Localization of laser-induced breakdown in aggregates of silver nanoshells

To cite this article: Honoh Suzuki et al 2006 Sci. Technol. Adv. Mater. 7 290

View the article online for updates and enhancements.
Localization of laser-induced breakdown in aggregates of silver nanoshells

Honoh Suzuki a,*, Tomoko Koike a, Izumi Suzuki a, Tokimasa Kawabata b, I-Yin Sandy Lee a

a Department of Chemistry, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan
b Department of Material Systems Engineering and Life Science, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

Received 30 October 2005; received in revised form 25 January 2006; accepted 26 January 2006
Available online 20 March 2006

Abstract

Nanoshells are useful in near-infrared (NIR) applications because of the red shift of the Mie resonance into NIR. Silica/gold/silver nanoshells were prepared via gold anchoring and characterized by Mie-theoretical calculations and transmission electron microscopy, which indicated a broad and enhanced NIR absorption and a partially coated, mottled Ag/Au structure on the silica core. The mottled nanoshells were found to spontaneously aggregate in solution to form irregular islands. Their surface roughness was examined by the fractal dimension analysis. When the aggregates were irradiated with 1064-nm laser pulses, highly localized emission due to laser-induced breakdown was observed, which is attributed to the non-uniform metal distribution over the aggregate surface and the localization of the optical field induced by the disordered arrangement of the nanoshells in the aggregate.

© 2006 NIMS and Elsevier Ltd. All rights reserved.

Keywords: Laser-induced breakdown; Ag nanoshells; Mie theory; Localized emission; Nanoparticle aggregates

1. Introduction

Nanoshells are a new class of nano-composite material, which consists of a core sphere and a surrounding thin layer [1]. If the core is a dielectric and the outer layer is metallic, the shell structure causes a significant red-shift of the Mie surface mode, compared with that for analogous metal nanoparticles, leading to the enhanced interactions with near-infrared (NIR) laser light. The surface plasmon band is sensitive to the core size and the layer thickness, so that it can be tailored to various application needs [2]. This feature makes nanoshells promising in NIR applications such as cancer therapy [3] and non-linear optics [1].

Recent theoretical and experimental studies also show the importance of nanoparticle aggregation in non-linear optical interactions [4,5]. When nanoparticles aggregate, they often form a fractal-like structure due to self-similarity inherent in the cluster–cluster aggregation mechanism over many length-scales [6]. The rough surface with the fractal disorder induces localization of the laser field near the aggregate surface [7], and results in strong microscopic enhancement of non-linear optical effects such as two-photon fluorescence [4].

In view of the strong enhancement in the case of nanoparticles, it is prompting to examine laser interactions with nanoshell aggregates in the NIR region. In this paper, we report preparation and characterization of silver/gold/silica nanoshells and their aggregates, and microscopic observation of the interaction of the aggregates with NIR laser pulses. Upon laser irradiation, the aggregates are found to emit white light due to laser-induced breakdown (LIB). Microscopic images of LIB reveal that the spatial profiles of the emission are highly localized.

2. Experimental section

All chemicals used are of reagent grade. Solutions are prepared with deionized water. Silica/gold/silver nanoshells have been prepared via gold anchoring [2,8,9]. Mono-disperse silica nanoparticles with the diameter of 100 nm are prepared by hydrolytic polymerization of tetraethyl orthosilicate (TEOS; Aldrich) [8], where 1.5 ml (6.4 mmol) of TEOS is added to a mixture of 25% ammonia solution (3 ml) and dry ethanol (50 ml). The solution is stirred overnight for the reaction to be complete. The surfaces of the silica nanoparticles are functionalized by the addition of 25 μl (0.14 mmol) of (3-aminopropyl)trimethoxysilane (APTM; Aldrich), followed by overnight stirring and heating at 70–80 °C for 1 h [9]. The nanoparticles are
then repeatedly centrifuged and re-dispersed in ethanol to remove excess reactants. Because of the difficulty in direct coating of silver on silica, small gold nanoparticles (2–3 nm in diameter) are separately prepared and attached to the core surface as anchors for silver coating. The gold hydrosol is made by adding 2 ml (50 μmol) of 25 mM chloroauric acid (Wako) to a reductant solution, which is a mixture of 1% tetrakis(hydroxymethyl)phosphonium chloride (THPC; Aldrich) solution (1 ml; 50 μmol) with 6 mM NaOH (47 ml). The resulting orange solution is added to the suspension of the functionalized silica nanoparticles (5 ml) and allowed to react for 2 h, followed by repeated centrifugation and re-dispersion. Silver is then coated onto the surface of the gold-decorated silica by reduction of Ag⁺. The silica solution (50 μl) is mixed with 0.15 mM silver nitrate solution (25 ml; 3.8 μmol) and, while being stirred vigorously, 37% formaldehyde solution (0.25 ml) and 25% ammonia solution (0.10 ml) are simultaneously and quickly added to it [2]. The grayish solution prepared according to this protocol has been found to gradually turn colorless, with the precipitation of black powders; however, surfactants such as sodium dodecyl sulfate (SDS) can prevent aggregation and stabilize the solution for weeks. Absorption spectra are recorded with a UV–visible spectrophotometer (Shimadzu UV-160).

