Bulgarian Chemical Communications, Volume 48, Special Issue G (pp.142 -146) 2016

Characterization of gold nanoparticles synthesized on the surface of organanoclay

V. A. Angelov*, E. H. Ivanov, R. K. Kotsilkova

Institute of Mechanics, Bulgarian Academy of Sciences Acad. G. Bonchev St., bl. 4, 1113 Sofia, Bulgaria

Received October 10, 2016; Revised November 16, 2016

This article studies two methods for synthesis of gold nanoparticles over organoclay – wet impregnation with UV treatment and wet chemical method (using sodium citrate as reducing agent). The study is focused on the determination of the size of gold nanoparticles synthesized with the two methods using TEM and XRD analysis with the corresponding computer software. The methods show a good match in the determined size of gold nanoparticles. The TEM analysis of the sample prepared with the wet chemical method showed better control over the size of the gold nanoparticles.

Keywords: Synthesis, gold nanoparticles, organoclay, TEM, XRD, software application

INTRODUCTION

The interest in the synthesis of metal nanoparticles has been growing because of their unique electronic, optical, thermal and catalytic properties and promising applications in interdisciplinary fields [1]. Various wet chemical methods have been used for synthesis of gold nanoparticles, the most common involve reduction of chloroauric acid ($H[AuCl_4]$) solution using a reducing agent. Two widely used reducing agents: sodium citrate and sodium borohydride are postulated by Turkevich method and Brust method, respectively. Another method for synthesis of gold nanoparticles is wet impregnation, well known in the development of heterogeneous catalysts. It comprises of adding the gold nanoparticles precursor ($H[AuCl_4]$) onto support component (organoclay).

The decoration of gold nanoparticles on layered silicates has been also reported in the scientific literature by Zhang *et al.* [2]. They suggest a simple wet chemical method to synthesize clay-APTES-Au nanocomposites. APTES (3-aminopropyltriethoxy-silane) acts as the linkage. The silane terminal of APTES formed bonds with the clay surface, while the other $–NH_2$ terminal bonds to gold nanoparticles.

Boev *et al.* [3] describe the preparation of hybrid organic-inorganic nanocomposites containing uniform distributions of metal nanoparticles prepared by mixing a preformed nanoparticle colloid with the precursors of ureasil, prior to the sol-gel transition.

Tamoto *et al.* [4] describe new methods to prepare gold nanoparticle/silica nanohelix hybrid nanostructures which form a 3D network in the aqueous phase. Nanometric silica helices and tubules obtained by sol-gel polycondensation on organic templates of self-assembled amphiphilic molecules were further funcionalized with (3-aminopropyl)-triethoxysilane (APTES) or (3-mercaptopropyl)-triethoxysilane (MPTES).

EXPERIMENTAL

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 gold nanoparticle synthesis. Tetrachloroaurate trihydrate (HAuCl4·3H2O) from Sigma-Aldrich was the precursor for the synthesis of gold nanoparticles. Trisoduim citrate dihydrate (Na3C6H5O7.2H2O) from Merck was used as a reducing agent for the synthesis of gold nanoparticles.

Synthesis methods

Impregnation Method in Water (IM wt)

A variation of the wet impregnation method for "decoration" of clay with gold nanoparticles is proposed using water solutions of $HAuCl_4$ as a precursor. Quaternary alkylammonium MT2EtOH, as the organoclay intercalate was used to attach the gold nanoparticles onto organoclay and as a

* To whom all correspondence should be sent:
E-mail: v.angelov@imbm.bas.bg

reducing agent. Solution of $HAuCl_4$ in distilled water was prepared with concentration: 1.73 wt % (3.35 g, 0.00017 mol $HAuCl_4$). After that HAuCl4 water solution was mixed with 1.71 g clay for 30 min. The resulting mixture was further dried in an oven at 80 °C for 8 h then irradiated for several hours using UV light until the color of the treated clay turned to dark gray. Thus, both the organoclay modifier and the UV treatment produced a subsequent reduction of the gold cations to neutral gold atoms forming the gold nanoparticles on the clay platelets. The result of this synthesis was clay decorated with 1.92 wt% of gold nanoparticles with average size ranged from 5 to 150 nm, as described in details in our previous work [14].

