A New Way to Prepare Nanostructured Materials: Flame Spraying of Microemulsions

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Received: June 1, 2001; In Final Form: January 8, 2002

In this report we describe a new method to obtain nanostructured coatings or powders based on the flame decomposition of microcompartmentalized solutions. Metal nanoclusters of well-defined size are obtained by reduction of a metal salt inside the water compartment of water in oil (w/o) microemulsions, formed by water in hexane and stabilized by an appropriate surfactant. Metal nanoclusters can be separated from the mother solution by spraying the microemulsion solution into an air/acetylene flame. In this way, nanostructured coating or powder, almost preserving the original structure of the nanoparticles synthesized in the microemulsion system, can be obtained in quantities sufficient for industrial applications. As an example we report the flame spraying of gold microemulsions to produce gold coating onto silicon wafers. To the best of our knowledge, this study reports a new method allowing the use of a microemulsion synthetic pathway for the production of consistent amount of nanoparticles. This method could be of great utility in many applications involving nanoparticles in the fields of physics, chemistry, biotechnology, and biology.

Introduction

Nanomaterials have a relevant importance for industrial applications since they have unique mechanical, optic, and magnetic properties. It is well-known that certain physical and mechanical properties of materials considerably change as their grain size is reduced. For example, improvements in hardness, ductility, and dielectric properties can be obtained. Unfortunately, at present only a few methodologies are available for the synthesis of nanostructured powders or coatings at the industrial level.[1]

Nanopowders can be directly synthesized by using a microemulsion system.[2−5] This method is probably the most powerful because it allows the size and shape of the formed nanoparticles to be controlled. However, the separation of the nanoparticles from the mother microemulsion solution has proven to be very difficult and, even after a tedious procedure of separation, the quantity of powder obtained is scarce and cannot be used for industrial purposes.

Another method to obtain nanostructured coatings or powders consists in the use of thermal spraying systems.[6] Thermal spraying is a complex process that combines particle injection, melting, quenching, and consolidation in a single process. Thermally heated and melted particles are propelled toward a substrate (or simply obtained as a powder) where they are flattened and quenched in a very short time. The gases, combustion gases, or plasma are the sources of the thermal and kinetic energy heating the particles and propelling them to the substrate. As in any coating process, the properties of the coating are a complex function of the process variables. Key parameters are the spray characteristics, the chemical composition, the surface preparation and the temperature of the substrate, the physical properties of the feeding materials (especially density), melting point, and latent heat of fusion. Moreover, the flame temperature and the plasma electric power are fundamental in controlling the final product quality.

One of the most common thermal spraying methods operates with powders[7−9] as feeding material in a plasma or flame spraying system. With this method the operating conditions can be imposed so that the individual grains do not melt upon impacting the substrate. The main drawback of this procedure is that it requires powders with grain sizes greater than 1−5 μm, because of the difficulty in handling powders of smaller grain size. Conventional plasma spraying processes normally use a 10−100 μm sized feedstock to form the coating. When finer particles are used, they have a tendency to flow badly or to agglomerate heavily. The use of liquid solutions instead of powders can in principle overcome this problem.[10] However, the "liquid method" has obtained limited industrial success because of the poor control of the structure of the coated film obtainable by the conventional technology. In particular, the only way to control the grain size of films obtained by flame spraying of a liquid is to control the droplet size, which is really a demanding task. Furthermore, when the droplets are into the flame, they may undergo complex phenomena that are also very difficult to control. Direct continuous ink jet printers have been used to obtain uniformly spaced droplets by superimposing a periodic disturbance on a high velocity ink stream.[11] Also dispersion of powders in various solvents has been used as feedstock materials,[11] but in any case it has not been possible to obtain materials containing nanostructured "units" lower than about 5 μm.

