Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Chil Seong Ah, Hyouk Soo Han, Kwan Kim & Du-Jeon Jang (1999): Preparation, Characterization, and Photolysis of Dodecanethiol-Derivatized Noble Metal Nanoparticles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 209-212

To link to this article: http://dx.doi.org/10.1080/10587259908023414

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 209-212
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Preparation, Characterization, and Photolysis of Dodecanethiol-Derivatized Noble Metal Nanoparticles

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Dodecanethiol-derivatized nanoparticles of Ag, Ag/Au, and Au with an average size of 5.5 nm have been prepared via a two-phase synthetic route in water/toluene and characterized with various methods. In particular, their photochemical dynamics and mechanisms have been studied with laser flash photolysis. The surface plasmon absorption peak varies linearly from 532 to 429 nm as the Ag fraction of Ag/Au alloy clusters, in which Ag atoms are more abundant at the outer part, increases. Excited silver nanoparticles dispersed in cyclohexane undergo dethiolation in 8 ns and then fragmentation in 40 ns. Thereafter, the fragments gradually aggregate owing to the presence of less soluble bare metal sides.

Keywords: nanoparticles; dodecanethiol-derivatized; noble metals; bimetallic clusters; fragmentation and aggregation

INTRODUCTION

Nanoparticles have a variety of unique spectroscopic, electronic, and chemical properties that germinate from their small sizes and high surface/volume ratios[1-5]. Particularly, colloidal nanoparticles of noble metals exhibit excellent photochemical activities as well as striking colors that arise from their unusual electronic properties such as surface plasmon absorption[2,3,5]. Bimetallic and trimetallic composite noble metal nanoparticles may show similar but unique physicochemical properties. Furthermore, derivatization of the nanoparticles with organic molecules makes the metal clusters dissolvable in desiring solvents, extending their application capabilities[4,6].

In this paper we report that we have prepared dodecanethiol-derivatized nanoparticles of Ag (S-Ag), Au (S-Au), and bimatallic Ag/Au (S-Ag/Au) and

characterized their physicochemical properties with various methods including laser flash photolysis.

METHODS, RESULTS, AND DISSCUSION

Stabilized noble metal nanoparticles were prepared via a two-phase synthetic route in water/toluene as described previously[6].

The spectra of Fig. 1(a), measured using a UV/vis spectrometer (Sinco, UV2040), reveal that the peak absorption wavelength of surface plasmon band decreases linearly from 532 to 429 as the mole fraction of Ag in Ag/Au bimetallic composite nanoparticles increases from 0 to 1. As a mixture of monometallic S-Ag and S-Au samples in any proportion shows a simple combination of UV/vis spectra of two individual samples, the single surface plasmon absorption band of S-Ag/Au should arise from Ag/Au composite clusters rather than a simple mechanical mixture of two different monometallic clusters.

The spectra of Fig. 1(b) taken with an IR spectrometer (Bruker, IFS) suggest that the alkyl chains of the dodecanethiolate species on all alloy clusters take fully-extended trans zigzag conformations. However, the fact that the antisymmetric CH_2 stretching frequency of bimetallic S-Ag/Au sample is much the same as that of monometallic S-Ag one implies that Ag atoms are more enriched on the surface part of bimetallic alloy clusters. XPS peaks from the same bimetallic nanoparticles also support this implication.

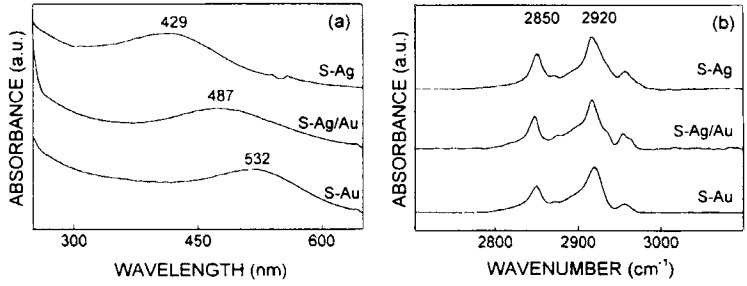

FIGURE 1 UV/vis (in n-hexane) (a) and IR (in KBr matrices) (b) absorption spectra of dodecanethiol-stabilized noble metal nanoparticles. The positions of surface plasmon absorption maxima and standard CH_2 stretching modes are shown in (a) and (b), respectively.

