Published in final edited form as:

Nanoscale. 2012 April 7; 4(7): 2281–2287. doi:10.1039/c2nr12053d.

Microwave-assisted synthesis of gold nanoparticles self-assembled into self-supported superstructures

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Abstract

Passivated gold nanoparticles were synthesized through a microwave-assisted process in a two-phase system, in the presence of 1-dodecanethiol. An average particle size of 1.8 nm of the gold nanoparticles obtained and 0.35 S.D. was determined through HRTEM and STEM analysis. It was observed that these nanoparticles spontaneously self-assemble into self-supported superstructures of 1 μm in diameter avg and 400 nm thickness, yielding an off-white powder which can be handled as a simple powder. XRD analysis indicates that *n*-alkanethiol molecules used as a passivating compound, besides protecting against crystal growth, interact to form cubic ordered arrays between the nanoparticles. This interaction leads to the superstructure formation, with an average distance between nanoparticles in the array, of 3.56 nm. Theoretical calculations and molecular dynamics simulations were performed to analyze the resulting structure.

Introduction

Nanoscale materials have been extensively studied over the last decade, evidencing thoroughly that a reduction in size to a few nanometres modifies the known chemical and physical properties of bulk materials.¹ Such a feature allows the possibility of designing devices with new or improved performance in different technological fields and the tailoring of properties of materials for a specific application.² This has attracted materials science researchers worldwide toward the development of different techniques to produce materials within the size range of a few nanometres. A number of approaches to synthesize

nanomaterials with a controlled size and shape have been reported, wherein the final characteristics of the nanostructure are affected by the fabrication methods and processing conditions.^{3–7} Included are top down dispersion techniques such as sputtering,⁷ laser ablation,^{8,9} mechanical attrition,¹⁰ and others, where sophisticated equipment, high vacuum or pressure conditions are required. Another approach is bottom up, condensation methods, such as those based on colloidal chemistry: inverse micelles,^{11,12} chemical reduction in aqueous,^{5,13,14} organic¹⁵ and two-phase/phase transfer systems,^{16–18} that require the use of external reducing agents such as hydrides or citrate.

In 1986 the use of microwaves was first reported by Gedye *et al.*¹⁹ for rapid organic synthesis, observing the advantages of this technique such as fast heating and reaction completion.^{19–22} This technique has been applied now to develop an alternate methodology to synthesize metallic nanoparticles at relatively short times, allowing a good control of size distribution, and of great importance, it does not require necessarily the use of additional reducing agents.²³ Reduction takes place during the interaction of microwave radiation with reagents in the reaction system forming reducing species *in situ* without the need of mixing other chemicals as reducing agents, thus eliminating additional contamination sources. In this microwave approach, thermal and non-thermal effects can take place, where an increase of thermal energy occurs due to absorption of microwaves as a function of the dielectric properties of the irradiated molecules from chemicals in the reaction system. Solvents can reach temperatures above their boiling points as superheated liquids. Based on this, a kinetic or thermodynamic product can be designed.²⁴ In this process the reaction is controlled through the setting of temperature, power and time of reaction.

Another technological breakthrough in the field of nanomaterials is the formation of 3D nanostructured materials obtained through the assembling of nanoparticles, in which it has been reported that properties can be tuned by the nature of these particles as chemical composition, size, shape and of great importance, by the spacing between them.^{2,25,26} The success of this process is highly dependent on the careful manipulation of nanostructures to position them in a specific array.^{27,28} A particular interest in the generation of ordered arrays of nanoparticles has been raised due to the potential applications of these superstructures, resulting from the collective physical properties of nanoparticles, such as optical and electrical properties. These applications include advanced photonics, surface enhanced Raman scattering (SERS)-based sensors, and electric nanodevices.^{6,29–32}

Here we report on the synthesis of gold nanoparticles passivated by 1-dodecanethiol in a two phase system (toluene/water), based on a microwave induced method. It was found that under the conditions studied, nanoparticles self-assemble spontaneously into flower-like self-supported superstructures, showing domains of ordered nanoparticles. The final product was studied by electron microscopy techniques, X-ray diffraction and infrared spectroscopy. A comparison between this two-phase microwave assisted reaction and the product obtained through the conventional colloidal two-phase^{16,18} method is presented.

