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Liquid-phase synthesis of thiol-derivatized silver nanocrystals

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Abstract

A liquid-phase method is reported for the preparation of dodecanethiol-derivatized silver nanocrystals. Toluene sols of this material maintain as sols in air at room temperature at least on the timescale of months. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are used to obtain size and structural information about the nanocrystal core while solubility properties and energy dispersive X-ray spectroscopy (EDS) are used to identify the passivating layer. Laser desorption time-of-flight mass spectra (LDTOFMS) of this material show broad peaks in the mass range from 40 to 300 *k*amu. These results are consistent with the synthesized material being a dodecanethiol-derivatized silver nanocrystal material with a mean crystalline silver core of 3.1 ± 0.6 nm.

Keywords: Silver nanocrystals; Thiol-derivatization; Self-assembled monolayers; Nanoscale metal-organic composites; TEM

1. Introduction

Nanometer sized crystallites possess novel properties which make them important for applications in diverse high technologies such as optoelectronics, magnetic data storage systems, structural materials and chemical catalysis [1–4]. Colloidal solutions of nanometer sized metallic crystallites can be prepared by reducing metallic ions in suitable liquids in the presence of stabilizers [4,5]. These stabilizers can be ions such as chloride and citrate ions which adsorb

on to the nanocrystal surface or large molecules such as polymers which coat the nanocrystal surface and, thereby, prevent aggregation [6]. A number of recipes based on this approach have been developed for the preparation of nanometer sized gold and silver colloids of narrow size distributions [4–7]. Colloidal silver solutions prepared by such an approach need to be handled in oxygen free atmospheres as they react with oxygen and deteriorate upon exposure to air [8].

A further limitation which appears to be rather general for such colloidal solutions of nanometer sized metallic particles is that they cannot be as easily manipulated as some newer versions of molecularly passivated nanocrystal materials. In particular, they cannot be precipitated and redispersed in liq-

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uids. Further, they do not form ordered superlattices upon drying on surfaces. It is necessary to use techniques such as electrophoretic deposition in order to make ordered superlattices from charged nanocrystals [9]. These limitations have been largely overcome in the newer versions of molecularly passivated nanocrystals. For example, dodecanethiol-derivatized gold nanocrystals can be precipitated and redissolved [10]. In addition, populations of narrow size distributions (isolated by size selective precipitation) form ordered superlattices upon being dried from solution on suitable substrates [11]. The passivating layers also protect the gold nanocrystals from attack in highly acidic and basic media [11].

Long chain alkanethiols are suitable candidates for the derivatization of gold and silver surfaces as they are known to form self-assembled monolayers (SAMs) on these surfaces [12]. Since thiol-derivatization of gold nanocrystals leads to the formation of a new molecularly derivatized nanocrystal material, it is reasonable to expect that thiol-derivatization of silver nanocrystals could lead to the production of a similar type of material that forms stable sols which can be handled in air. In this paper, we report a liquid-phase technique for the preparation of thiol-derivatized silver nanocrystals which have been characterized by techniques such as X-ray diffraction (XRD) [13], transmission electron microscopy (TEM) [14], laser desorption time-of-flight mass spectrometry (LDTOFMS) [15] and energy dispersive X-ray spectroscopy (EDS) [14].

2. Experimental

$\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (≈ 100 mg) is dissolved in an ethanol solvent (30–100 ml). 1-dodecanethiol (≈ 150 μl) is then added to this solution after which argon is bubbled through it (solution A). NaBH_4 (≈ 100 mg) is added to about 50 ml of an ethanol solvent and argon is also bubbled through this solution (solution B). Solution B which is under an argon atmosphere is then slowly added to solution A (also under an argon atmosphere) by means of a transfer needle while solution A is being vigorously stirred. After the addition is complete, the solution is sealed under an argon atmosphere and is continued to be vigorously stirred for a few hours. This solution which contains a dark precipitate is then opened to air and