A transmission electron microscope (TEM; TOPCON EM-002B) is employed to take the electron micrographs of the aggregates. The air-dried sample is placed on a copper mesh and loaded into the microscope. The elemental analysis of the single nanoshell is performed by an energy dispersive X-ray spectroscopy (EDS; EDAX International). The size distribution of the silica cores (the average diameter and its standard deviation) has been estimated by measuring 34 samples randomly selected from 12 micrographs.

For laser-induced emission experiments, the wet aggregates are sampled from the solution and placed under a homemade optical microscope, which is equipped with an objective (Nikon CF M Plan SLWD 40×, numerical aperture = 0.40) that has a long working distance of 15 mm. The exceptionally long working distance is advantageous to the on-site observation of laser-induced events. The slide glass is slightly tilted, for the aggregate sample to be suitably irradiated with a horizontal laser beam. The absence of shading effects has been confirmed by altering the tilt angle of the slide. The laser source is a Q-switched Nd: yttrium–aluminum–garnet (YAG) laser (1064 nm) with a pulse width of 5 ns and attenuated pulse energy of 200 mJ (Continuum Surelite I-10). The collimated beam has a spot diameter of 3 mm and TEM₀₀ near-Gaussian profile. Each single pulse causes breakdown at the aggregate surface, the emission from which is captured with a microscope CCD camera (Kodak MDS-100).

3. Results and discussion

The nanoshells have enhanced absorption bands extending into the near-IR region, compared with a typical absorption of silver nanoparticles with a similar diameter (Fig. 1a). The broad absorption band over 400–1100 nm is qualitatively very similar to those reported for silver nanoshells [2]. To characterize the spectra, we performed a model calculation based on the classical Mie theory for a spherical core–shell structure (i.e. coated sphere) [10], which is a straightforward extension of the standard Mie theory of a homogeneous isotropic sphere. The Maxwell equations are solved in terms of vector spherical harmonics and appropriate boundary conditions, and the extinction cross section is calculated from the scattering coefficients as a function of the core size, the shell thickness, and the incident wavelength. The wavelength-dependent optical constants (complex refractive indices) of silica, silver and water are taken from the literature [11,12], whereas the contribution from the gold anchors is ignored. The calculated spectra (Fig. 1b) show that the redshift highly depends on the shell thickness, and is greater as the shell becomes thinner. The observed peak position (730 nm) approximately corresponds to the model having the silver thickness of 10 nm. The observed band is, however, much broader than those of the models, which indicates significant dispersiveness in the silver thickness of the prepared nanoshells. As the Mie scattering in general strongly depends on the particle size and shape [10], the size...
distribution and possible non-sphericity of the silica core may also contribute to the observed broadening. Comparison of the spectra of the freshly prepared solution with those of the SDS-stabilized one has suggested that the effect of the aggregation on the solution spectra is minor.

In contrast to the reported stability of nanoshell suspensions [2], our nanoshells spontaneously aggregate in solution, thus also suggesting the possibility of incomplete coating. TEM images of the aggregates (Fig. 2) show that it is actually the case: most of the silica spheres (94 ± 10 nm in diameter) are partially coated, leaving significant areas of bare silica surfaces. The coating structure is extremely rough with the maximum coating thickness of 10–14 nm. This ‘mottled’ coating structure is likely to have resulted from the less-than-ideal anchoring in our protocol, and may explain the broad absorption band and the tendency for aggregation. The elemental analysis of single nanoshells indicates that the coating is mainly composed of silver (7–64 at.%); the gold content (0.3–7.9 at.%) is always minor. It is noted that the observed maximum content of silver is close to the value (67 at.%) which would correspond to an idealized silver/silica nanoshell having the core diameter of 100 nm and the shell thickness of 10 nm. Therefore, we may consider that the core–shell model based on the Mie theory has some relevance to the actual structure in this particular case, in spite that the theory is in general inapplicable to particles with non-uniform shell structures, and a more elaborated theory would be necessary to fully characterize the broad absorption band.