Experimental procedure

Synthesis

Gold nanoparticles were synthesized through a microwave induced reaction, starting with a two phase system. No phase-transfer catalyst or external reducing chemical was required. All reagents were used as received. In a microwave high pressure vessel, 0.2 mmol of HAuCl_4 dissolved in 6 ml of H_2O are added to a solution of 1.25 mmol of 1-dodecanethiol in 15 ml of toluene. The system was introduced into an ETHOS EZ Digestion System MicroWave (Milestone, 2.5 GHz, sensor ATC400) equipment. To synthesize the gold nanoparticles this system was continuously irradiated for 60 seconds at 400 W, followed by 60 seconds at 800 W and finally at 1200 W for another 60 seconds, reaching a temperature of 200 °C. After irradiation, samples were cooled at room temperature. At the end of the reaction the product was obtained as an off-white powder and purified in ethanol.

Characterization

For the analysis of the samples, the final product was suspended in toluene. A drop of this sample was mounted over a carbon coated copper TEM grid. Scanning electron microscopy (SEM) was performed in a cold field emission gun (CFEG) Hitachi S-5500 ultrahigh resolution electron microscope (0.4 nm at 30 kV) with a BF/DF Duo-STEM detector. The EDS analysis was performed using a Bruker AXS Quantax spectrometer attached to the SEM microscope. For TEM characterization, the samples were analyzed using a JEOL JEM-2010F (FEG-TEM) microscope operated at 200 kV with a 0.19 nm lattice resolution, which was employed to record high resolution (HRTEM) images of the samples. Also, the samples were analyzed by scanning transmission electron microscopy (STEM) with a JEOL JEM-ARM200F (FEG-STEM/TEM) at 200 kV with a 0.08 nm resolution, equipped with a Cs-corrector (CEOS GmbH) for the electron probe. The probe size used for acquiring simultaneously the high-angle annular dark-field (HAADF) STEM as well as the bright-field (BF) STEM images, was 9 C (23.2 pA) and the CL aperture size was 40 μm . HAADF-STEM images were acquired with a camera length of 8 cm and the collection angle of 50–180 mrad was used, easily satisfying the requirement for the detector to eliminate contributions from unscattered or low-angle scattered electrons. The BF-STEM images were obtained using a 3 mm aperture and a collection angle of 11 mrad was used. The alignment of the microscope was verified through the CESCOR software. The HAADF as well as the BF images were acquired using a Gatan DigiScan camera.

In order to ‘clean’ the raw data and to reduce the noise of the images recorded, the images were filtered using the Richardson–Lucy/Maximum Entropy algorithm implemented by Ichizuka.²⁷

Theoretical calculations

A model of 1-dodecanethiol molecules array was built with the Cerius2 (MSI, 1997) program by molecular dynamic simulation. The minimum energy configuration of this model was achieved through a geometric optimization process. The same optimization procedure was performed to generate a model of decahedral gold nanoparticles with 39 atoms. The geometrical optimization allows refining the geometry of an atomic structure

through an iterative process, which allows adjusting the atomic coordinates and lattice parameters until the system reaches a structure of minimum energy, accomplishing a defined convergence criterion of tolerance. For this study, a convergence criterion of 0.0005 eV was defined with 25 000 iterations. The algorithm applied for calculations was SMART, which is a combination of methods of descending steps,³³ conjugated gradient³⁴ and Newton Raphson.³⁵ A universal potential was applied.³⁶

A model of the superstructure was generated by the above procedure, alternating 1-dodecanethiol molecules and gold nanoparticles. A simulated diffraction pattern of this superstructure model was obtained by Bragg's Law theory with the Cerius2 program (MSI, 1997). The parameters used were a Siemens D-5000 diffractometer, using a copper X-ray source, wavelength of 1.54178 Å and a 2θ display range from 0 to 45°.

Results and discussion

Microwave processing of the two-phase reaction system allowed the reduction of metallic ions to form metallic gold followed by nucleation to form the gold nanoparticles. Arrested growth and stabilization of these nanoparticles was controlled through the presence of the 1-dodecanethiol used as the passivating agent.

The use of microwaves increases the temperature of the two-phase system when energy is absorbed mainly due to the presence of polar molecules which have a high dielectric loss and loss tangent values, such as water,²² while other less polar liquids such as toluene can be heated by conduction through the heated water. Both phenomena control the characteristics of the final product.

An important feature of the synthesis method applied is that the energy supplied from the microwave source can induce the formation of reducing species from the dissociation of chemicals in the reaction system that will allow the reduction of Au^{3+} to Au^0 . Vargas-Hernandez *et al.*²³ reported the reduction of gold under microwave irradiation conditions based on water dissociation ($\text{H}_2\text{O} \leftrightarrow \text{H}_{\text{aq}}^+ + \text{OH}_{\text{aq}}^-$) and self-ionization processes (which might lead to $2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}_{\text{aq}}^+ + \text{OH}_{\text{aq}}^-$). From these reactions, it has been proposed that recombination reactions occur producing electrons that can reduce gold ($\text{H}_{\text{aq}}^+ + \text{OH}_{\text{aq}}^- \leftrightarrow (\text{H}_2\text{O})_{\text{liq}} + e_{\text{aq}}^-$).

