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Perfluorocarbon-stabilized silver nanoparticles manufactured from layered silver carboxylates

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Perfluorocarboxylate-stabilized silver nanoparticles have been prepared uniformly *via* the thermal decomposition of layered silver perfluorocarboxylates ($AgCO_2(CF_2)_nCF_3$, n = 10, 12, 14 and 16).

Particles in the nanometer size range have been attracting increasing attention due to their fascinating electronic and optical properties originating from their quantum-scale dimensions. In this connection, a tremendous effort is currently underway to develp nanodevices by organizing the nanoparticles into controlled architectures.[1] One of the prerequisites for attaining such a goal is for the particles to be prepared in advance in a stable condition. The stabilization is usually accomplished by capping the particles with suitable surface passivating agents. The choice of the agent is very critical since it determines the stability, solubility, reactivity, and even the size and shape of the nanoparticles during the synthesis.[2] Specifically, a capping agent which can form a covalent linkage to nanoparticles endows the nanoparticles with enhanced stability. Aliphatic or aromatic thiols, for instance, have thus been widely used as stabilizing agents for metal and semiconductor nanoparticles.[3]

Considering their characteristics of low friction, excellent insulation, and chemical inertness, perfluorocarbons must comprise very promising stabilizers. Nanoparticles derivatized with perfluorocarbons are presumed to possess highly enhanced stability against mechanical friction, thermal stress, and extreme acid/base conditions.[4] In spite of these merits, however, it is difficult to fabricate fully perfluorinated nanoparticles owing to the solvophobic (water/oil insoluble) nature of the perfluoro molecules. Nonetheless, a few efforts have been directed towards the preparation of silver or gold nanoparticles derivatized with semifluorinated hydrocarbons.[5] In this communication, we describe a novel synthetic route to produce perfluorocarbon-derivatized silver nanoparticles simply from the thermal decomposition of the layered silver carboxylates.

Silver alkane carboxylate ($AgCO_2R$) is one class of heterostructured materials that show a well-developed progression of intense X-ray reflections. These intense X-ray reflections are associated with the three-dimensionally stacked silver carboxylate layers.[6] $AgCO_2R$ is also proven to decompose at ~520 K (in an atmosphere of N_2) into highly monodisperse alkane carboxylate-derivatized silver nanoparticles.[7,8] On these grounds, after synthesizing silver perfluorocarboxylates, we have attempted to verify whether perfluorocarbon-derivatized silver nanoparticles are also produced by thermal decomposition of the samples.

Silver perfluorocarboxylates ($AgCO_2(CF_2)_nCF_3$, n = 10, 12, 14 and 16) were prepared by the two-phase method† and characterized by various analytical tools such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy, UV/VIS spectroscopy, and transmission electron microscopy (TEM).‡ The XRD pattern is composed of a series of peaks that can be indexed to (0*k*0) reflections of a layered structure (Fig. 1). The interlayer spacing is observed to increase linearly with the number of CF_2 units, indicating that all the samples in fact share a common layered structure. In the IR spectra, the characteristic CF_2 and COO^- group vibrational bands are also clearly identified [Fig. 3(a)]. The carbonyl stretching band observable at ~1700 cm^{-1} in free acids is completely absent in silver perfluorocarboxylates, indicating that the obtained samples are not contaminated with free acids.

Regarding the thermal behavior of the materials, DSC and TG analyses have been performed. The DSC measurement reveals that an endothermic phase transition occurs sharply at 554–566 K for all samples (data not shown). These endotherms are associated with the chain melting process of the fluorocarbon moieties. Immediately after the endothermic transition, a rather complex exothermic transition is identified in the DSC traces. This phenomenon can be ascribed to the decomposition of the silver perfluorocarboxylate. Much the same observations are made from the TGA experiments. On these grounds, we have characterized the decomposition products which were obtained by heating the silver perfluorocarboxylates at 573 K for 10 min in an N_2 environment. The heated samples were rinsed thoroughly with hot chloroform and ethanol to remove free acids or possible impurities. The remaining solids were soluble in fluorocarbon media such as hexafluorobenzene but insoluble in common organic solvents such as ethanol, acetone, chloroform, hexane and benzene. This suggests that the decomposition products exist in perfluoronated moieties. Fig. 2(a) shows the TEM image for a typical product obtained from $AgCO_2(CF_2)_{16}CF_3$. The image reveals that silver nanoparticles are indeed formed by the thermal decomposition of the silver perfluorocarboxylate. It is remarkable that the core sizes of the nanoparticles are uniform with an average diameter of ~5 nm regardless of the perfluorocarbon chain length; the sizes observed in the TEM images are 5.2 ± 0.8 (n = 16), 5.5 ± 0.5 (n = 14), 5.1 ± 0.9 (n = 12) and 5.0 ± 1.0 nm (n = 10).