In this report we propose an innovative method, consisting in the firing of a microemulsion. This allows production of large quantities of 10−200 nm monodisperse nanoparticles with a good control of the coated films. This new method can be used

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to produce both nanopowders and nanostructured coatings. As an example of the new method to prepare nanostructured gold coatings by flame spraying, we describe two different kinds of microemulsions, both formed by water in hexane. A gold salt is directly reduced into reverse micelles of ammonium laurate or Brij30 by using hydrazine hydroxide. UV−Vis spectroscopy, light scattering, and transmission electron microscopy (TEM) investigations show the formation in the microemulsions of metallic nanoclusters having diameters between 10 and 100 nm. Suspensions so prepared are then used to feed the flame spraying system and to create nanostructured gold films upon a silicon substrate. Gold films have been investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Results clearly demonstrate that the size of the nanoclusters, present in the microemulsion systems, is preserved upon microemulsions flame spraying, allowing the preparation of nanomaterials of controlled size and shape starting from a relatively simple methodology. In our opinion, this new process for production of nanosized materials overcomes the intrinsic limitations of most of the methods currently used for nanoparticles and nanocoating production. This new method will extend the application of nanotechnologies from the laboratory to industrial scale in chemistry, biology, biotechnologies, and physics.

Experimental Section

The reagents have been chosen in order to obtain a microemulsion that can be easily fired. Brij30, a nonionic surfactant with a short hydrocarbon chain, (tetraethyleneglycododecyl ether: $CH_3(CH_2)_{11}(CH_2CH_2O)_4OH$ purchased from Fluka, purity >95%), and ammonium laurate, anionic surfactant with a relatively short chain and without a metal counterion, $(C_{11}H_{23}COO^−NH_4^+)$, were employed to stabilize microemulsions. Ammonium laurate (Pfalts & Bauer, Inc.) was recrystallized three times from ethanol before use. Hydrazine hydroxide (Merck-Schuchardt, purity >99%) was employed as reducing agent since it can be completely decomposed once fired. The continuous oil phase was hexane (Sigma-Aldrich, purity 95% HPLC grade). Tetrachloroauric acid was purchased from Aldrich Chem. Co. (purity >99%).

Gold nanoparticles have been prepared using the well-known microemulsion technology.[2,3,12,13] The synthesis of the nanoclusters consists of mixing two w/o microemulsions with the same w_0 (w_0 = [H$_2$O]/[surfactant]) value, one containing tethrachloroauric acid and the other containing hydrazine hydroxide. Microemulsions containing the metallic salt have been prepared by adding different amounts of a 1 M aqueous solution of $HAuCl_4\cdot3H_2O$ to a 0.2 M surfactant solution in hexane, to obtain the desired w_0 value. The final metal concentration, expressed as moles of metallic salt over total volume, was always of the order of $10^{−3}$ M.

In the same way, microemulsions containing the reducing agent have been prepared by adding an aqueous solution of hydrazine hydroxide to a 0.2 M surfactant solution in hexane. The concentration of hydrazine was 10 times higher than that of gold because a lower stoichiometric ratio caused the slow precipitation of gold clusters.

Mixing the two microemulsions produces a colloidal suspension of gold nanoclusters. The reaction is instantaneous in the case of Brij30, while it is much slower with ammonium laurate. In both cases, once gold reduction is complete, the colloidal suspension is deep red colored, as typically observed for suspensions of gold nanoclusters.

The temperature has been kept at 25 °C during the entire preparation for the microemulsion with Brij30 and at 30−35 °C for ammonium laurate, since in the latter case microemulsions are not stable at lower temperatures, being the reduction of gold salt too slow.

The formation of gold nanoparticles has been confirmed by UV−Vis spectra obtained with a Lambda 5 Perkin-Elmer Spectrometer. An Applied Photophysics SX 18MV Microvolume Stopped-Flow Reaction Analyzer was used to follow kinetic processes for time scales <10 s. Quasi-elastic light scattering experiments were carried out at a temperature of 25 or 30 °C with a Brookhaven Instrument apparatus (BI9000AT correlator and BI 200 SM goniometer). The light scattered from the sample has been collected at 90° with respect to the impinging 532 nm laser light radiation, double frequency of a pumped Nd:YAG diode from Coherent-Compass 315M, whose power output was 100 mW.

The autocorrelation function has been analyzed by the method of cumulants[15] and the apparent hydrodynamic radius was obtained from the measured diffusion coefficient using the Stokes−Einstein relationship. To obtain a size distribution, the autocorrelation function has been also Laplace-inverted using the CONTIN routine,[16] provided by the Brookhaven software package.

Transmission electron microscopy investigations have been carried out by using a Philips EM201C apparatus operating at 80 kV. To remove the surfactant and to obtain clear TEM images, gold nanoparticles have been flocculated and then washed by ethanol. Samples were prepared by placing a 100 μL drop of ethanol dispersion onto a carbon-coated copper grid. During the deposition the TEM grid was placed on a filter paper and it was dried in a nitrogen atmosphere for 2 days.