Based on these reactions, in the presence of 1-dodecanethiol the following overall reduction reaction can occur in a two phase system of toluene ($\Phi\text{-CH}_3$) and water:

1-dodecanethiol molecules can also contribute to the reduction of gold precursors. It has been reported that alkanethiol molecules can reduce gold atoms from Au(III) to Au(I) forming alkanethiolate complexes with gold.^{3,37,38}

On the other hand, recent work by Huo *et al.*³⁹ and Lu *et al.*,⁴⁰ reported the formation of nanostructures based on the complexation of Au(I) and Au(III) species to organic molecules,

specifically to oleylamine, followed by slow reduction of gold to Au(0). Huo has reported a Au(III) to Au(0) 90.9% and Au(I) 9.1% conversion after 96 h of reaction. This led to the formation of 1D gold nanostructures with diameters of 1.5–1.8 nm, located between layers of oleylamine strands. Also, Shen *et al.*⁴¹ have prepared 2D self-assembled arrays of gold nanoparticles synthesized by microwave processing in the presence of amine compounds, where the organic chains interact with the metallic nanoparticles through the amine group. Another common practice to form superlattices of metallic nanoparticles is based on the use of chemically functionalized hard templates as inorganic unidimensional nanostructures, or soft templates as polymers or biological molecules with specific binding sites, where the assembly will be designed based on the template shape, synthesizing previously passivated nanoparticles with a controlled size.⁴²

In our case, complexation between 1-dodecanethiol and the gold precursor can occur forming a gold alkanethiolate.^{38,43–46} Reduction to Au(0) under a microwave assisted process is carried out within minutes.²³ Results indicate that passivation of growing nuclei occurs before the particles can reach each other, thus preventing their coalescence. These thiol-capped gold nanoparticles were found to form flower-like superstructures with an average size of 1.11 μm and a S.D. of 0.11, as shown in the SEM images in Fig. 1. These superstructures can be handled as a simple powder. It is observed that these superstructures grow radially in two directions, with a thickness of 400 nm avg, maintaining a stable morphology, even when the product is dry (Fig. 1). “Petals” outgrow from the center of the superstructure, mainly towards the sides of the structure as a two-dimensional growth.

The chemical composition was determined by EDS (Fig. 2), showing the presence of 53.66 wt% C, 6.63 wt% S and 39.7 wt% Au. Elemental mapping indicates an even distribution of S and Au throughout the whole superstructure.

According to the analysis performed through different electron microscopy techniques it was observed that most of the gold nanoparticles in the superstructures show a FCC crystal structure (Fig. 3). Very few nanoparticles with a pentagonal symmetry were detected. This indicates that overall, the structure of FCC nanoparticles at these sizes remains stable within the superstructure. These arrested growth processes controlled the formation of the gold nanoparticles to reach an average particle size of 1.8 nm with an S.D. of 0.35, as calculated from HRTEM and STEM images.

It is known that particles of this size grown by the Brust method^{16,18} will tend to have icosahedral cores. However, a clear cut result from our work is that most of the produced nanoparticles tend to exhibit a FCC crystal structure (basically octahedron shape with {111} facets). No doubt that this is related to the fact that the growth is very rapid and the shapes are non-equilibrium shapes but rather dominated by the growth kinetics.

The conventional colloidal two-phase method^{16,18} yields alkanethiol-passivated gold nanoparticles with a slightly wider size distribution, where, in order to select nanoparticles with a narrower size distribution an additional processing has to be applied, such as fractionated crystallization.³⁸ Then, to prepare a superlattice of these nanoparticles, also

different techniques have been reported, such as crystallization in solvent vapors,¹⁷ and self-assembling onto a substrate through micellar systems of gold nanoparticles.³⁰

At higher magnifications, HAADF-STEM analysis of the distribution of gold nanoparticles within the superstructure allows observing large domains of ordered nanoparticles, as the one indicated in the inset in Fig. 4a. The average spacing between nanoparticles in these arrays is 3.56 nm (Fig. 4b and c). The flower-like structure is the result of the intertangled alkanethiol molecules, produced during growth. We believe that this intertangement between alkanethiol molecules happens in the case of most growth methods and has been largely overlooked, considered as a contamination. When these structures are observed at low magnification, nanoparticles are not visible and are missed. On the other hand the very common practice of cleaning the samples with a plasma cleaner or other radiation will destroy the flower superlattice.