Citrate Method (Cit)

The Turkevich method [5] was applied for the synthesis of gold nanoparticles using trisodium citrate as a chemical reducing agent. 10 mL of 2.05 wt % HAuCl4 solution were 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 were added. The citrate was selected with the appropriate concentration in order to get the following mole ratio: $[Au^{3+}]$/[citrate] = 0.0006 mol/0.0035 mol = 0.17. After the citrate was 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 $[Au^{3+}]$/[citrate] mole ratio was between 10 nm and 30 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 and then left for 1 day to let the gold nanoparticles further grow on the surface of the clay platelets. The mixture was then filtrated and the gold nanoparticles decorated clay (AuNPs/clay) was dried in oven for 16 h at 80 °C. Synthesis protocol is described in details in Ref. [6].

Characterization methods

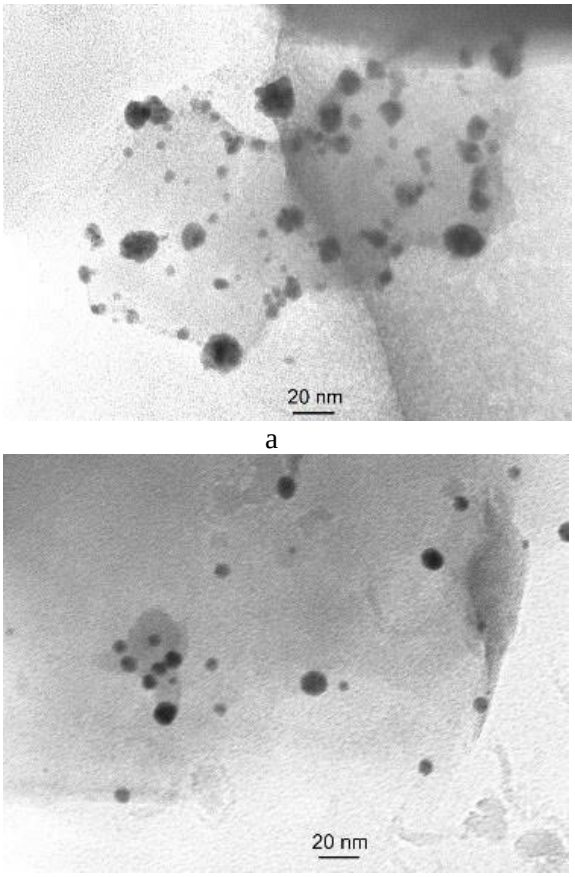
Transmission electron microscope JEOL JEM 2100 was used for characterization of the morphology of the samples. Powder samples were deposited on the standard TEM grids. High magnification TEM has been provided with magnification 40 000 times, 50 000 times and 200 000 times.

The X-ray diffractograms were obtained by using Bruker D8 Advance diffractometer with Cu Kα radiation (λ= 0,15418 nm) and LynxEye detector.

RESULTS AND DISCUSSIONS

TEM characterization of gold nanoparticles

Fig. 1 shows the TEM images of synthesized gold nanoparticles using wet impregnation method on the surface of organoclay before and after the UV treatment of the powder.



a

b

Fig. 1. TEM images with 200 000 times magnification of a sample obtained using wet impregnation method: a) before; b) after UV treatment

The size and the shape of the gold nanoparticles shown in the TEM images 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 are obtained by fitting intensity

models to the TEM micrograph [7]. The success of each fitting procedure is characterized by a fitting score (GoF). GoF summarize the discrepancy between the observed values and the values expected under the intensity model in question. Lower GoF values means that the intensity model better fits to the observed nanoparticle's morphological parameters.

Using Pebbles software, the gold nanoparticles shown in Fig. 1a) are analyzed and most of them can't be fitted by the standard intensity models with an acceptable fitting score (GoF < 1000) suggesting that the process of formation is still in progress. In Fig. 1b) all of the shown gold nanoparticles are clearly shaped and can be fitted into the standard intensity model of spheres with acceptable fitting score suggesting that the process of formation is significantly advanced compared to the fresh synthesized sample due to the process of photoreduction caused by the UV treatment [8].

