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Photochemical Synthesis of Silver Nanodecahedrons under Blue LED Irradiation and Their SERS Activity

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Received: 15 February 2020; Accepted: 2 March 2020; Published: 4 March 2020

Abstract: Silver nanodecahedrons were successfully synthesized by a photochemical method under irradiation of blue light-emitting diodes (LEDs). The formation of silver nanodecahedrons at different LED irradiation times (0–72 h) was thoroughly investigated by employing different characterization methods such as ultraviolet–visible spectroscopy (UV–Vis), transmission electron microscopy (TEM), and Raman spectroscopy. The results showed that silver nanodecahedrons (AgNDs) were formed from silver nanoseeds after 6 h of LED irradiation. The surface-enhanced Raman scattering (SERS) effects of the synthesized AgNDs were also studied in comparison with those of spherical silver nanoparticles in the detection of 4-mercapto benzoic acid. Silver nanodecahedrons with a size of 48 nm formed after 48 h of LED irradiation displayed stronger SERS properties than spherical nanoparticles because of electromagnetic enhancement. The formation mechanism of silver nanodecahedrons is also reported in our study. The results showed that multihedral silver nanoseeds favored the formation of silver nanodecahedrons.

Keywords: silver nanodecahedron; SERS; photochemical synthesis; LEDs

1. Introduction

Recently, silver nanomaterials have gained much attention due to their various applications in the areas of electronic and sensor engineering, catalysis, biomedicine, and surface-enhanced Raman scattering (SERS) [1,2]. For the most part, these applications are based on unique optical properties of silver nanomaterials, particularly their light absorption and scattering ability as a result of surface plasmon resonance [1,3]. The optical properties depend on the shape and size of the nanoparticles, therefore in the last decade, many groups all over the world have studied the synthesis of silver nanomaterials with shape- and size-controlled anisotropy, such as plate-, cube-, wire-, rod-, pyramid-, and decahedron-shaped silver [1–4]. Among these, silver nanoplates (AgNPs) and silver nanodecahedrons (AgNDs) have been

studied because of their localized surface plasmon resonance in a longer wavelength region. In particular, AgNDs with multihedral structure display a remarkable scattering ability [3,4]. So far, AgNDs have been synthesized by a chemical method using hydrazine as a reductive agent and trisodium citrate as a stabilizer [5]. However, only few AgNDs are obtained with this method. The synthesis of AgNDs using a photochemical method based on irradiation by light-emitting diodes (LEDs) for a better control of their shape has gained much attention [3,4,6–10]. One of the first researchers to study AgNDs were Stamplecoskie and Scaiano. In their study, AgNDs were synthesized via two steps: firstly, the synthesis of 3 nm spherical AgNPs with the optical reductive agent I-2959 and, secondly, their irradiation using 455 nm blue LEDs. However, the reaction mechanism is not known [6]. Jamil Saade et al. also synthesized AgNDs by irradiating 3–5 nm AgNP seeds with blue LEDs, but no applications of AgNDs were mentioned [7]. Shan-Wei Lee et al. first reported the synthesis of AgNDs based on the two aforementioned steps but using 520 nm green LEDs at low temperature for SERS applications. Although these authors claimed that the obtained AgNDs have better SERS properties than AgNPs, no persuasive explanation was given [8]. While studying the thermodynamics of formation of AgNDs, Haitao Wang et al. realized that using LEDs at a low temperature would facilitate the formation of AgNDs. They studied the mechanism of AgNDs formation but did not consider the surface plasmon effect, one of the important surface properties of silver nanomaterials [9]. Cardoso-Avila et al. also applied LED irradiation on quartz cuvettes containing AgNPs to synthesize AgNDs; however, neither the reaction mechanism nor the SERS effects were thoroughly investigated [10,11].

In this study, we synthesized AgNDs under blue LED irradiation via a two-step photochemical method. The formation of AgNDs was investigated at different LED irradiation times. The SERS effects of the synthesized AgNDs were also studied in comparison with those of AgNPs in the detection of 4-mercapto benzoic acid (4-MBA), a Raman tester able to bind to silver nanoparticles through Ag–S bonds, enhancing the SERS effects [12–14].