The home-built flame spraying setup is formed by a simple airbrush, modified in order to be used with a mixture of air and acetylene (purity index 99.6%) and designed to spray the microemulsions as an aerosol directly into the flame. During the deposition of the nanoparticles the pressure of the air/acetylene mixture was about 1.5 bar, while the air/acetylene ratio was about 1. In these conditions the flame reaches a temperature of about 1200 °C. The length of the flame was 25−30 cm. The aerosol was fed into the flame from a nearly parallel direction to the flame direction. The droplet size and the velocity of the stream (microemulsions and combustion gases) were optimized to make sure the residence time of the microemulsion droplets into the flame was sufficient in order to complete the combustion process.

Nanoparticles were sprayed upon chips of silicon (about 1 × 1 cm²). This substrate ensured a good heat resistance and a smooth surface for scanning electron microscopy and atomic force microscopy analysis. Each deposition was performed using 25 mL of microemulsion, as a function of w_0, but keeping constant the oil/surfactant ratio.

SEM images were obtained with a Philips 514 microscope, without metal coating the samples.

AFM has been used to characterize the shape and size distribution of the gold nanoclusters deposited by flame spraying onto the silicon substrate. Samples were scanned in contact mode and at room temperature with an Explorer TMX 2000 (Topometrix) using a 130 μm air scanner and a silicon nitride microfabricated cantilever with integrated pyramidal tips for contact imaging. Images were taken with on-line filtering and subsequently processed by flattening to remove the background slope.
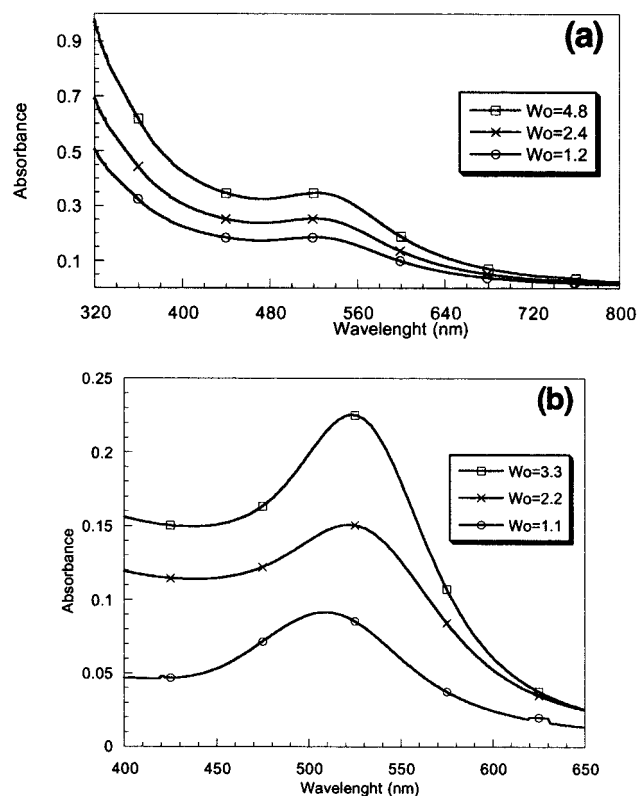
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Figure 1. UV−Vis absorption spectra of gold suspensions obtained with ammonium laurate (a) and Brij30 (b) as surfactant and for different values of w_0.

Figure 2. UV−Vis absorption as a function of time for gold microemulsions obtained with ammonium laurate (a) and Brij30 (b) surfactants and with different values of w_0.

Results and Discussion

It is well-known that when surfactants are dissolved in organic solvents they form aggregates called reversed micelles.[2,3,5] Water can be easily dissolved in the polar core constituted by the surfactant polar headgroups, forming the so-called "water-pool", whose size depends on the mole ratio between the added water and the surfactant, $w_0 = [H_2O]/[surfactant]$. The water pool has been proved to be a useful microreactor for the synthesis of several nanoparticle systems, such as metallic particles, oxide particles, magnetic fluids, and semiconductors.[12] The advantage of using this synthetic pathway is mainly related to the control of the size and shape of the nanoparticle.

As described in the Experimental Section, we prepared nanosized gold particles in microemulsions. The formation of the gold nanoparticles in the microemulsion has been confirmed by UV−Vis absorbance, quasi elastic light scattering (QELS), and transmission electron microscopy (TEM).