is either filtered or centrifuged in order to separate the solid material from the liquid phase. Toluene is then added to the solid material. A certain amount of the solid material dissolves in toluene. The material is then taken through one or more cleaning cycles in order to remove toluene soluble unreacted matter. In a cleaning cycle, around 400 ml of an ethanol solvent is added to around 10 ml of toluene containing the solid material which is then placed in a low temperature bath (-18°C) for a few hours. The resulting precipitate is separated from the liquid phase by filtration and washed with an ethanol solvent in order to remove the unreacted matter. The yield of toluene soluble solid material after the clean up cycle(s) is around 40 mg.

The material is then characterized by XRD, TEM, LDTOFMS and EDS. Samples for XRD were prepared by drying toluene sols of the material on suitable substrates (silicon or glass). X-ray diffractograms were obtained by using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). The (111) and (200) reflections are fit by Lorentzian line shapes and from the FWHM of the (111) peak fit the size of the silver nanocrystal core is obtained using the Scherrer formula [13]. Samples for TEM and EDS were prepared by drying toluene droplets containing the material in suitable concentrations on amorphous carbon coated copper grids and studied in a Hitachi HF-2000 FE transmission electron microscope (equipped with an EDS unit) at an electron energy of 200 keV. Silver nanocrystal core sizes obtained from TEM measurements are within an accuracy of 20%. Samples for LDTOFMS were prepared by drying a concentrated solution containing the material on a stainless steel probe tip. This film was irradiated by laser pulses (532 nm, 5 ns) and the negative ion mass spectrum was recorded using a custom-built 1.2 m time-of-flight instrument that is optimized for high-mass detection [15,16]. The mass spectra are averaged over several laser pulses.

3. Results and discussion

Fig. 1 is an X-ray diffractogram of the material. The peak positions can be assigned to that of fcc silver. The peaks are substantially broadened, thereby, indicating that the material is composed of very small silver crystallites. The silver core size

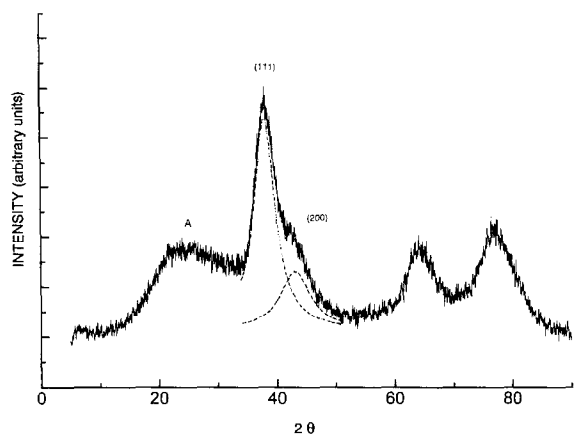


Fig. 1. X-ray diffractogram of the synthesized material. The solid line is from experiment. The dotted lines are Lorentzian fits. The broad feature labelled A is from the substrate.

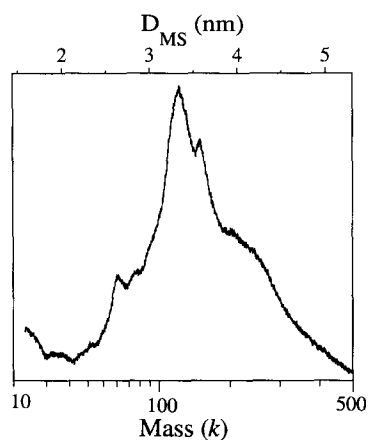


Fig. 3. LDTOF mass spectrum of the synthesized material. The upper scale gives the equivalent diameter of the silver core calculated on the basis of assumptions mentioned in the text.