Nanoparticles organize themselves into these self-supported flower-like arrays, without the need of any templates or sophisticated equipment, and their distance is dictated by the length of the passivating agent. Spontaneous formation of these superstructures opens the possibility for a new nanoengineered technology for preparing nanostructured materials with homogeneous sized metallic nanoparticles, where properties of the overall material can be tuned as a function of the separation distance between the metallic centers. These superstructures are formed by gold nanoparticles and 1-dodecanethiol, as corroborated by the presented electron microscopy images and IR spectroscopy analysis below. It was corroborated through the IR spectra of the samples that the alkanethiol molecules remain in the sample, with no apparent structural modification caused by microwave irradiation. Fig. 5 shows the infrared spectrum of the superstructures which indicates the main absorption peaks from 1-dodecanethiol, C–H stretch from CH₂ at 2917, 2848 and from CH₃ at 2954 and 2872 (w) cm⁻¹, C–H from –CH₂– deformation (bending or scissoring) at 1467 and from CH₃ at 1376 cm⁻¹. At 720 cm⁻¹ a peak from rock-twist –CH₂– was observed.

X-Ray diffraction (XRD) analysis of the superstructures reveals wide diffraction peaks located at 38.18° 2θ which indicate the presence of a gold phase corresponding to the gold nanoparticles (Fig. 6). Similar XRD analysis was performed on randomly arranged 1-dodecanethiol passivated nanoparticles obtained through the conventional colloidal two-phase method,^{16,18} and in this sample, no distinctive diffraction peaks were present between 5 and 30° 2θ, the only visible signal corresponds to a characteristic small particles peak at 38° 2θ and one at 3.2° 2θ which could be related to the distance between gold nanoparticles.

Also, it was observed that XRD analysis of the self-assembled superstructures showed additional diffraction peaks at 2.36, 4.9, 7.32, 10.48, 11.41, 19.9, 22.78 and 25.66° 2θ.

The origin of these additional diffraction peaks can be attributed to packing of alkyl chains from 1-dodecanethiol.

To study this packing of alkyl chains, theoretical XRD calculations were performed based on simulated arrays of 1-dodecanethiol molecules packed in a cubic cell, with a tilting of 45° in planes (010) and (001) as presented in Fig. 7. Tilting was induced since this is the most stable configuration of the proposed model of the superstructure presented in Fig. 8. This

analysis allowed assigning those additional peaks between 5 and $26^\circ 2\theta$ to a cubic ordered array of 1-dodecanethiol molecules.

In this model the distance between equivalent carbon atoms in adjacent alkanethiol chains is 0.41 nm, and the distance between equivalent sulfur atoms in adjacent alkanethiol chains is 0.47 nm.

A model was constructed by introducing the same alkanethiol molecules into the cubic cell, now attached to gold nanoparticles, as presented in the model of Fig. 8. These calculations were based on the work reported by Naro *et al.*⁴⁷ and Iwasa and Nobusuda.⁴⁸

X-Ray diffraction peaks obtained experimentally and theoretically from the model of the superstructures in Fig. 7 and 8 are presented in Table 1. It was observed that matching of the XRD peaks obtained experimentally and theoretically is very close. Also, experimentally a peak on $2.36^\circ 2\theta$ was also detected, which corresponds to a distance of 3.7 nm.

Slight distortions from the theoretical values can be explained due to the fact that nanoparticles in the experimental superstructure are larger than the ones used in the model, and also due to their behavior as soft matter. As reported previously,¹⁷ alkanethiol molecules attached to the gold nanoparticles from the sulfur atom can have some mobility during the synthesis and they can either expand slightly or contract along the backbone chain.

It is proposed that these superstructures are formed as indicated by the model calculated in Fig. 8. According to this model, nanoparticles attach to the sulfur from alkanethiol molecules, and the self-assembling occurs between alkyl chains probably through Van der Waals interactions⁴⁹ in a similar way as reported for superlattices formed in solvent vapors.¹⁷ However, in this microwave assisted process, this packing occurs in a liquid system under more critical conditions of pressure and temperature. It is observed that the assembled structure in these layers induces a slight bending of the superstructures after the model has been energetically relaxed, in a similar fashion as observed for the experimentally obtained superstructures, this could explain the formation of “petals” in the flower-like superstructures.

Calculations of the system based on this model allowed determining the length of an attached 1-dodecanethiol molecule yielding a value of 1.5 nm, and the distance between two rows of gold nanoparticles (edge-to-edge) theoretically has been calculated as 1.79 nm average. According to this value and the measured size of gold nanoparticles (the mean is 1.8 nm), the average distance from center to center between assembled rows of gold nanoparticles should be 3.59 nm average. These results are close to the XRD peak located at $2.36^\circ 2\theta$.