Figures 1a and 1b show the UV−Vis absorption spectra obtained upon mixing two precursor microemulsions as a function of water droplet size. It has been reported[17−22] that metallic nanoparticles show an absorption band in the UV−Vis due to the excitation of surface plasmons. For gold nanoparticles the surface plasmon absorption peak appears between 490 and 550 nm, depending on the size of the particles (see Figure 1 and Table 1). The intensity of the absorption maxima shows a distinct dependence on the w_0 value, while the maximum wavelength is red-shifted upon droplet size increased, as it has been well established in previous reports.[17,18,23] This is evident for particles synthesized in Brji30 microemulsions, while nanoparticles obtained from ammonium laurate are too large to show this effect.

The reduction kinetic of the gold salt shows a marked dependence on the surfactant film charge, as shown in Figures
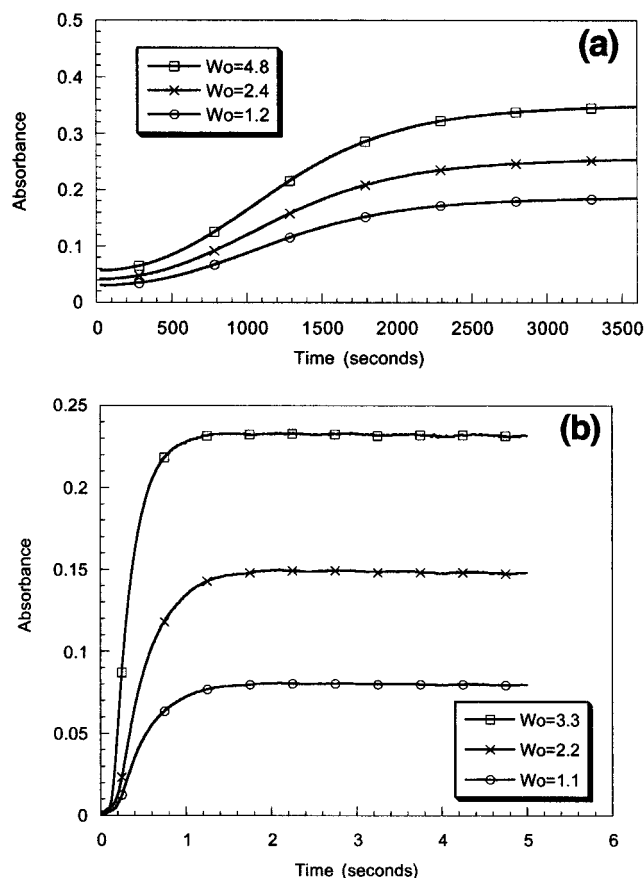
TABLE 1: Plasmon Absorption Peak of Nanoparticles Synthesized with Different Surfactants as a Function of the Water-to-Surfactant Ratio (w_0) and Nanoparticle Mean Diameter

surfactant	W_0	λ_{max}	mean diameter (nm)
Brij 30	3.3	524 nm	∼19.0
Brij 30	2.2	521 nm	∼15.0
Brij 30	1.1	510 nm	∼9.7
ammonium laurate	4.8	523 nm	∼59.0
ammonium laurate	2.4	521 nm	∼46.0
ammonium laurate	1.2	521 nm	∼46.0

2a and 2b. Gold nanocluster formation is practically instantaneous in the case of the Brij 30, while the process is considerably slowed for ammonium laurate/hexane microemulsions. This is probably due to the net negative charge of the surfactant monolayer at the surface water droplet that makes, in the presence of the cationic gold salt, the kinetic exchange among droplets slower than in the case of noninteracting nonionic surfactants.