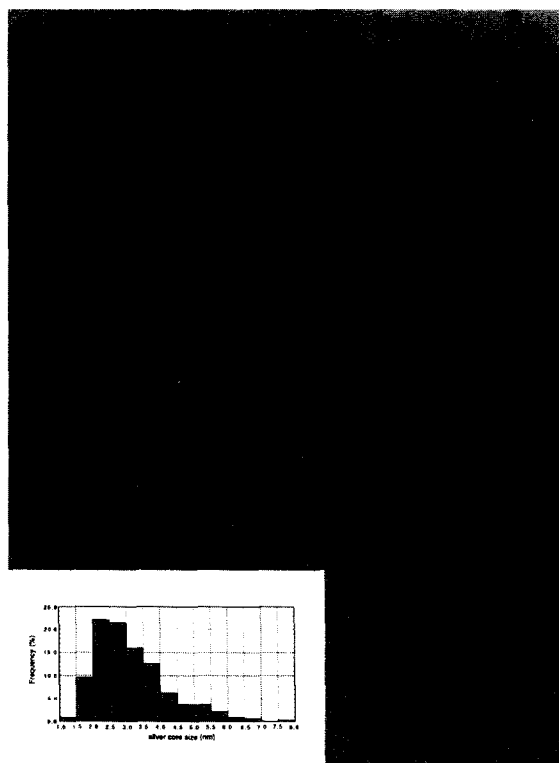


Fig. 2. (a) TEM image of the synthesized material. The inset is a histogram of silver nanocrystal cores measured from the micrograph. Irregular particles such as the one labelled A in the micrograph have not been considered in the particle count.

calculated from the FWHM of the (111) peak using the Scherrer formula is 2.1 nm. Fig. 2 shows a TEM image of the material. Irregularly shaped particles such as the one labelled A in the micrograph which may have been formed by the coagulation of incom-

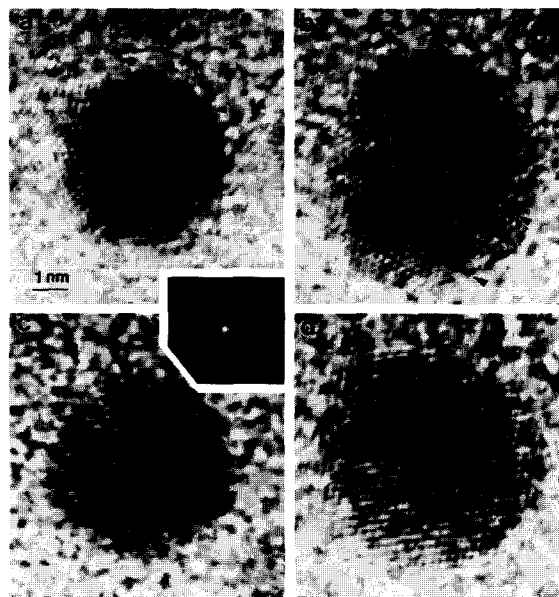


Fig. 4. HRTEM image of thiol-derivatized silver nanocrystals. The arrows in (a) and (b) indicate twin boundaries. Figure (c) shows a multiply twinned particle. The inset is a Fourier transform of this HRTEM image. Figure (d) shows a single crystal silver nanocrystal.

pletely passivated nanocrystals comprise less than 3% of the population. The majority of the nanocrystals contain a silver core in the size range from 1.5 to 4.5 nm. The mean size of silver nanocrystal cores is 3.1 ± 0.6 nm. The mass spectrum of this material is shown in Fig. 3. Broad peaks in the mass range from 40 to 300 kamu are observable. We calculate an effective diameter for the silver cores in the mass spectrum by assuming that the residual surfactant mass contributes negligibly and by taking the density of the core to be that of bulk fcc silver. The size of the silver cores obtained by this procedure lie in the range between about 2.5 and 5 nm with the most abundant peak being at about 3.3 nm. Within experimental uncertainty, the silver core sizes obtained from TEM, LDTOFMS and XRD are in good agreement with each other. Nonetheless, the smaller silver core size obtained from XRD may be an indication that large silver nanocrystals are twinned. Indeed, examination of several large silver nanocrystals by high-resolution TEM indicates that the nanocrystals can be twinned as shown in Fig. 4. Nanocrystals in Fig. 4a and 4b contain one and two twin planes, respectively. The nanocrystal shown in Fig. 4c is a multiply twinned particle as is further evident from

the Fourier transform of the high-resolution image shown as an inset. Twinned particles appear smaller in XRD as the XRD peak width is an indication of only the size of the single crystal domain.

