductivity in materials based on the decorated organoclay. The second reason for the observed agglomeration is that in the first method we have used isopropanol as a solvent to prepare the suspension of organoclay. The intention of using isopropanol as solvent has been to improve the dispergation of organoclay, due to the presence of organic compound (quaternary alkyl-ammonium cations) in the organoclay. As part of the preparation process, it has indeed been observed that the

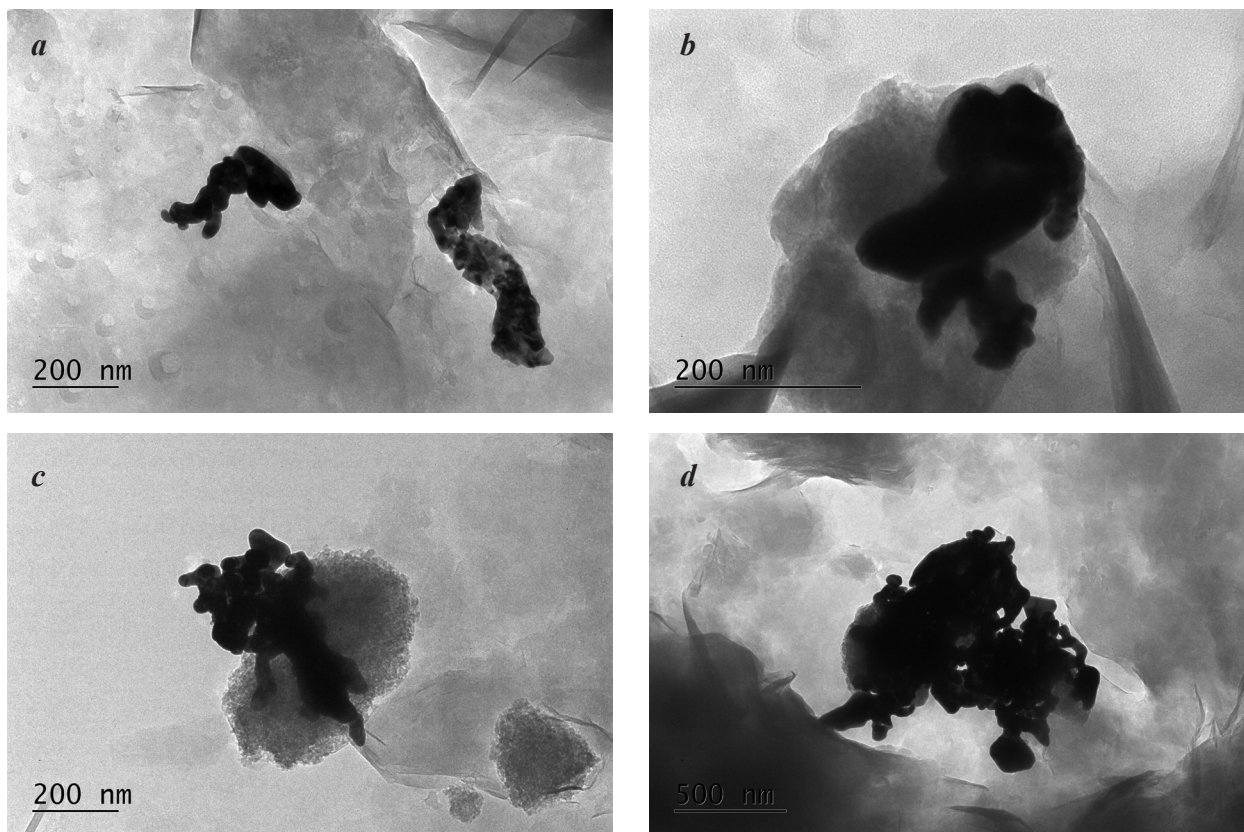


Fig. 1. (a–d) TEM images of the powder samples 10.6 wt % Au/organoclay synthesized using i-propanol.



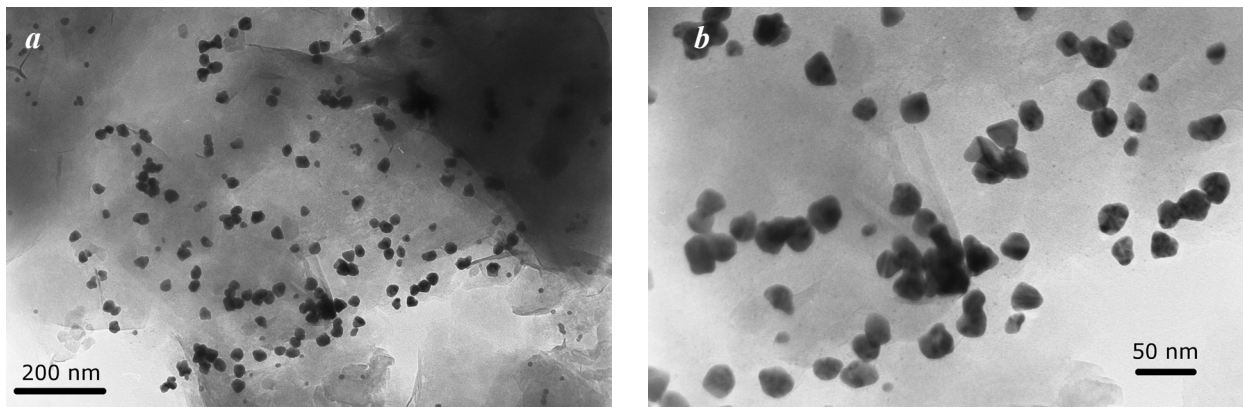


Fig. 2. (a–b) TEM images of the powder samples 0.5 wt % Au/organoclay synthesized using distilled water.