The mean diameter of the particles has been estimated by dynamic light scattering measurements.[22,24,25] An increase of the water/surfactant ratio leads to an increase of the gold nanoclusters dimensions, as already observed for metal nanoclusters[13,19,23] (see Table 1). Size distributions obtained by light scattering of different microemulsions (see Figure 3) show that microemulsion technology allows a size control of the nanoparticles simply by changing w_0 and/or the surfactant. Moreover, microemulsions obtained from ammonium laurate as surfactant do not allow synthesis of particles with diameter smaller than about 46 nm. It is worth noticing that the "contrast" between

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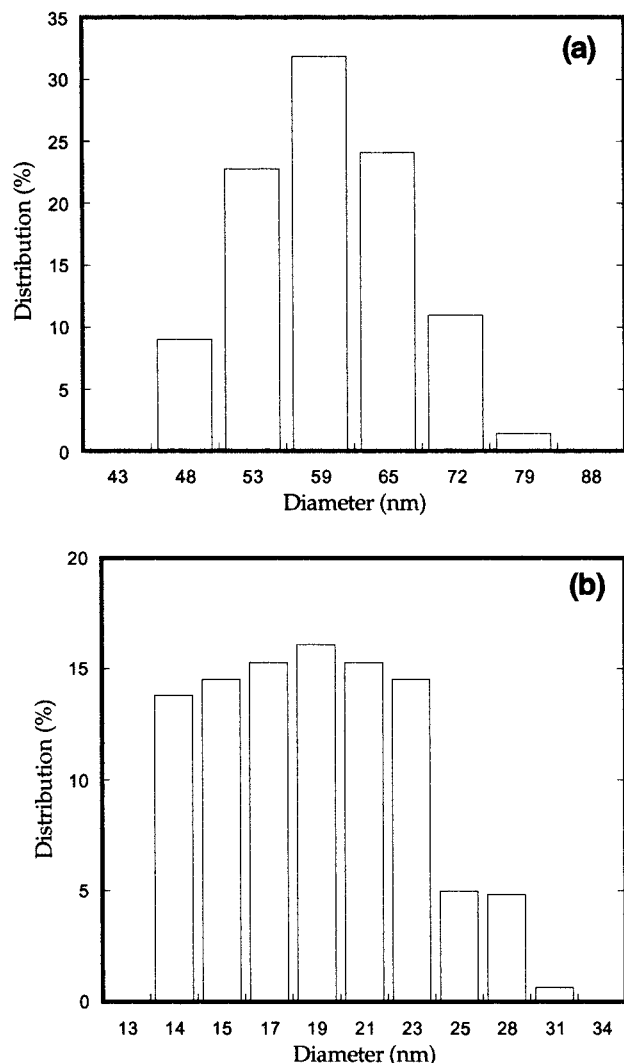*J. Phys. Chem. B, Vol. 106, No. 24, 2002* **6181**

Figure 3. Size distribution of gold nanoclusters in microemulsions obtained from light scattering analysis. Microemulsions have been prepared with (a) ammonium laurate with $w_0 = 4.8$ and with (b) Brij30 with $w_0 = 3.3$.
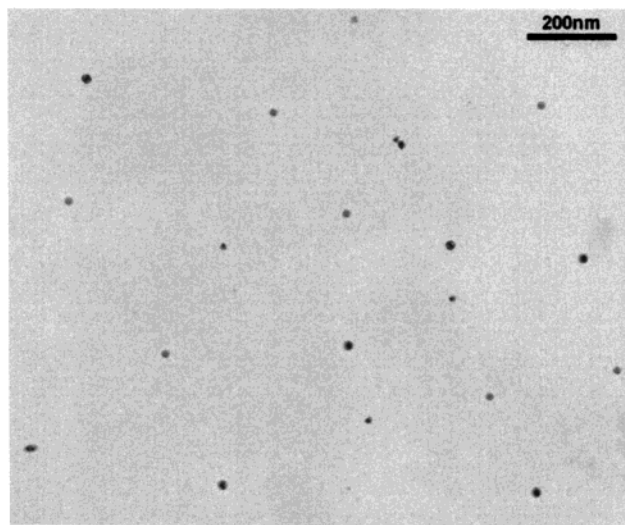

Figure 4. TEM image of a sample obtained from a microemulsion prepared with Brij30 as surfactant ($w_0 = 3.3$).