During the aggregation process, the absorbance of the solution monotonically decreases with a half-life of 3–4 h, and black aggregates gradually precipitate; after 1 day, the solution becomes colorless and the aggregation is essentially complete. The peak position and shape of the absorption band show little change during the aggregation process, suggesting that the aggregation mainly proceeds without significant changes to the size and shell thickness of the nanoshells. Comparison of TEM images of the aggregates with those of SDS-stabilized nanoshells (not shown) confirms that the structure of single nanoshells is essentially intact before and after the aggregation. Accordingly, the driving force of aggregation is attributable to the chemical activity of the uncoated, functionalized silica surfaces on the mottled nanoshells.

Many aggregation processes in nature are known to generate fractal and fractal-like structures. When the interparticle force is short-ranged and the interparticle contact causes a strong and
irreversible attachment, such as in the case of the aggregation of the mottled nanoshells, the cluster–cluster aggregation (CCA) mechanism [6,13] is likely to operate. In fact, an optical microscopic observation shows that many of the nanoshell aggregates form irregularly-shaped islands (Fig. 3) that have a striking resemblance to fractals generated by computer simulations [13].

To examine the possibility of fractal nature of the aggregates, we have analyzed optical microscope CCD images of the aggregate samples. The fractal dimension of island shapes can be evaluated from the relationship between the perimeter $P$ of the coastlines versus the area $A$ of the islands

$$P = cA^{D/2},$$ (1)

where $c$ is a constant and $D'$ is the fractal dimension of the coastlines [14]. The fractal dimension in the three-dimensional space $D$ is calculated by

$$D = D' + 1.$$ (2)

To obtain $D$, we have analyzed 19 optical microscopic images: the edges of the aggregate islands are first recognized by comparing the color of the adjacent pixels with the background color, then their perimeters and areas are determined by counting the number of the edge pixels and that of the pixels surrounded by the edges. The fractal dimension of $D \approx 2.60$ has been estimated from the logarithmic (Richardson) plot (Fig. 4). It should be noted that this value is of qualitative and tentative nature because of the scattering in the plot and the limited span of the length scales of the optical microscopy. Nevertheless, it may serve as a useful measure of the irregularity and roughness of the surface structure of the nanoshell aggregates.

For fractal structures under laser irradiation, a strong local enhancement of the near-surface optical field is theoretically predicted [5]. To test this, we have performed a microscopic observation of laser-induced breakdown (LIB) at the surface of the nanoshell aggregates.

The LIB process in general is an inherently complicated phenomenon and is in active research because of its importance in plasma physics and environmental analysis. The LIB emission from bulk water–metal interfaces, however, turns out to be comparatively simple; it can be understood essentially in terms of a spatially-uniform blackbody radiation from a thin layer of plasma at the surface, which has been generated by laser heating and cools down in a 10-ns time scale [15]. Atomic and ionic emissions from ablated fragments are totally quenched in water, in contrast to the case of dry (e.g. air–metal) LIB where...
they are commonly observed and spread out over several millimeters in space [16]. The short duration and the absence of spatial blur of the visible LIB emission in water are expected to be advantageous to the microscopic imaging, as they prevent ‘washing-out’ of hot-spot images by thermal and ablative diffusion. Thus, the wet LIB emission can be a useful tool for the microscopic probing of near-surface phenomena in solution.