Evidence for the dodecanethiol-derivatization of these silver nanocrystals is obtained from several different observations which are outlined here. The cleaned solid material can be repeatedly precipitated from and redissolved in nonpolar solvents such as hexane and toluene. However, it cannot be dissolved/dispersed in polar solvents such as water and ethanol. TEM images of densely packed regions of nanocrystals show that the silver cores are separated from each other by regions which appear to have the same contrast as the background carbon film. 1-dodecanethiol consists largely of carbon and hydrogen and is not expected to show any observable differences in contrast with respect to the background carbon film under these experimental conditions. Hence, the fact that the silver nanocrystal cores of adjacent nanocrystals are prevented from touching each other can be attributed to the derivatization of the nanocrystal surfaces by dodecanethiol. Peaks corresponding to carbon, sulfur, silver, oxygen and silicon are observed in the EDS spectrum shown

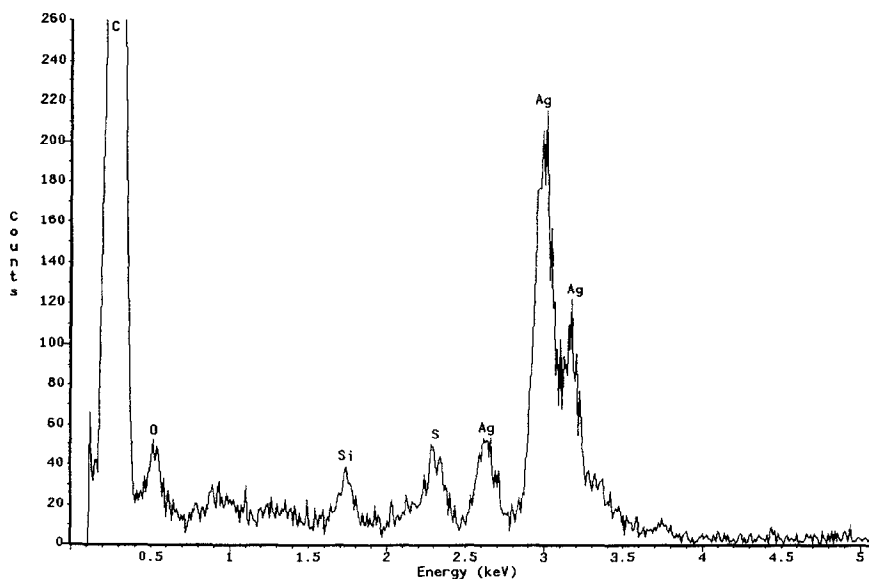


Fig. 5. EDS spectrum of the synthesized material on amorphous carbon coated copper grids indicating that the material is thiol-derivatized.

in Fig. 5. Peaks corresponding to carbon, oxygen and silicon are known to appear in the EDS spectra of neat carbon coated copper grids. The peaks corresponding to sulfur and silver arise exclusively from the nanocrystal material. The solubility properties of the material, TEM of densely packed regions of nanocrystals and their chemical analysis by EDS are all consistent with the surfaces of the silver nanocrystals being derivatized by dodecanethiol.

In conclusion, a liquid-phase technique has been developed for the preparation of dodecanethiol-derivatized silver nanocrystals. This is an important development because it may be possible to develop strategies on the basis of this synthetic procedure for linking this new type of metal–organic composite material to one another and to surfaces through chemical bonds. The resulting materials could possess novel and interesting properties of importance to nanoelectronics. Further studies are in progress in our laboratories to examine these issues.

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