2. Materials and Methods

2.1. Chemicals

Silver nitrate ($AgNO_3$, >99%, Sigma-Aldrich, Darmstadt, Germany), trisodium citrate tribasic dihydrate (TSC, >99%, Sigma-Aldrich, Darmstadt, Germany), polyvinylpyrrolidone (PVP K30, Prolabo, Kennersburg, NJ, USA), L-arginine (L-A, 99%, Merck, Darmstadt, Germany), sodium borohydride ($NaBH_4$, 98%, Merck, Darmstadt, Germany), 4-mercapto benzoic acid (4-MBA, 99%, Sigma-Aldrich, Darmstadt, Germany), and DI water (standard HPLC, Merck, Darmstadt, Germany). Chemicals were used without any purification.

2.2. Synthesis of Silver Nanodecahedrons

AgNDs were synthesized in 2 steps: (i) synthesis of AgNPs as seeds and (ii) irradiating the seeds with blue LEDs to grow AgNDs with the aid of L-A [3,11]. The synthesis procedure is described in Figure 1.

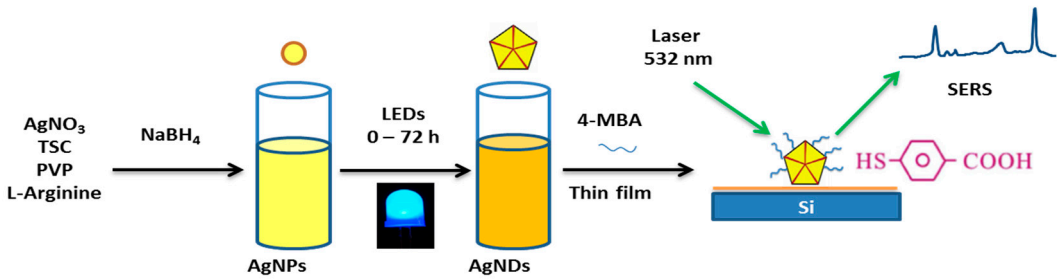

Figure 1. Schematic illustration of the fabrication and surface-enhanced Raman scattering (SERS) measurement of nanodecahedrons (AgNDs). TSC: trisodium citrate tribasic dihydrate, PVP: polyvinylpyrrolidone, AgNPs: silver nanoplates, LEDs: light-emitting diodes, 4-MBA: 4-mercapto benzoic acid.

2.3. Synthesis of Seeds

All glass equipment and magnetic stirrers were treated with aqua regia before use. In total, 5 mL of 50 mM TSC, 150 µL of 50 mM PVP, 2 mL of 5 mM $AgNO_3$, and 250 µL of 5 mM L-A were mixed in a beaker, then milli-Q water was added into the mixture to 100 mL. The mixture was magnetically stirred at 500 rpm for 5 min. Afterwards, 800 µL of 100 mM $NaBH_4$ was rapidly added to the solution. The color of the solution immediately changed into light yellow, then yellow, indicating the presence of AgNPs in the solution. The solution was stirred at room temperature and aged in the dark overnight.

2.4. Synthesis of AgNDs

A volume of 20 mL of the as-synthesized AgNPs solution stored in a glass bottle (Wheaton-Germany) was exposed to blue LEDs (Dragon—Taiwan, 460 ± 12 nm, output: 10 W) for 6, 12, 24, 48, and 72 h; the color of the solution changed from yellow to orange.

2.5. Characterization

The morphological structure of the synthesized AgNDs was studied through a JEOL JEM-1400 (Jeol Ltd., Tokyo, Japan). The samples were dropped onto 3 mm-diameter copper grids, dried at room temperature, and analyzed by TEM (Jeol Ltd., Tokyo, Japan) at 100 kV. The light absorption spectra of AgNDs and intermediates were analyzed by a V-750 UV/Vis spectrophotometer (Jasco Co., Tokyo, Japan, 100 nm scanning speed per minute).

2.6. SERS Measurements

SERS in the presence of the reductive agent 4-MBA by silver nano-seeds and AgNDs obtained after 48 h of LED irradiation was measured on a Si wafer. The wafer was cut into 1 × 1 cm slices and treated with piranha solution to remove all organic compounds. Then, 2 mL of AgNDs (or AgNPs) solution was centrifuged at 12,000 rpm for 15 min to obtain a precipitate. The precipitate was then redispersed into 1 mL of DI water; 50 µL of 10^{-5} M 4-MBA solution was mixed with 450 µL of the sample solution for 1 h at room temperature. Afterwards, 20 µL of the obtained mixture was dropped on the Si wafer and dried at room temperature, obtaining a 4-MBA@AgNDs (or AgNPs) @Si wafer ready for Raman analysis, carried out with HORIBA XploRA ONE TM, Palaiseau, France, equipped with a 532 nm laser source and a 10x optical microscope lens. The sample was analyzed at 10 random locations to obtain an average value. For comparison, the Raman spectrum of a 10^{-4} M 4-MBA solution without AgNDs or AgNPs was also recorded with the same procedure.