Based on these calculations, peaks related to the gold nanoparticle ordering appear at higher distances (lower 2θ values) and those originated by the packing of alkyl chains from thiol molecules are located between 5 and $25^\circ 2\theta$ (between 1.5 and 3.4 nm). As for metallic gold distinctive nanoparticle peaks appear at $38.1^\circ 2\theta$ (0.235 nm).

In general, the synthesis of nanoparticles using microwave radiation allows very rapid heating and cooling of the sample. This results in a much better control of the size and shape of the nanoparticles because Ostwald ripening effects are reduced.

From this research and previous reports,^{21,23,37} it is expected that the superstructure formation, morphology and spacing between nanoparticles in the arrays will be influenced by the nature and size of the ligand, the nature of chemicals in the reaction system and the processing conditions of microwave irradiation.

Conclusions

A novel method based on microwave radiation has been proven to yield gold nanoparticles in short reaction times with a high size and shape selectivity. No additional contaminants from reducing agents were incorporated into the product, thus simplifying the processing stage dedicated for purification. Another important feature of this method is the spontaneous formation of superstructures of homogeneous gold nanoparticles, which can be handled as a simple powder, based on the interaction between alkyl chains from 1-dodecanethiol molecules. Results obtained open the possibility for a new nanoengineering technological field for the preparation of nanostructured materials in short times and high yields.

Acknowledgments

The authors would like to acknowledge the following agencies: The Welch Foundation Agency, project AX-1615: Controlling the Shape and Particles Using Wet Chemistry Methods and its Application to Synthesis of Hollow Bimetallic Nanostructures, the National Science Foundation (NSF) PREM grant number: DMR-0934218: Oxide and Metal Nanoparticles: The Interface Between Life Sciences and Physical Sciences. The authors would also like to thank the International Center for Nanotechnology and Advanced Materials (ICNAM) at UTSA, and the RCM Center for Interdisciplinary Health Research (CIHR), and the project award number 2G12RR013646-11 from the National Center for Research Resources, and ININ project CA-216. Authors thank Prof. Necip Guven (University of Texas at San Antonio) for XRD experiments.

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Fig. 1.
SEM image of flower-like superstructures of gold nanoparticles/1-dodecanethiol.

Fig. 2. EDS analysis of the superstructures, showing a chemical composition of C, S and Au, and mapping of S and Au.

Fig. 3. HRTEM image of one section of a flower-like superstructure synthesized by microwave processing. Note that most of the particles have a FCC structure. Inset shows a HAADF-STEM image of a typical nanoparticle from the superstructure.

Fig. 4. (a) HAADF-STEM image of a superstructure. (b) Magnification of the ordered array indicated in (a). (c) Analysis of the section indicated in (b) shows a separation of 3.56 nm avg between gold nanoparticles.

Fig. 5.
Infrared spectrum of the superstructures.

Fig. 6. X-Ray diffractograms of nanoparticles obtained through (a) the two-phase colloidal method and (b) the microwave assisted process.

Fig. 7.
Models of 1-dodecanethiol arrays used to simulate the XRD analysis.

Fig. 8. Model of self-assembled gold nanoparticles–1-dodecanethiol. (a) Side view and (b) top view.

Table 1

Experimental X-ray diffraction peaks of the gold nanoparticle superstructures and calculated peaks and distances of the modeled alkanethiol packing

Experimental 2θ	Experimental d/nm	Corresponding planes from a cubic structure	Calculated 2θ alkanethiol superlattice	Calculated d alkanethiol superlattice/nm	Calculated 2θ Au-alkanethiol superlattice	Calculated d from Au-alkanethiol superlattice/nm
2.36	3.74				2.5	3.531
					3.95	2.235
					4.35	2.029
4.9	1.8	[100]	5.65	1.562	5.6	1.577
7.39	1.195	[110]	8.35	1.058	7.3	1.209
			9.9	0.892	8.1	1.090
			10.5	0.841	9.9	0.892
10.48	0.843	[111]	11.5	0.768	10.6	0.833
11.41	0.774	[200]	14.45	0.612		
		[211]	18.8	0.471	18.8	0.471
19.93	0.445	[310]	19.85	0.446	19.9	0.446
22.78	0.39	[311]	22.2	0.400	22.2	0.400
25.66	0.3469	[321]	25.15	0.353	25.15	0.353
26.00	0.34242	[400]	25.85	0.344		
			26.75	0.332	26.8	0.3329
38.160	0.235	[111] ^a				

^a From the gold phase according to JCPDS 4-784.