When a laser pulse hits the aggregate, a bright emission is observed (Fig. 5). A bright-field observation has confirmed that the incident intensity is well above the LIB threshold for the aggregate surface: on each laser incidence, a significant amount of nanoshells at the aggregate surface get fragmented and diffuse away (Fig. 6). Hitting the same sample by subsequent laser pulses initially increased and then gradually diminished the emission intensity, possibly owing to the initial increase of the LIB-active surface area, followed by the ablative loss of the metal coating and the eventual destruction of the aggregate. The fragmentation may well be expected from the penetration depth of silver (10 nm) at the laser wavelength and the high temperature ($\sim 10^4$ K) of the plasma sheath at the surface of LIB events [15]. The formation of bubbles (Fig. 6c) also indicates the laser-induced cavitation caused by the local optical heating. On the basis of these observations, the emission can be identified mainly with the wet LIB emission; other light-emitting processes such as supercontinuum and non-linear rainbow are considered to be minor once the LIB threshold is reached. It is noted that granular aggregates with less roughness, also in sight in Fig. 5(a), do not emit light upon laser irradiation. It implies a lower LIB threshold for the structure with rougher surfaces. An attempt to determine the accurate LIB threshold of the aggregate was so far unsuccessful due to the invasive and destructive nature of the LIB events and the variance of the threshold for each aggregate sample.

The observed white-light emission is in the shape of bright ‘speckles’ randomly located over the aggregate surface (Fig. 5b). The spatial profile of the emission intensity [17] (Fig. 5c) reveals that, in contrast to the case of bulk metal surfaces, the LIB emission from the aggregate is highly localized. Each of the hot spots is found to be at most of the size of the Airy disk, i.e. the Rayleigh resolution limit (0.6 $\mu$m) that approximately corresponds to $2 \times 2$ CCD pixels in our optical system.

The origin of the observed localization of the LIB emission is an open question. One possibility is that it might simply reflect a highly non-uniform distribution of metal coating over the aggregate surface. As the TEM and EDS results show the significant variance of the silica surface coverage of the nanoshells, it sounds straightforward that metal-rich regions on the aggregate surface become hot spots upon laser irradiation. On the other hand, the spot size of our resolution limit has the dimension of 25–30 nanoshells, and what we observe is the spatially averaged emission from a collection of such nanoshells. If the arrangement of metal-rich nanoshells is more or less random, the non-uniform metal distribution is expected to be smeared out by the spatial averaging, and thus it is rather unlikely that this effect alone could produce strong localization in the emission profile (unless the emission threshold depends on the surface coverage very sharply). The LIB threshold may also be a function of the size and shape of the silica core, but the Mie theory suggests that it is a slowly varying one in our case, so that the distribution of the core size and shape is not expected to be the major cause of the localization either. Another possibility is the one predicted in the theory of laser-fractal interactions: the interference and local self-amplification of the incident optical field near the disordered, fractal-like metal surface [5]. Such effect is collective in nature, and more relevant to the geometrical disorder and fluctuations in the nanoshell arrangement (e.g. scaling properties of the correlation, the asymptotically zero mean density [18], and the lack of translational symmetry) at many length scales, so that the localized dipolar eigenmodes are randomly located over the aggregate [19], and the resolution limit does not necessarily exclude the observation of strong localization. This mechanism is also related to well-known optical phenomena such as the surface-enhanced Raman effect. Although the non-uniformity of the metal distribution within monomer particles was not considered in the original theory, we infer that it could also contribute to the observed LIB localization in two ways: it could enhance the incident laser field via the so-called antenna effect, and the resulting concentration of laser energy could in
turn heat up the metal-rich region effectively. Thus, the localized LIB event may be attributable to the combination of the mottled metal coating and the disordered arrangement of the nanoshells in the aggregate.

The laser-fractal theory also predicts that the enhancement is spatially very local and microscopic; when averaged over a macroscopic scale, there may be no net enhancement [4]. Therefore, the localization may not be advantageous for the overall enhancement of the LIB emission. On the other hand, it may find applications where the spatial self-concentration of the laser energy is valuable. For example, it may allow photo-acoustic shock-wave generation at microscopic sites with a low-power NIR laser, which could be useful in medical and therapeutic applications such as laser lithotripsy [20]. In this regard, the mottled nanoshells prepared in this work turn out to have two unexpected advantages: they have the characteristic NIR absorption very similar to fully-coated nanoshells, and they have the tendency to spontaneously form aggregates having very rough surfaces, which can be used as a host for a variety of surface-enhanced optical phenomena, such as microscopic LIB and microplasma generation, in the NIR region.

