Surface-enhanced fluorescence from silver fractallike nanostructures decorated with silver nanoparticles

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Fluorescence emission of fluorophore molecules in the close vicinity of a nanostructured metal surface can be enhanced through a local electromagnetic field with the help of surface plasmon resonance. The fluorescence enhancement effect is very sensitive to the topography and dielectric property of the metal substrate. In the current work, metal substrates with complex structures, which are made of silver fractallike structures and nanoparticles (NPs), are prepared through electrochemical reduction followed by physical deposition. The surface-enhanced fluorescence of Rhodamine 6G monolayer molecules deposited on the prepared complex substrates are investigated with the laser spectroscopic technique. The experimental results show that the fractallike structure decorated with silver NPs presents stronger fluorescence enhancement, compared with silver NPs or pure silver fractallike structures. © 2011 Optical Society of America

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1. Introduction
The surface-enhanced fluorescence (SEF) technique is known as one of the most sensitive spectroscopic tools for the detection of a wide range of adsorbate molecules down to the single molecule detection limit [1–4]. It is widely accepted that the locally enhanced electromagnetic (EM) field formed at a nanostructured surface is mostly responsible for the SEF effect [5,6]. The sizes and shapes of metallic nanostructures have strong impacts on the distribution of local EM fields [7,8] and the effect of enhancement. In this regard, many methods have recently been developed for producing metal substrates with various surface configurations, which include the polish of the surface [9], the vapor deposition method [10], self-assembly of metal colloids [11], and the chemical reduction method [12,13]. However, efforts to pursue a more convenient and controllable avenue are still of great interest for the application of SEF. Compared with other methods, such as vapor deposition and the self-assembly technique, the electrochemical deposition method is very useful for the preparation of nanostructures with novel topography and specific characteristics; it is economical, highly productive, and readily adoptable [13–15].

In this paper, a fractallike structure formed on a glass surface decorated with silver nanoparticles (NPs) was prepared. The fluorescence enhancement was investigated by forming a monolayer of Rhodamine 6G (Rh6G) molecules on the fractallike structure decorated with Ag NPs, a pure fractallike structure, an Ag NP monolayer deposited on clean glass, and a bare glass surface as a control. The enhancement factor (EF) was defined as the ratio of fluorescence intensity on the metallic surface to fluorescence intensity on the glass slide.

2. Experimental Section
A. Materials
Rh6G (laser grade) was purchased from Exciton (USA) and used as received. p-aminothiophenol (PATP) and 3-aminopropyl trimethoxysilane (APS) were purchased from Sigma-Aldrich and used as received. Analytical grade silver nitrate (99.8%), citric acid (99.5%), sodium borohydride (98.0%), silver foil,
microscope slides, and tin(II) chloride used for fractal growth were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the experiments (>18 MΩ cm).

B. Synthesis of Silver Colloids

Silver colloids were prepared according to the literature with slight modification [16]. Silver colloids of about 40 nm in size were obtained through reduction of sodium borohydride and citric acid under ice bath conditions, and characterized by transmission electron microscopy (TEM) [see Fig. 2(a)]. The detailed process is as follows: First, citric acid of 2.1 g and sodium borohydride of 1.9 g were dissolved in 20 ml deionized water and stirred for about 10 min. Then 50 ml of 0.1 mol/l AgNO₃ was added slowly to the mixed solution with continuous stirring for 2 h under the ice bath. As the color of the mixture turned from yellow to yellow–brown, the solution was collected, centrifuged, and washed with water, and then ultrasonicated for several minutes at room temperature. The sample Ag colloids were obtained by repeating the process several times.

C. Electrochemical Growth of Silver Fractals

Silver fractals were prepared by the electrochemical method following a procedure from the literature [13,14]. Briefly, two microscope slides were thoroughly sonicated with Alconox soap, isopropyl alcohol, ethanol, and distilled water before they were soaked in 10⁻⁴ M tin(II) chloride for a few hours. Two pieces of silver foil (25 mm × 30 mm × 1 mm each) were held about 25 mm apart between two microscope slides. The space between the two microscope slides was filled with deionized water. A direct current of 100–200 μA was maintained between the two silver foil electrodes for about 20 min, then the fractallike silver structures on the glass were obtained.

D. Sample Preparation

1. Formation of Silver Colloid Monolayer on Glass

The glass slides were first soaked in a 7:3 (v/v) mixture of H₂SO₄ (95%–98%) and H₂O₂ (30%) overnight before the deposition. (Caution: piranha solution is extremely caustic. Use only with extreme care.) Then the glass slides were silanized with APS by immersing the slides into 1.6% APS ethanol solution for 5 h. After being thoroughly rinsed with ethanol and water to remove unbound monomers from the surface, the APS-coated glass slides were incubated with prepared silver colloid for 6 to 12 h, and a monolayer of the Ag NPs was formed on the surface of the slides. The surface morphology can be modified by properly controlling the incubating time. Finally, the Ag-NP-covered slides were rinsed with deionized water and dried with a stream of nitrogen gas, as shown in Fig. 1(a).

2. Fabrication of Fractal/PATP SAMs/Ag NP Sandwich Structures

PATP was chosen as the coupling molecule because PATP is a bifunctional molecule whose -SH group is easily cleaved to form a metal–S bond when adsorbed on a metal surface. Protonated amino groups can adsorb on the metal surface through the electrostatic force between the protonated amino group and the negative charged metal NPs. Therefore, the glass slides electrodeposited by the silver fractal structure were immersed in 0.1 mM PATP ethanol solutions for 12 h to form PATP. Then the surface was thoroughly washed with ethanol and water, and immersed in the silver colloid for 6 h. Then the sandwich structure consisting of the Ag fractal structure, PATP, and Ag NPs was formed, as shown in Fig. 1(b).

