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Seedless, Surfactantless Room Temperature Synthesis of Single Crystalline Fluorescent Gold Nanoflowers with Pronounced SERS and Electrocatalytic Activity

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Nanostructured noble metal particles have received considerable interest in the recent years due to their fascinating optical, electronic, and catalytic properties.[1,2] Among the many different nanomaterials, nanosized Au and Ag particles are very attractive for various applications, mainly because of their unique optical, catalytic, and electrocatalytic properties. The properties of the nanostructured metal particle can be easily tuned by tailoring their size and shape. Colloidal Au and Ag nanoparticles are of special interest in surface-enhanced Raman scattering (SERS) as a substrate, mainly because they strongly scatter light and their optical properties depend on the size, shape, and aggregation state.[3] Because dramatic enhancement in the scattering can be observed for the molecules adsorbed on the nanostructured particles, single molecule spectroscopy is possible by SERS.[4] Furthermore, the nanosized metal particles are known to show excellent electrocatalytic activity, and the catalytic behavior depends on their shape and size.[5a] Various approaches have been made to synthesize nanoparticles of different shape.[5,6] Only a handful of papers report the synthesize of nanoparticles having flower-like morphology by chemical and electrochemical routes.[7] In this communication, we describe a simple one-pot approach for the synthesis of fluorescent nanostructured Au particles with marigold (nMG) like morphology without any extra control, seed, surfactant, and so forth and its SERS and electrocatalytic activity for the first time.

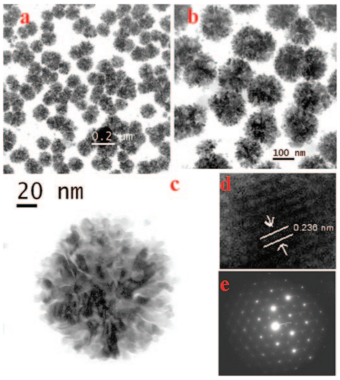

Figure 1. Representative TEM images (a–c) and SAED pattern (e) obtained for nMGs. (c) HRTEM image of nMg shown in c.

The nMGs were obtained by the simple mixing of an aqueous solution of 5-hydroxyindole-3-acetic acid (HIAA) (0.075 mM) and $HAuCl_4$ (0.3 mM) at room temperature and stirring the solution for 30 min. The color of the solution turned to salmon immediately after mixing, indicating the formation of Au nanoparticles. Figure 1 shows the representative TEM images obtained for the nanoparticle. Interestingly, the TEM images show nanocrystals having peculiar shape and morphology, very similar to the marigold flower. The nMGs have an average size of 150 ± 10 nm. The hexagonal nature of the selected area electron diffraction (SAED) pattern (Figure 1e) reveals that nMGs are single crystalline with a (111) lattice plane. High-resolution TEM images of selected nMGs were taken to further examine the morphology. The lattice fringe spacing of the nMGs was determined (Figure 1d) to be 0.236 nm, corresponding to the (111) plane spacing of face centered cubic (fcc) Au. It is known that the formation of anisotropic nanostructure in liquid media involves the utilization of a caping agent such as a surfactant to kinetically control the growth rate. In our case, the anisotropic particles have been obtained without such surfactants. HIAA not only functions as a reducing agent but also controls the growth of the particles as the surfactants. It should be mentioned here that the concentration of HIAA controls the shape and surface morphology of the nanoparticles (vide infra). The energy dispersive spectrum (EDS) confirms that the nMGs consist of only Au (Supporting Information). The X-ray diffraction (XRD) pattern recorded for nMGs self-assembled on a glass slide shows only one peak corresponding to the (111) plane of fcc (Figure

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(1) (a) Shipway, A. N.; Katz, E.; Willner, I. *Chem. Phys. Chem.* **2000**, *1*, 18. (b) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293. (c) Katz, E.; Willner, I. *Angew. Chem., Int. Ed* **2004**, *43*, 6042.

(2) (a) Rosi, N. L.; Mirkin, C. A. *Chem. Rev* **2005**, *105*, 1547. and the references cited therein. (b) Tsai, C.-S.; Yu, T.-B.; Chen, C.-T. *Chem. Commun.* **2005**, 4273. (c) Liu, J.; Lu, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 90.

(3) (a) El-Sayed, M. *Acc. Chem. Res.* **2001**, *34*, 257. (b) Kely, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.

(4) (a) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102. (b) Graham, D.; Smith, W. E.; Linacre, A. M. T.; Munro, C. H.; Watson, N. D.; White, P. C. *Anal. Chem.* **1997**, *69*, 4703. (c) Orendorff, C. J.; Gearheart, L.; Jana, N. R.; Murphy, C. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 165.