4. Conclusion

We have prepared and characterized partially coated nanoshells and their aggregates. The rough surfaces of the aggregates are examined by fractal dimension analysis. We have also observed microscopic localization of the LIB emission on the surface of the aggregates. A combination of the enhanced NIR absorption of the nanoshells and the mottled, disordered structure of the aggregates leads to the LIB events in the microscopic hot spots, which may find applications where the low incident laser energy is a concern and the spontaneous energy concentration is valuable.

Acknowledgements

We acknowledge the support by Grants-in-Aid for Scientific Research No. 17510086 from the Ministry of Education, Science and Culture of Japan.

References

[1] J.B. Jackson, S.L. Westcott, L.R. Hirsch, J.L. West, N.J. Halas, Controlling the surface enhanced Raman effect via the nanoshell geometry, Appl. Phys. Lett. 82 (2003) 257–259.

[2] J.B. Jackson, N.J. Halas, Silver nanoshells: variations in morphologies and optical properties, J. Phys. Chem. B 105 (2001) 2743–2746.

[3] L.R. Hirsch, R.J. Stafford, J.A. Bankson, S.R. Sershen, B. Rivera, R.E. Price, J.D. Hazle, N.J. Halas, J.L. West, Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance, Proc. Natl Acad. Sci. 100 (2003) 13549–13554.

[4] W. Wenseleers, F. Stellacci, T. Meyer-Friedrichsen, T. Mangel, C.A. Bauer, S.J.K. Pond, S.R. Marder, J.W. Perry, Five orders-of-magnitude enhancement of two-photon absorption for dyes on silver nanoparticle fractal clusters, J. Phys. Chem. B 106 (2002) 6853–6863.

[5] V.M. Shalaev, Electromagnetic properties of small-particle composites, Phys. Rep. 272 (1996) 61–137.

[6] R. Jullien, R. Botet, Aggregation and Fractal Aggregates, World Scientific, Singapore, 1987.

[7] A.K. Sarychev, V.A. Shubin, V.M. Shalaev, Anderson localization of surface plasmons and nonlinear optics of metal-dielectric composites, Phys. Rev. B 60 (1999) 16389–16408.

[8] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, J. Colloid Interface Sci. 26 (1968) 62–69.

[9] S.L. Westcott, S.J. Oldenburg, T.R. Lee, N.J. Halas, Formation and adsorption of clusters of gold nanoparticles onto functionalized silica nanoparticle surfaces, Langmuir 14 (1998) 5396–5401.

[10] C.F. Bohren, D.R. Huffman, Absorption and Scattering of Light by Small Particles, Wiley, New York, 1983.

[11] E.D. Palik (Ed.), Handbook of Optical Constants of Solids, Academic Press, New York, 1985.

[12] D.J. Segelstein, MS Thesis, University of Missouri-Kansas City, 1981.

[13] T. Vicsek, Fractal Growth Phenomena, World Scientific, Singapore, 1989.

[14] J.C. Sánchez-López, A. Fernández, TEM study of fractal scaling in nanoparticle agglomerates obtained by gas-phase condensation, Acta Mater. 48 (2000) 3761–3771.

[15] H. Suzuki, H. Nishikawa, I.-Y.S. Lee, Laser-induced breakdown spectroscopy at metal water interfaces, Phys. Chem. Commun. 5 (2002) 88–90.

[16] D.E. Kim, K.J. Yoo, H.K. Park, K.J. Oh, D.W. Kim, Quantitative analysis of aluminum impurities in zinc alloy by laser-induced breakdown spectroscopy, Appl. Spectrosc. 51 (1997) 22–29.

[17] The plot was made with the program: P. Ramachandran, MayaVi: a free tool for CFD data visualization, Fourth Annual CFD Symposium, Aeronautical Society of India, August 2001.

[18] A.V. Butenko, P.A. Chubakov, Yu.E. Danilova, S.V. Karpov, A.K. Popov, S.G. Rautian, V.P. Safonov, V.V. Slabko, V.M. Shalaev, M.I. Stockman, Nonlinear optics of metal fractal clusters, Z. Phys. D 17 (1990) 283–289.

[19] V.M. Shalaev, R. Botet, D.P. Tsai, J. Kovacs, M. Moskovits, Fractals: localization of dipole excitations and giant optical polarizabilities, Physica A 207 (1994) 197–207.

[20] A.J. Coleman, J.E. Saunders, A review of the physical properties and biological effects of the high amplitude acoustic fields used in extracorporeal lithotripsy, Ultrasonics 31 (1993) 75–89.