The formation of silver nanoparticles can also be confirmed from UV/VIS spectroscopy. A distinct absorption peak is observed at *ca.* 400 nm for a sample dispersed in hexafluorobenzene [see Fig. 2(b), solid line]. This must arise from the surface plasmon absorption of silver nanoparticles. The absorption band for the perfluorocarbon-tethered silver nanoparticles in hexafluorobenzene is significantly broader than that

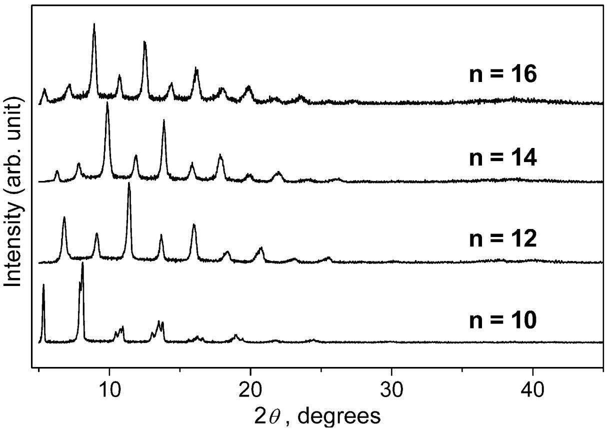

Fig. 1 XRD patterns for as-prepared $AgCO_2(CF_2)_nCF_3$.

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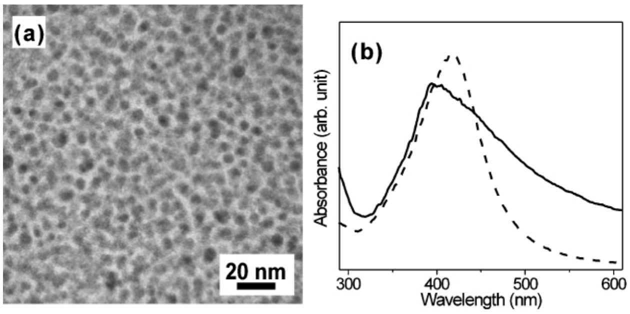

Fig. 2 (a) TEM image of thermally decomposed $AgCO_2(CF_2)_{16}CF_3$. (b) UV/VIS spectra of silver nanoparticles formed by thermal decomposition of $AgCO_2(CF_2)_{16}CF_3$ (solid line) and $AgCO_2(CH_2)_{16}CH_3$ (dashed line).

for similarly sized hydrocarbon-tethered nanoparticles in hexane [see Fig. 2(b), dashed line]; the hydrocarbon-tethered nanoparticles were obtained by the thermal decomposition of silver stearate. Shah *et al.*[5a] also observed a similarly broad band for monodisperse semifluorinated silver nanoparticles. Referring to the Drude model,[9] in which the band width should be inversely proportional to the mean free path of the electrons, the electronegative fluorocarbon layer was presumed by them to decrease the electron mean free path in the silver nanoparticles. The broad band may occur, however, due to the aggregation of particles in solution although the TEM image in Fig. 2(a) suggests little aggregation in the dry state.