(5) (a) Li, Y.; Shi, G. *J. Phys. Chem. B* **2005**, *109*, 23787. (b) Malikova, N.; Pastoriza-Santos, I.; Schierhorn, M.; Kotov, N. A.; Liz-Marzan, L. M. *Langmuir* **2002**, *18*, 3694. (c) Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3673. (d) Chu, H.-C.; Kuo, C.-H.; Huang, M. H. *Inorg. Chem.* **2006**, *45*, 808. (e) Shankar, S. S.; Rai, A.; Ankamwar, B.; Singh, A.; Ahmad, A.; Sastry, M. *Nat. Mater.* **2004**, *3*, 482. (f) Shao, Y.; Jin, Y.; Dong, S. *Chem. Commun.* **2004**, 1104. (g) Li, C.; Shuford, K. L.; Park, Q.-H.; Cai, W.; Li, Y.; Lee, E. J.; Cho, S. O. *Angew. Chem., Int. Ed.* **2007**, *46*, 1. (h) Bakr, O. M.; Wunsch, B. H.; Stellaci, F. *Chem. Mater.* **2006**, *18*, 3297. (i) Lu, G.; Li, C.; Shi, G. *Chem. Mater.* **2007**, *19*, 3433.

(6) (a) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T. *J. Phys. Chem. B* **2005**, *109*, 13857. and the references cited therein. (b) Nehl, C. L.; Liao, H.; Hafner, J. H. *Nano Lett.* **2006**, *6*, 683. (c) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957.

(7) (a) Jena, B. K.; Raj, C. R. *Langmuir* **2007**, *23*, 4064. (b) Guo, S.; Wang, L.; Wang, E. *Chem. Commun.* **2007**, 3163. (c) Wang, T.; Hu, X.; Dong, S. *J. Phys. Chem. B* **2006**, *110*, 16930. (d) Duan, G.; Cai, W.; Luo, Y.; Li, Y.; Lei, Y. *Appl. Phys. Lett.* **2006**, *89*, 181918. (e) Duan, G.; Cai, W.; Luo, Y.; Li, Z.; Li, Y. *Appl. Phys. Lett.* **2006**, *89*, 211905.

10.1021/cm7019608 CCC: $40.75

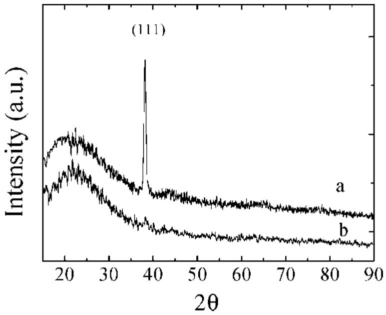

Figure 2. XRD pattern obtained for (a) after and (b) before the self-assembling of nMGs.

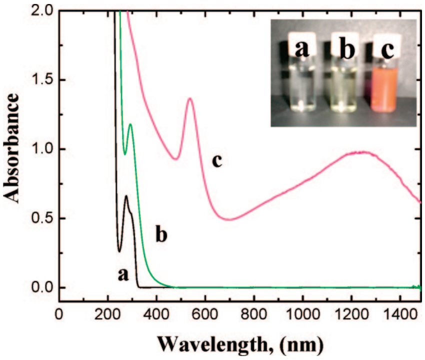

Figure 3. UV−visible NIR spectra obtained for (a) HIAA, (b) $HAuCl_4$, and (c) colloidal nMGs. Inset shows the photograph of the corresponding solutions.

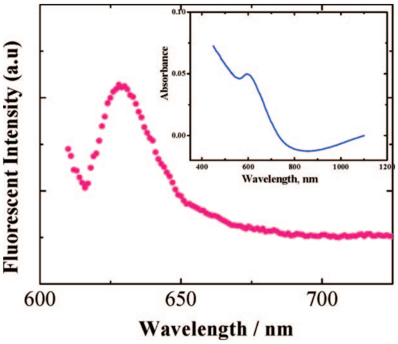

Figure 4. Emission spectrum obtained for self-assembled nMGs. Excitation wavelength: 600 nm. Inset shows the corresponding UV−visible spectrum of nMGs.

2), indicating that the nMGs are indeed Au(111) single crystals.

Figure 3 is the optical absorption spectra obtained for $HAuCl_4$, HIAA, and the colloidal nanoparticles. The absorption band at 298 nm for $HAuCl_4$ completely disappears upon the addition of HIAA, and the color of $HAuCl_4$ changes to salmon (Figure 3, inset), indicating the reduction of Au^{3+} and the formation of Au nanoparticles. The nMGs has peculiar color and is largely different from the conventional spherical shape nanoparticles. The colloidal nMGs show two plasmon absorption bands, at 545 and 1250 nm. The band at 1250 nm is rather broad. The anisotropic nanoparticles are known to exhibit characteristic bands corresponding to transverse and longitudinal plasmon absorption.[3a] The longitudinal band is tunable with aspect ratio of the nanoparticles from the visible to NIR region.[3a] In our case the two bands observed at 545 and 1250 nm are ascribed to the transverse and longitudinal absorptions, respectively.