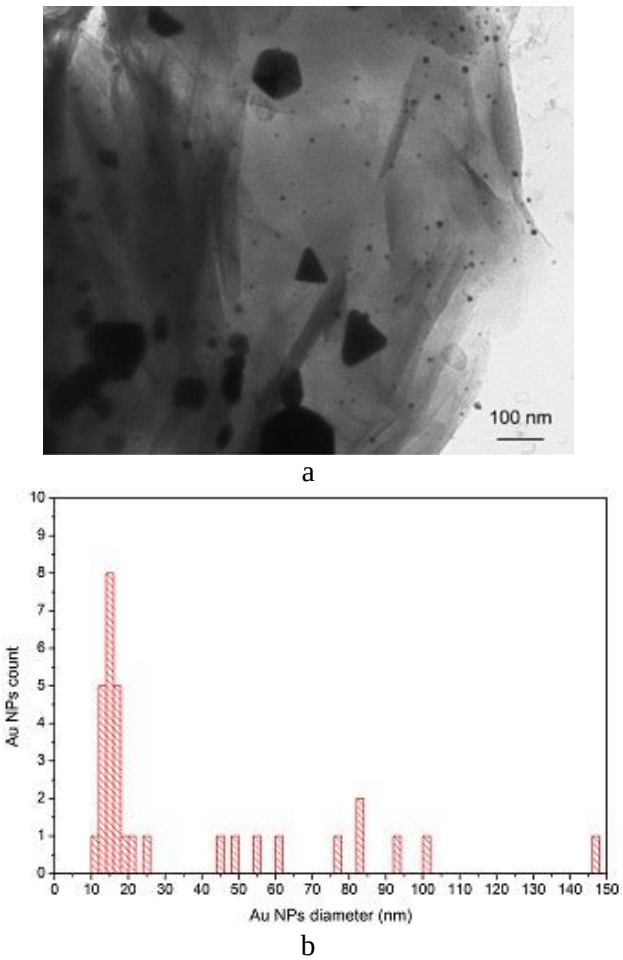


Fig. 2. a) TEM image with 50 000 times magnification of the sample after UV treatment; b) Histogram showing size distribution of 32 gold nanoparticles observed in Fig. 2a.

Fig. 2a shows TEM image of the sample shown in Fig. 1b), but with a smaller magnification of 50 000 times. Fig. 2b shows a high variation of the size of the nanoparticles, especially in the interval 40 nm to 150 nm. The observed nanoparticles have various shapes, mostly spherical, but also with ellipsoid, cylindrical, triangular or pentagonal basis. The agglomeration effect can be contributed to the UV treatment that induces further aggregation of gold nanoparticles [9].

The size variation can be improved by using a wet chemical method (citrate method) shown in Fig. 3.

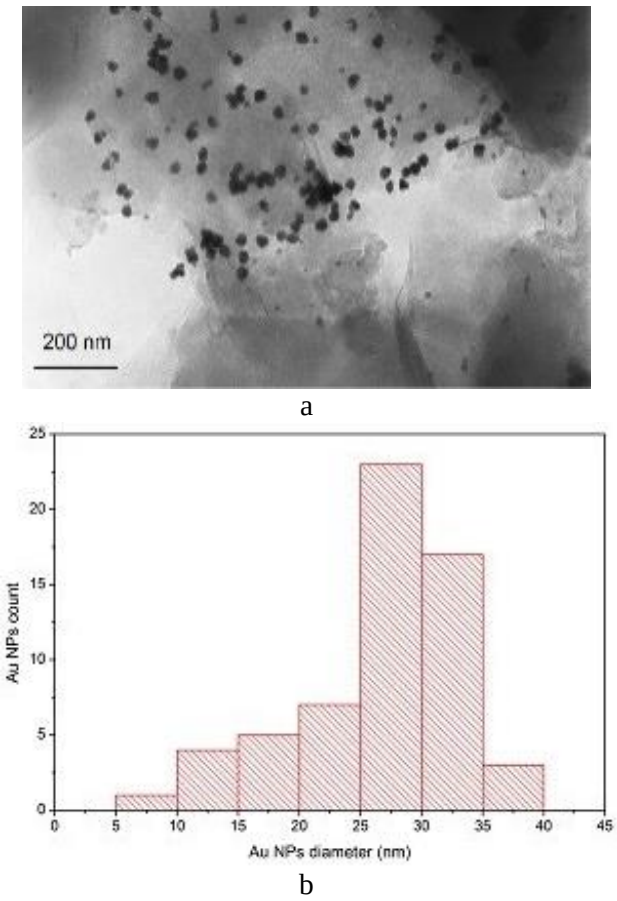


Fig. 3. a)FTEM image with 40 000 times magnification of the sample synthesized using citrate method; b) Histogram showing size distribution of 60 gold nanoparticles observed in Fig. 3a.

Almost all of the particles are with similar size, but the variance in the shape of the gold nanoparticles is still high. The particles sizes are normally distributed with mean value around 28 nm, fitting into the size range defined by the preparation protocol.

Table 1 illustrates a comparison between the results of the statistical analysis of the TEM images of the two studied methods illustrating that the

citrate method provides better control over the size the synthesized gold nanoparticles compared to the wet impregnation method with UV treatment.