3. Results

3.1. Synthesis of Silver Nanodecahedrons

The UV–Vis results in Figure 2 show the formation of silver nanoseeds (at 0 h) which presented an absorption peak at 400 nm (peak 1). A yellow color indicated the presence of spherical silver nanoparticles in the solution [4–9]. After irradiating with LEDs for 6 h, this peak showed a red shift to 407 nm, and another peak (peak 2) appeared at 460 nm, corresponding to the vibration of dipole resonance of AgNDs [6–9]. It was concluded that AgNDs were formed after 6 h of LED irradiation. After increasing the irradiation time to 12 h, the UV–Vis spectra showed red shifts of both peak 1 and peak 2 toward higher wavelengths, i.e., 413 nm and 470 nm, respectively. On the other hand, the absorbance of peak 1 decreased, while that of peak 2 increased rapidly due to the generation of more AgNDs from AgNPs after 12 h of irradiation. After 24 h, peak 1 was shifted toward 404 nm, and the absorbance decreased from 1.1 to 0.5 a.u., proving the number of AgNPs in the solution continued to decrease under LED irradiation. Peak 2 showed a decrease in the absorbance from 2.0 to 1.3, but the wavelength did not change much. On the other hand, after 24 h, peak 3 appeared at 345 nm, in accordance with AgNDs' out-of-plane quadrupole resonance [6,9]. When we continued to increase the

irradiating time to 48 and 72 h, we did not observe significant changes in the UV–Vis spectra. In fact, compared to the 24 h spectrum, peak 1 and peak 3 intensity almost did not change, while the intensity of peak 2 (464 nm), corresponding to AgNDs's dipole resonance, increased to 1.81. In conclusion, 48 h of irradiation was a suitable time to transform AgNPs to AgNDs.

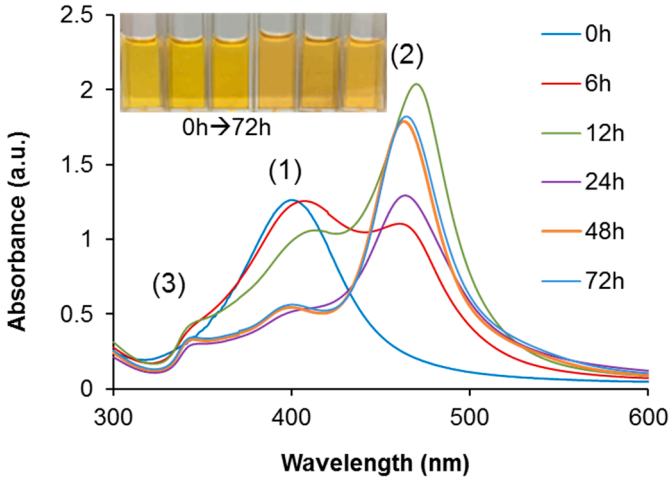

Figure 2. UV–Vis spectra of silver nanoparticles at different LED irradiation times.

The TEM images in Figure 3a revealed that AgNDs with average size of 30 nm and AgNPs smaller than 10 nm on average were the dominant species in the sample irradiated for 6 h. After 48 h of irradiation, the TEM image showed the presence in the sample of AgNDs with average size of 48 nm, in addition to AgNPs smaller than 10 nm on average. Moreover, the TEM results also indicated that increasing the LED irradiation time would result in the combination of AgNPs, leading to the formation of AgNDs, which was consistent with the UV–Vis results.