E. Morphological and Optical Characterization

Figure 2 shows a typical atomic force microscopy (AFM, SPM-9500J3) image of a prepared substrate of Ag NPs [Fig. 2(b)], and the fractallike silver structure decorated without [Fig. 2(c)] and with Ag NPs [Fig. 2(d)].
Fluorescence measurements were conducted at room temperature. An SP2750i Spectrometer (Acton Research Corporation, USA) and a PIXIS100 CCD system (Acton Research Corporation) were employed for fluorescence collection and detection. The laser excitation was at 532 nm. A properly selected notch filter was used to eliminate the scattered light in spectroscopic measurement.

3. Results and Discussion
A two-dimensional Ag NP cluster with a fractal transition boundary was formed on the glass substrate when a constant current was applied. The silver fractals exhibit a nonuniform and highly localized anisotropy property [as shown in Fig. 2(c)].

For pure fractallike and fractallike structures decorated with Ag NPs, an obvious difference between them is obtained from the AFM picture. Figure 2(d) shows the morphology of the fractallike structure decorated with Ag NPs. Ag NPs deposited on the fractallike structure form a three-dimensional nanostructure, while Fig. 2(c) shows only a two-dimensional distribution of the fractallike silver structure deposited on the glass slide. The deposition of Ag NPs on the fractallike structure formed a three-dimensional nanostructure, which may produce more hot spots, leading to a good enhancement of the local EM field.

The fluorescence emissions of Rh6G molecules on the substrates are shown in Fig. 3. Spectra (a) to (d) in Fig. 3 correspond to the fluorescence of a Rh6G monolayer on Ag NPs deposited on a glass substrate, silver fractal structures deposited on a glass substrate, and a fractal structure decorated with an Ag NP sample. The enhancement of the fluorescence emission can be ascribed to the local EM field enhancement. The EM field may originate from strong internanoparticle coupling among closely distributed Ag NPs assembled on the glass substrate. The coupled local EM field in the assembled multilayer on the glass substrate also supports the current experimental results [17,18]. For a pure fractallike silver structure and Ag NPs on the glass substrate, only a two-dimensional nanostructure was formed, and the hot spots within the structure occupied a small volume, resulting in a smaller enhancement of the local EM field and the fluorescence emission.

Figure 4 represents the SEF intensity histogram of 103 selective detected sample points on the sample surfaces at random. The fluorescence was measured at different sample points, and the emission signals were averaged. The maximum probabilities of the EFs as obtained from the spectral measurement are around 4.0, 6.0, and 12.0. As is shown in Fig. 4, the Rh6G monolayer deposited on a clean glass surface is taken as the reference. In this histogram, the silver fractallike structure produces 6.0 times stronger signals than the Rh6G monolayer deposited on a glass sample, and only 1.7 times stronger than that on the NP-deposited sample [Fig. 2(c)]. However, the silver fractallike structure decorated with Ag NPs exhibits the strongest fluorescence, and produces 12.0 times stronger signals than the Rh6G monolayer deposited on the glass sample and 4 times stronger signals than Ag-NP-deposited sample (see the blue arrows in Fig. 4). The better enhancement effect from the fractallike sample was attributed to the fact that localized plasmons created more “hot spots” in the formed three-dimensional nanostructure.

The fractallike structures decorated with Ag NPs can be regarded as aggregates of Ag NPs with a three-dimensional distribution nanostructure, which are different from nanofractal structures, such as compact or periodic geometries. The optical properties for such structures have been extensively studied by Stockman [19] and Shalaev and co-workers [20]. The plasmon normal modes (collective surface plasmons) are so localized that enhancement resulting from the interaction of all of the particles through dipole–dipole coupling is concentrated in very small regions of the clusters, that is, the hot spots [21,22]. The model predicts the local fields in fractal structures can be many orders higher than the incident fields. Giant fluorescence signals are possible when
fluorophore molecules reside near these hot spots. In contrast, for compact or periodic structures, the normal modes of surface plasmons are delocalized over larger regions determined by long-range dipole–dipole interaction of the NP surface plasmons.

A large variability of SEF intensities for a silver fractallike structure was observed experimentally, consistent with the random deposition of the Ag NPs on the glass and fractallike structure (as shown in Fig. 4). The fluorescence intensity distributions for nonfractal structures are homogeneous. However, for fractal and fractal decorated with NP surfaces, the fluorescence intensity distributions are extremely inhomogeneous. More hot spots were observed in the fractal decorated with NP structure than the pure fractal surface. This qualitative agreement with the predictions on fractal surfaces [20] argues strongly that the dimensionality of the surface is the essential feature in localizing the field to produce giant enhancements. The larger volume of the local EM field that exists in the fractallike silver structure contributes to the enhanced fluorescence [23].

4. Conclusion

The fluorescence enhancement induced by a fractallike structure decorated with and without Ag NPs was observed and investigated for an Rh6G fluorescent monolayer. The largest fluorescence amplification was obtained from a fractallike structure decorated with Ag NPs, and it is larger than that of the pure fractallike structure. These effects are explained by coupled excitation of the local field around the fluorophore molecules. The enhancement factor integrated over the volume that contains the fluorophore molecules depends on both the field enhancement and the size of the near-field zone. A larger volume and more hot spots can be produced when Ag NPs are deposited on the fractal structure, thus a higher SEF effect was observed from the decorated structure. The work presented here has implications for ultrasensitive bioassays with improved detectability of biomolecules.

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References