Table 1. Statistical analysis of gold nanoparticle sizes showing a comparison between the two methods.

Method	Statistical analysis of gold nanoparticle sizes (nm)				
	Mean	Standard Deviation	Minimum	Median	Maximum
Wet impregnation with UV treatment	35.63	34.31	10.30	16.86	146.69
Wet chemical (using sodium citrate as reducing agent)	26.78	6.50	10.00	28.69	35.38

Table 2. Results from FIT software analysis of XRD diffractogram shown in Fig. 4.

k	λ (nm)	β (rad)	2θ (deg)	θ (deg)	L (nm)
0.94	0.15418	0.292 ± 0.0049	38.218	19.109	30.01

XRD characterization of gold nanoparticles

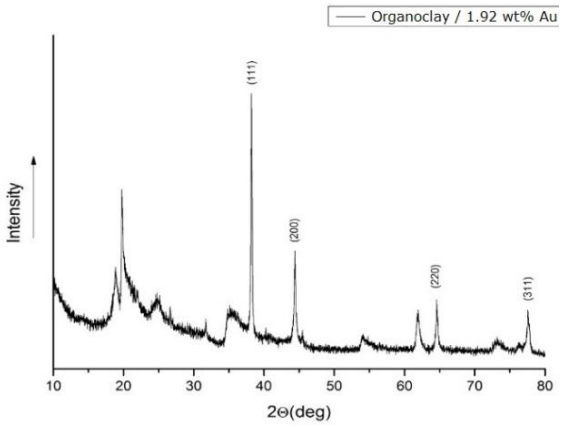


Fig. 4. XRD diffractogram of the sample synthesized using wet impregnation after UV treatment.

Fig. 4 shows the XRD diffractogram of gold nanoparticles synthesized over organoclay using the wet impregnation method after UV treatment. This XRD diffractogram is further analyzed to determine the mean size of the gold nanoparticles in the sample. The crystalline phases are identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files. The mean particle size (L) of gold nanoparticles is calculated based on the line broadening reflections, using the Scherer equation [10]:

$$L = \frac{k\,\lambda}{\beta\,cos\theta}$$

where: β is full width at half maximum of the highest phase in radians; λ is the X-ray wavelength; θ is the Bragg angle; *k* is a dimensionless shape factor.

The calculations are done using FIT software – an interactive software for decomposition and profile analysis of X-ray diffractograms [11]. FIT software uses full width at half maximum method for determination of the peak width and the shape of the observed gold nanoparticles is mostly spherical, therefore k = 0.94 is appropriate value for this case [10].

Table 2 shows the results of the analysis of XRD diffractogram. The mean size of the nanoparticles is calculated to be around 30 nm. This value is relatively close to the mean values calculated from the TEM image analysis.

CONCLUSION

In the present study gold nanoparticles over organoclay were prepared with two different methods – wet impregnation with UV treatment and wet chemical method (using sodium citrate as reducing agent). The gold nanoparticles were characterized using TEM at different stages of the preparation process – before and after the UV treatment. The results of this comparison

demonstrate that the UV treatment influence the formation process of gold nanoparticles. Citrate method showed better control over the size of the Au nanoparticles. XRD analysis was also performed and it provides similar results as TEM analysis.

Acknowledgement: *This work was inspired by the COST Action MP1202.*

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ХАРАКТЕРИЗИРАНЕ НА ЗЛАТНИ НАНОЧАСТИЦИ СИНТЕЗИРАНИ ВЪРХУ ПОВЪРХНОСТТА НА ОРГАНОГЛИНА

В. А. Ангелов, Е. Х. Иванов, Р. К. Коцилкова

Институт по Механика, Българска Академия на Науките

ул. „акад. Г. Бончев“, бл. 4, 1113 София, България

Постъпила на 10 октомври 2016 г.; коригирана на 16 ноември, 2016 г.

(Резюме)

Статията описва два метода за синтез на златни наночастици върху повърхността на органоглина – мокро импрегниране с последващо УВ облъчване и мокър химичен метод (т. нар. цитратен метод, при който се използва натриев цитрат, като редуциращ агент). Фокусирана е, върху определянето на размера на златните наночастици получени по тези два метода чрез използване на ТЕМ и РФА анализ със съответните компютърни програми. Методите показват добро съвпадение на получените резултати в размера на наночастиците, чрез различните компютърни програми. ТЕМ анализът на образеца, получен чрез цитратен метод показва, че по този метод имаме по-добър контрол върху размера на получените златни наночастици.