We can confirm from IR spectroscopy that the silver nanoparticles are indeed passivated by perfluorocarboxylates. The IR spectra taken for a sample before and after the thermal decomposition of $AgCO_2(CF_2)_{16}CF_3$ are shown in Fig. 3(a) and (b), respectively. The vibrational bands arising from the fluorocarbon sequences $(–CF_2–)_n$, *e.g.*, the symmetric ($\nu_s(CF_2)$) and the antisymmetric ($\nu_{as}(CF_2)$) CF_2 stretching modes, are clearly observed in both spectra. Consulting the IR spectra of the alkanecarboxylic acid monolayers on silver,[10] the intense peak at 1371 cm^{-1} in Fig. 3(b) can be attributed to the symmetric stretching vibration of the carboxylate group ($\nu_s(COO^-)$). These spectral features indicate that the silver nanoparticles are derivatized with perfluorocarboxylate. It may appear curious that the antisymmetric carboxylate stretching band ($\nu_{as}(COO^-)$) is absent in Fig. 3(b) while the corresponding band is very intense in Fig. 3(a). However, this can be understood by recalling our previous finding that the usual infrared surface selection rule is applicable even to the surface of fine metal particles.[10,11] In light of this, the absence of the $\nu_{as}(COO^-)$ band in Fig. 3(b) dictates that the carboxylate group is bound to the surfaces of silver nanoparticles symmetrically *via* its two oxygen atoms.

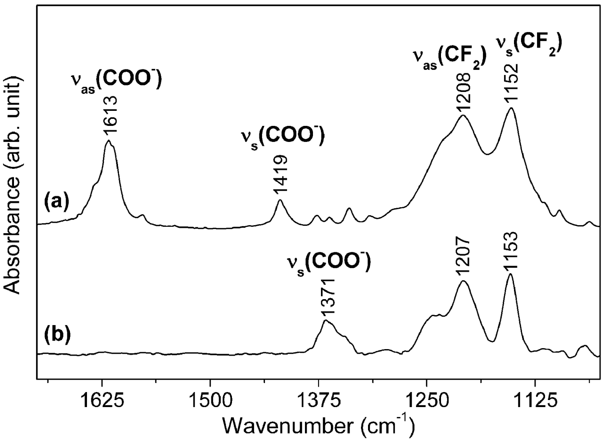

Fig. 3 (a) IR spectrum of as-prepared $AgCO_2(CF_2)_{16}CF_3$ and (b) that for silver nanoparticles formed from the thermal decomposition of $AgCO_2(CF_2)_{16}CF_3$.

In summary, we demonstrate that small and monodisperse perfluorocarbon-stabilized silver nanoparticles can be obtained simply from the thermal decomposition of layered silver perfluorocarboxylates. More detailed thermal characteristics of the silver perfluorocarboxylates will be reported in the near future. Nontheless, it should be mentioned that the present discovery will open up new avenues for the development of various novel engineering nanomaterials. For instance, when memory storage devices are fabricated with perfluorinated magnetic nanoparticles, the low dielectric layers will effectively insulate the active charge-storing elements. Perfluorocarbon-stabilized nanoclusters may also be used as coating agents endowing the target materials with chemical and mechanical inertness.

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Notes and references

† All perfluorocarboxylic acids ($CF_3(CF_2)_nCOOH$, n = 10, 12, 14 and 16; >95%) and hexafluorobenzene (>98%) were purchased from Fluorochem and used as received. $AgNO_3$ (1 mmol) in 20 mL of methanol was added dropwise to an equimolar perfluorocarboxylic acid in 20 mL of hexafluorobenzene. After the mixture was stirred for 3 h, the white precipitate was filtered and then washed several times with hexafluorobenzene and hot chloroform. The resulting powder was dried in vacuum for 3 h.

‡ X-Ray diffraction patterns were obtained on a Philips X'PERT-MPD diffractometer for a 2θ range 5–50° at an angular resolution of 0.02° using Cu-Kα (1.5419 Å) radiation. DSC and TGA were performed on TA Instrument DSC-2010 and TGA-2050, respectively, in a nitrogen atmosphere (50 ml min^{-1}) between 298 and 773 K at a heating rate of 5 K min^{-1}. Infrared spectra were measured using a Bruker IFS 113v FT-IR spectrometer equipped with a globar light source and a liquid N_2-cooled wide-band mercury cadmium telluride detector. Spectra were measured at a resolution of 4 cm^{-1} using previously scanned pure KBr as the background. TEM images were acquired for thermally decomposed samples using a JEM-200CX transmission electron microscope at 160 kV after placing a drop of hexafluorobenzene solution on carbon-coated copper grids (150 mesh). UV/VIS spectra were obtained using a SCINCO S-2130 spectrophotometer.

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