gold and the oil phase (including both the surfactant chain and the hexane) is so large that in this specific case light scattering
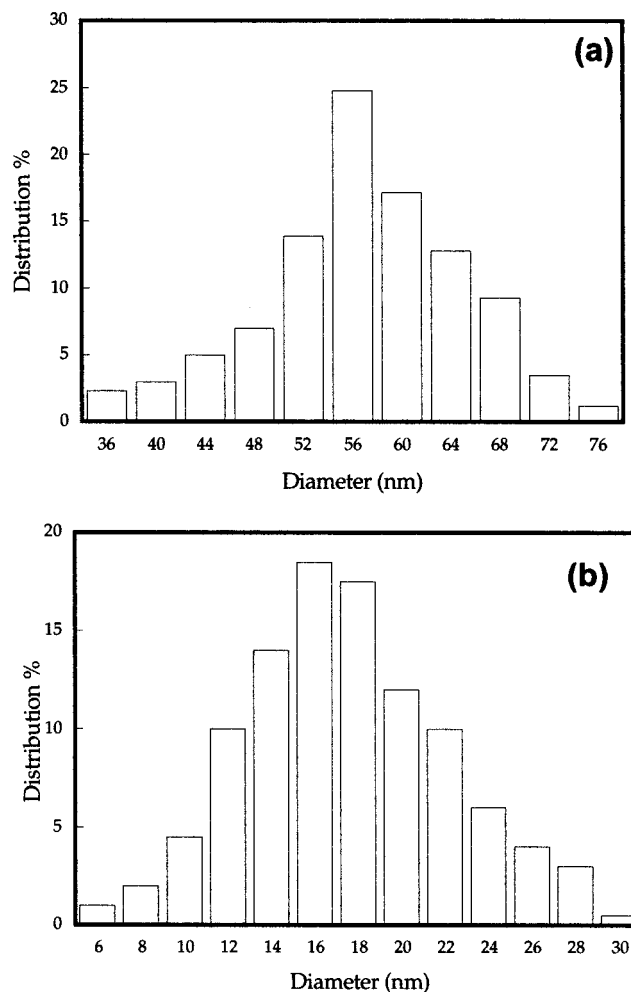

Figure 5. Histograms obtained from TEM images of microemulsions prepared with (a) ammonium laurate ($w_0 = 4.8$) and (b) with Brij30 ($w_0 = 3.3$).
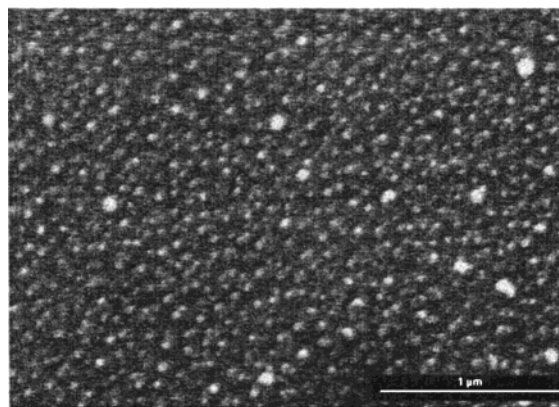

Figure 6. SEM image of a sample obtained by flame spaying of a microemulsion prepared with Brij 30 as surfactant ($w_0 = 2.2$).

only detects gold particles. The size of the particles obtained in this way may be considered in good approximation as the size of the gold clusters. To confirm this point we performed a transmission electron microscopy analysis (see Figure 4). TEM images were collected for samples prepared in microemulsions of Brij 30 ($w_0 = 3.3$) and ammonium laurate ($w_0 = 4.8$). To obtain a good statistic, several different regions of the sample have been investigated. Histograms reported in Figure 5 are obtained by measuring the diameter of about 500 particles. The
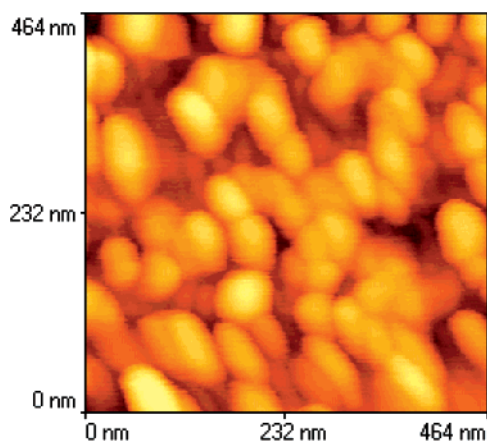
Figure 7. AFM image of a sample obtained by flame spaying of a microemulsion prepared with Brij30 ($w_0 = 2.2$).

particle size obtained by transmission electron microscopy (a mean diameter of about 18 nm for $w_0 = 3.3$ Brij30 and 56 nm for $w_0 = 4.8$ ammonium laurate) are in good agreement with quasi elastic light scattering results (see Table 1).