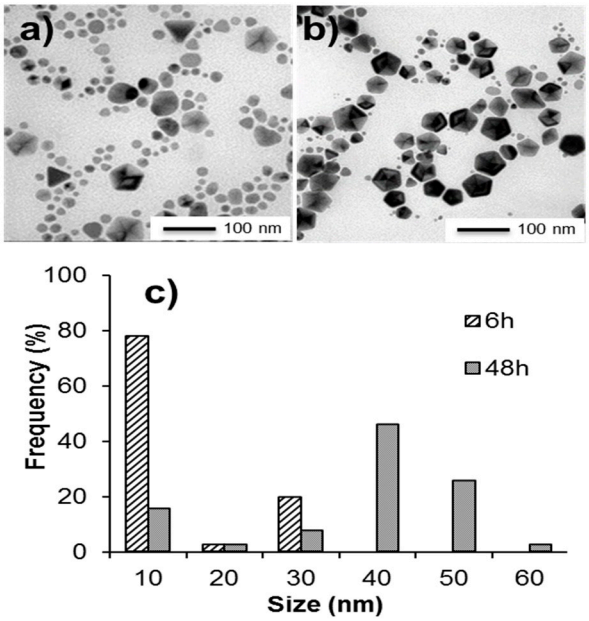

Figure 3. (**a**,**b**) TEM images and (**c**) particle size distribution of silver nanoparticles after 6 h and 48 h of irradiation.

The formation mechanism of AgNDs under blue LEDs is shown in Figure 4. Due to their surface plasmon resonance properties, the silver nanoparticles were able to combine to form anisotropic silver nanoparticles with larger size when they were irradiated by LEDs, which provided enough energy for

surface plasmon resonance [9]. The combination is illustrated in Figure 4. We propose two plausible growth processes for the formation of Ag decahedrons.

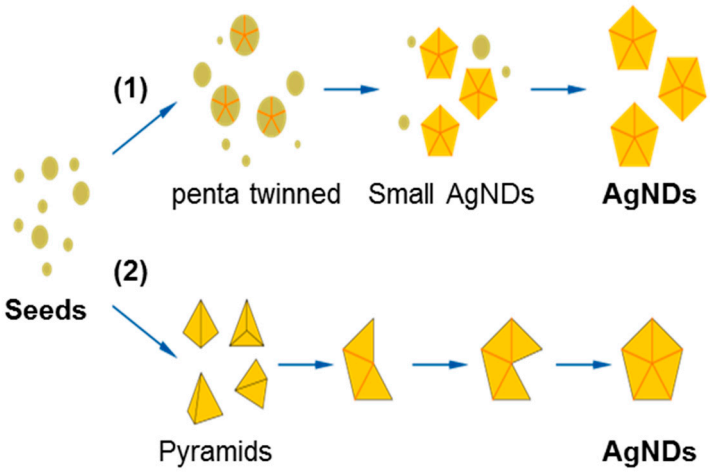

Figure 4. Proposed mechanisms of formation of AgNDs.

Mechanism 1: AgNP seeds were first generated as multihedral seeds with a small size, then combined with new-born seeds to form larger AgNDs [3,4,7,9]. It is widely accepted that the shape of multihedral seeds strongly depends on the excitation wavelength. For example, irradiation with blue LEDs would result in the formation of penta-twinned AgNDs [4,7,9,15], while planar twinned seeds can be generated under green LEDs [6–8]. The TEM results of AgNDs formed after 6 h of LED irradiation in this study showed the existence of AgNDs with sizes smaller than 20 nm, supporting this mechanism.

Mechanism 2: Silver nanopyramids were first generated due to the combination of AgNPs. Five pyramids were then combined along their side edges to form AgNDs during LED irradiation [4,7]. The TEM results of AgNDs observed after 48 h of irradiation (Figure 3) showed the presence of some silver nanopyramids and incomplete AgNDs, providing a proof of this mechanism.

In general, both mechanisms are possible during LED irradiation. Compared to mechanism 2, mechanism 1 is favored because of the low probability of forming AgNDs from five pyramid nanoparticles. Moreover, according to the UV–Vis results, the dramatic decrease in intensity of both peak 1 and 2 after 24 h of LED irradiation, as well as the gradual increase in intensity of peak 2 and the negligible change in intensity of peak 1 as the LED irradiation time of the silver solution kept increasing up to 48 h, indicated the aggregation of small AgNDs into larger AgNDs, which further supports mechanism 1.

3.2. SERS Properties of AgNDs

The Raman spectra of 4-MBA powder shown in Figure 5c revealed two peaks at 1091 and 1597 cm^{-1}, corresponding to the aromatic ring vibration, and two peaks at 1150 and 1180 cm^{-1}, corresponding to the COO^- vibration [12–14]. The SERS spectra of the mixture of 10^{-5} M 4-MBA and AgNPs or AgNDs showed that the peaks of the aromatic ring were shifted toward 1082 and 1589 cm^{-1} (Figure 5a,b). The remarkably higher intensity of the Raman peaks compared with the flat Raman signal of 10^{-4} M 4-MBA (as well as of 10^{-5} M 4-MBA) (Figure 5d) indicated that both materials were capable of enhancing SERS; in particular, AgNDs showed better SERS enhancement than AgNPs.