Transmission electron micrographs (TEMs) obtained with a transmission electron microscope (JEOL, JEM2000) have revealed that our prepared noble metal nanoparticles are considerably homogeneous in size with an average size of about 5.5 nm. While the TEM image of S-Au does not change with irradiation, the image of S-Ag does quite notably as shown in Fig. 2. S-Ag particles are photolyzed into smaller ones with sizes less than 2 nm, although agglomerated ones with largely increased sizes are found together after irradiation.

Absorption spectral change with irradiation in Fig. 3(a) also indicates that S-Ag nanoparticles decompose with a good quantum efficiency to form particles smaller than 2 nm which have significantly reduced plasmon absorption coefficients owing to their limitedly small sizes[1,5]. Transient absorption kinetic profiles and spectra were obtained by monitoring sample transmittance changes, made with excitation pulses from a 6 ns Nd:YAG laser (Quanta System, HYL101), with a CCD detector (Princeton Instruments, ICCD576G). The profile of Fig. 3(b) suggests that upon absorption of a photon S-Ag undergoes dethiolation in 8 ns and then fragmentation in 40 ns. After decomposition, absorption is significantly bleached due to reduced surface plasmon absorption coefficients. The absorption bleach partially recovers in a much slower time scale of 130 ms as the reduced solubility of newly exposed thiolate-free sides forces fragments to combine to form enlarged particles, which again aggregate later to turn into even larger agglomerates.

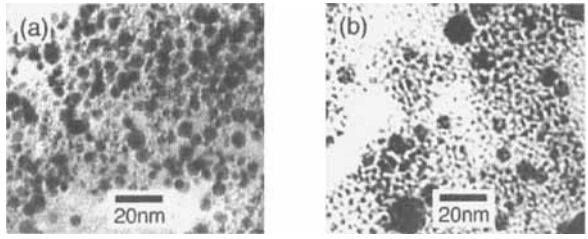

FIGURE 2 TEM images of S-Ag nanoparticles before (a) and after (b) 3 min irradiation of 355 nm, 30 ps, 0.6 mJ laser pulses at 10 Hz.

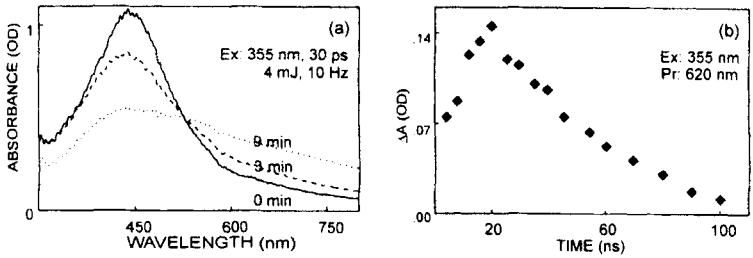

FIGURE 3 Absorption spectral changes with irradiation (a) and transient absorption kinetic profile (b) of S-Ag nanoparticles in cyclohexane. Excited and monitored conditions are shown inside.

CONCLUSIONS

Colloidal solution of S-Ag/Au alloy nanoparticles with an average size of 5.5 nm shows a single plasmon absorption band whose wavelength depends on Ag fraction. Ag atoms are relatively more abundant at the outer part of bimetallic composite nanoparticles, while the alkyl chains of adsorbed dodecanethiolates have fully extended all-trans conformations. S-Ag particles are photolyzed into smaller ones with sizes less than 2 nm which have notably reduced plasmon absorption coefficients. Following dethiolation within 8 ns, fragmentation takes place in 40 ns, although aggregation follows in a much slower time scale due to the reduced solubility of fragments.

Acknowledgments. This work was supported by the Basic Science Research Institute Program. KK and DJJ also acknowledge the Center for Molecular Catalysis and the Center for Molecular Science, respectively.

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