We notice that the size of the particle produced in the microemulsion water pool is not strictly related to the size of the water pool and to its increase as a function of the water addition. In fact particles here produced are generally larger than those expected from the water pool size. However, the surfactants used for the synthesis were not titrated with respect to their water content and, therefore, the actual w_0 might be larger than the value reported in Table 1, which only indicates the amount of water added to the hexane/surfactant solution.

Gold colloidal dispersions so prepared were directly used as feedstock materials, as described in the Experimental Section. The nanocoated wafers were investigated by scanning electron microscopy (SEM),[26,27] atomic force microscopy (AFM),[28] and X-ray photoelectron spectroscopy (XPS).

The SEM image of a sample obtained by flame spraying a Brij30 microemulsion ($w_0 = 2.2$) is reported in Figure 6. Gold

nanoparticles appear to have a diameter of about 25 nm. Light scattering experiments performed on the same microemulsion system provide a value for the diameter of nanoclusters of about 15 nm. The agreement between the results of the two techniques is fairly good. In fact, a flattening process with a subsequent increase of the nanoparticle diameter is expected to occur when the nanoparticles impact the substrate.

AFM was used to further characterize the shape and size distribution of the sprayed nanoclusters. The gold surfaces are covered in pebble-like clusters of regular dimensions. The nanostructure of the gold films is evident, as shown in Figure 7 for a sample obtained by flame spraying a Brij30 ($w_0 = 2.2$) microemulsion. The mean diameter of the nanoparticles is about 30 nm, in very good agreement with SEM results. The average height of the clusters in around 24 nm.

Figure 8 reports a 3D representation of an AFM image of a sample prepared with Brij30 ($w_0 = 3.3$) showing the shape and size homogeneity (mean diameter of about 35 nm) of the nanoparticles of the gold coating. Figure 9 shows the 3D representation of an AFM image of a sample obtained by flame spraying a microemulsion prepared with ammonium laurate ($w_0 = 4.8$). The mean diameter of the nanoparticles is about 75 nm.

AFM images also provide a qualitative estimation of the height of the nanoclusters on silicon substrate. The observed height is from about half to a third less than the diameter of the nanoclusters, which further confirms their morphology change from spherical to hemispherical caps upon impact with the surface.

XPS analysis[29,30] gives insight on the chemical composition of the flame sprayed coatings. XPS spectra show the presence of gold (4f and 4d core level from pure gold, binding energy $4d_{3/2} = 353$ eV, $4d_{5/2} = 335$ eV, $4f_{5/2} = 88$ eV, $4f_{7/2} = 84$ eV).[30] A 1s carbon graphitic peak (binding energy $= 284.5$ eV)[30] is also observed, while a chemical shift of the aliphatic carbon peak is not detected. These findings lead to the conclusion that the flame combustion of the microemulsion is complete, and no contaminants are present in the uniform film coating. No appreciable dependence of gold 4d and 4f levels on w_0 or on the kind of surfactant could be observed.
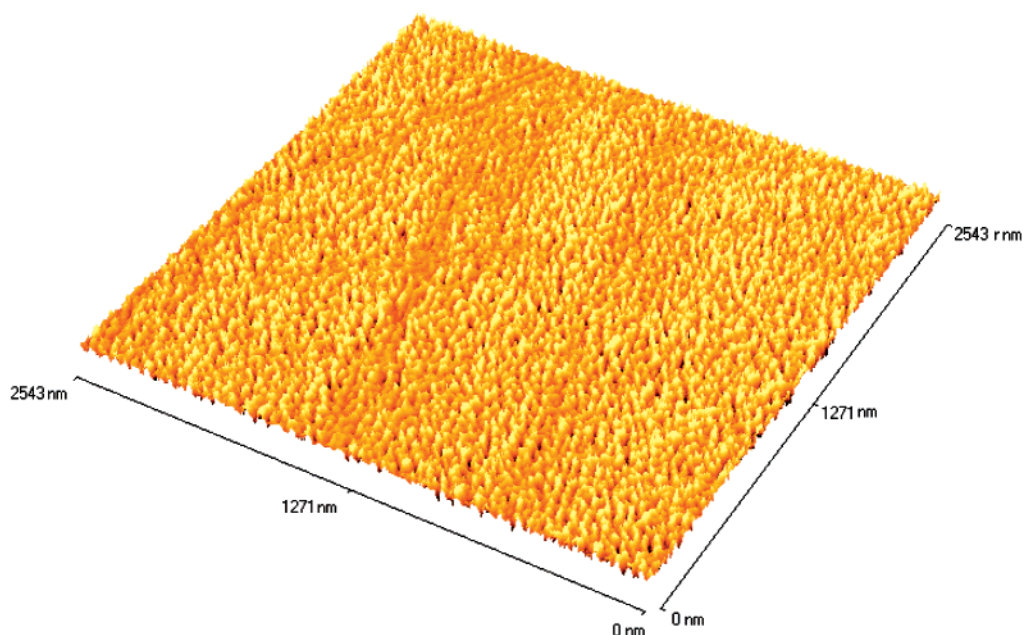