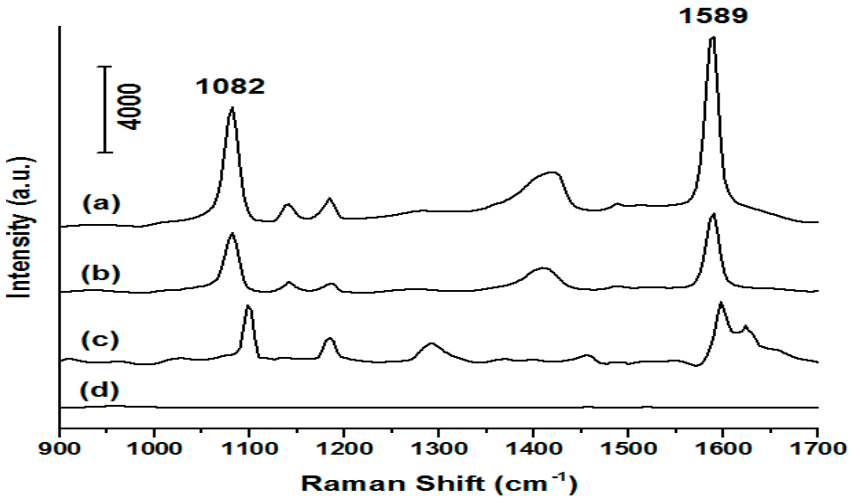

Figure 5. Raman spectra of the mixture of 4-MBA (10^{-5} M) and (**a**) AgNDs (after 48 h of LED irradiation) or (**b**) AgNPs; Raman spectra of (**c**) 4-MBA powder and (**d**) 4-MBA (10^{-4} M).

The enhancement of SERS was probably due to chemical and electromagnetic mechanisms [12,13]. The chemical mechanism depends on the binding of 4-MBA and nano-silver. Since both AgNPs and AgNDs were capable of binding 4-MBA through Ag–S bonds, the difference in SERS properties was due to the electronic mechanism, which is deeply related to the surface plasmon properties of nano-silver. AgNDs have better surface plasmon properties than AgNPs, as displayed by the UV–Vis results, showing a bipolar peak for AgNPs twice as big as that of AgNDs. On the other hand, because the excited wavelength was 532 nm, closer to the wavelength of the bipolar peak of AgNPs (464 nm) than to that of the peak of AgNDs (400 nm), AgNDs were capable of better enhancing SERS, in agreement with Haifei Lu's report [3]. Besides, energy-concentrating spots called "hot spot" formed on AgNDs' surface, which were located at the points and lines of the decahedrons [3,4,12,13] corresponding to face (111). These spots further enhanced the SERS properties of AgNDs.

4. Conclusions

We successfully synthesized silver decahedrons nanomaterials (AgNDs) by a photochemical method using blue 10 W LEDs. After 48 h of LED irradiation, silver nanoparticles with size smaller than 10 nm combined with each other, forming AgNDs with average size of 48 mn, which were analyzed by UV–Vis spectroscopy and TEM. The results indicated that AgNDs were formed through intermediates such as small AgNDs seeds or silver nanopyramids. Both silver nanoseeds and AgNDs exhibited good SERS enhancement in the presence of 4-MBA. AgNDs had better SERS effects than AgNPs, which can be explained by an electronic mechanism.

Author Contributions: Conceptualization, N.T.P.P. and D.H.N. methodology, N.T.P.P. and D.H.N. formal analysis, M.N.T.A., D.T.D.N., and N.V.K.T. investigation, M.N.T.A. and D.T.D.N. writing—original draft preparation, M.N.T.A. and M.-T.N.-L. writing—review and editing, M.-T.N.-L. supervision, M.-T.N.-L. administration, D.H.N. funding acquisition, D.H.N. and M.-T.N.-L. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the People's Committee of Ho Chi Minh City, performed with the support of the Board of Management of Saigon High-Tech Park (SHTP), the Research Laboratory of Saigon Hi-Tech Park (SHTPLABs), and the Institute of Applied Materials Science, Vietnam Academy of Science and Technology (IAMS).

Conflicts of Interest: The authors declare no conflict of interest.

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