organoclay dispergates better in i-propanol than in distilled water.

### 3.2. TEM characterization of gold nanoparticles over organoclay using the second method

TEM image of gold nanoparticles synthesized over organoclay using the citrate method and solvent distilled water are shown in Figure 2. Almost all of the particles are of similar size and they are placed on the surface of the organoclay. The variance in the shape of the gold nanoparticles is still high.

The size and the shape of the gold nanoparticles shown in the TEM image can be further analyzed using PEBBLES software – a user-friendly software

which implements an accurate, unbiased, reproducible, and fast method to measure the morphological parameters of a population of nanoparticles (NPs) from TEM micrographs. In this software, the morphological parameters of the projected NP shape have been obtained by fitting intensity models to the TEM micrograph [16].

Figure 3 shows the results of the measurement of 60 gold nanoparticles, analysed with statistical methods. The mean and the median size are around 27 nm and the standard deviation is just around 6 nm. This confirms that the majority of the gold nanoparticles, synthesized with the protocol described in Experimental Section 2.2.2, are of similar size, slightly larger than the one expected in the protocol.

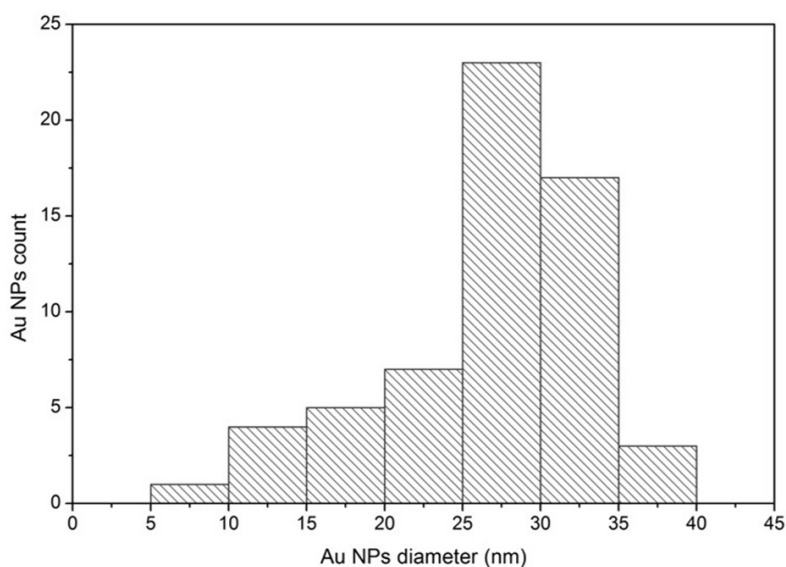


Fig. 3. Histogram and statistical analysis of gold nanoparticles size on TEM image shown in Figure 2.

**Table 1.** Statistical analysis of the size of the gold nanoparticles synthesized over organoclay by two different methods

Method	Statistical analysis of gold nanoparticle sizes (nm)				
	Mean	Standard deviation	Minimum	Median	Maximum
First method using solvent i-propanol	537.47 nm	254.63 nm	269.86 nm	505.42 nm	940.98 nm
Second method using solvent distilled water	26.78 nm	6.50 nm	10.00 nm	28.69 nm	35.38 nm

Table 1 illustrates a comparison between the results of the statistical analysis of the TEM images of the two studied methods. The mean (26.8 nm) and the median (28.7 nm) values in the second method (using distilled water) are much closer to each other compared to the mean (537.47 nm) and median values (505.42 nm) in the first method (using i-propanol). This confirms that citrate method and solvent distilled water (second method) provides better control over the size the synthesized gold nanoparticles compared to citrate method and solvent i-propanol (first method).

#### 4. CONCLUSIONS

In the present study the gold nanoparticles and the dispergation of the organoclay have been obtained with two different methods. The prepared organoclay decorated with gold nanoparticles has been characterized using TEM. The organoclay has been better dispergated in i-propanol, however using i-propanol as solvent and concentrated solutions of  $\text{HAuCl}_4$  with sodium citrate has led to the formation of big agglomerates (the mean size is around 537 nm). The TEM analysis of the samples prepared with the second method (using distilled water as solvent) has shown the formation of individual gold nanoparticles (the mean size is around 30 nm) that have not agglomerated.

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