Figure 8. 3D representation of an AFM image of a sample obtained by flame spaying of a microemulsion prepared Brij30 ($w_0 = 3.3$).

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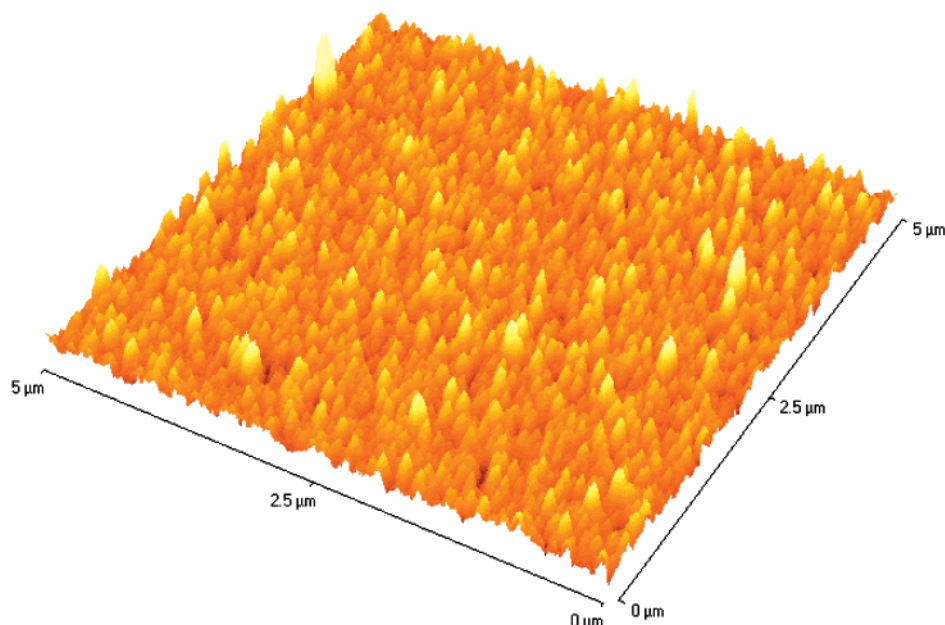*J. Phys. Chem. B, Vol. 106, No. 24, 2002* **6183**

Figure 9. 3D representation of an AFM image of a sample obtained by flame spaying of a microemulsion prepared with ammonium laurate ($w_0 = 2.4$).

Conclusions

Nanostructured materials can be prepared by combining microemulsions and flame spraying methods. Metallic nano-clusters of diameter between 10 and 100 nm have been synthesized in microemulsions. These microemulsions have been used to feed a flame spraying system and form a nanostructured gold film coating onto silicon substrates. Gold coatings have been investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The results clearly demonstrate that the structure and size of the nanoclusters in the microemulsions is preserved upon flame spraying, and that flame spraying can be used successfully to produce nano-coatings or nano-powders.

There are several advantages in obtaining nanostructured materials by combining the flame spraying and microemulsions synthetic techniques. The most relevant is the possibility of obtaining nanoparticles from 1 to several nanometers with a good control of their size and shape. This can be easily achieved by controlling the microemulsion synthetic pathway and the microemulsions structure. Both these aspects are not accessible to conventional flame spraying methods that can produce particles of micrometer size with poor control of the size and shape of the particles. On the other side, the microemulsion route alone produces only small amounts of nanoparticles that are usually of difficult separation from the mother microemul-sion solution, and in most cases the surfactant remains on the nanoparticle as a contaminant.

In conclusion, nanoparticles obtained by microemulsions firing can be produced with a good purity, shape, and size control, and in quantity useful for industrial applications, allowing their use in a very large number of applications in the fields of chemistry, physics, and biology.

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