It is very interesting to note that the nMGs are highly fluorescent. The nMGs either in colloidal solution or immobilized on solid surface exhibit an intense emission band when it was excited at the transverse band. The surface immobilized nMGs exhibit an emission band at 628 nm (Figure 4) whereas the colloidal nMGs show the emission at 585 nm (Supporting Information). The fluorescence of nMGs can be either associated with the shape and surface morphology of the nanoparticle or due to the oxidzed product of HIAA adsorbed on the nanoparticle surface. El-Sayed and co-workers demonstrated that the Au nanorods exhibit fluorescence and the intensity of fluorescence depends on the aspect ratio.[8] The fluorescence of Au nanorod was ascribed to the interband recombination of electron and hole.[8] It is believed that the presence of longitudinal surface plasmon resonance effectively amplifies the fluorescence of metallic Au.[8] It is well-known that the surface morphology and shape of the nanoparticles strongly depends on the concentration of reducing/stabilizing agent and the metal precursor. To find the origin of the fluorescence of nMGs, we have synthesized nanoparticles at high concentration of HIAA (0.15 and 0.3 mM) and investigated their spectral behavior and surface morphology. The optical absorption spectrum of these nanoparticles show a surface plasmon band at 552 and 577 nm (Supporting Information). The colors of these two colloidal nanoparticles are largely different from that of nMGs (Supporting Information). The TEM image obtained for these nanoparticles reveals that the shape and morphology of the nanoparticles are largely different from nMGs. More importantly, these two nanoparticles do not show any characteristic emission (Supporting Information) as in the case of nMGs, indicating that the emission of nMGs could be associated with the nanostructured particle. If the emission is originated from the oxidized product of HIAA, the nanoparticles obtained at high concentration should also exhibt fluorescence. As the nanoparticles obtained at higher concentration of HIAA do not show emission band, we suggest that the emission of nMGs could be due to its surface morohology and shape. It is worth pointing out here that the conventional spherical Au nanoparticle does not show such fluorescence (Supporting Information). The chemical and electrochemical oxidation of 5-hydroxyindoles are known to yield a mixture of several oligomeric products.[9] Although the electrochemical studies on the oxidation chemistry of 5-hydroxyindoles are well-known,[9b–d] to the best of our knowledge the fluorescence spectral properties of the oxidation products have not been reported. Further works are necessary to identify the oxidation products of HIAA generated during the formation of nMGs and to investigate their spectral properties.

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(8) (a) Link, S.; El-Sayed, M. A. *Annu. Rev. Phy. Chem.* **2003**, *54*, 331. (b) Mohamed, M. B.; Volkov, V.; Link, S.; El-Sayed, M. A. *Chem. Phys. Lett.* **2000**, *317*, 517.

(9) (a) Napolitano, A.; d'Ischia, M.; Prota, G. *Tetrahedron* **1988**, *44*, 7265. (b) Goyal, R. N.; Sangal, A. *J. Electroanal. Chem.* **2005**, *578*, 185. (c) Wrona, M. Z.; Drhurst, G. *Bioorg. Chem.* **1990**, *18*, 291. (d) Wrona, M. Z.; Drhurst, G. *J. Org. Chem.* **1987**, *52*, 2817.

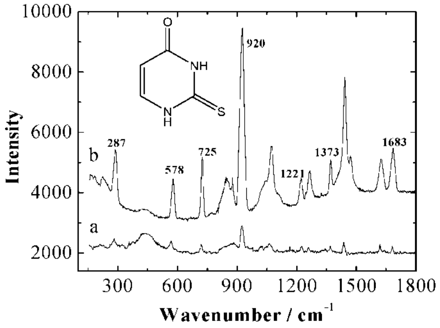

Figure 5. SERS spectra of 2-TU (1 μM) in the (a) absence and (b) presence of nMGs.

The surface enhanced Raman spectroscopy (SERS) is considerd to be a powerful analytical tool for determining chemical information of molecule adsorbed on the surface of coinage metal particles.[4,10] It can be successfully used for the ultrasensitive detection of different analytes. Surface morphology and structure of the substrate plays a key role in SERS. Because nMGs have peculiar morphology and surface structure, it would be very promising to utilize them for SERS application. We have chosen the biologically important 2-thiouracil (2-TU) as a target molecule to examine SERS activity of nMGs. 2-TU and its derivatives show high antithyroid, antiviral, and antitumor activity.[11] Sensitive detection of 2-TU at low concentration is of significant interest for pharmokinetic and clinical studies. Figure 5 is the SERS spectra of 2-TU in the presence and absence of aqueous colloidal nMGs. The overall spectral features obtained for 2-TU are consistent with those reported in the literature.[12] The spectral signals in the absence of nMG are very weak, and some of the bands are not seen clearly at the concentration used. However, dramatic enhancement in the peak intensity was observed in the presence of nMGs. Signficant enhancement in the intensity for the band at 920 cm^{-1} corresponding to the in plane bending of N(3)CC and ring[12a] was observed. In the absence of nMGs, the band observed at 1221 cm^{-1} corresponding to the in plane bending of C(5)−H and C(6)−H is not prominent. However, it is very prominent in the presence of nMGs. The assignments of different bands observed are given in TS 1 (Supporting Information). It is generally accepted that the SERS effect at the nanostructured surface is the result of a combination of enhancement of localized electromagnetic field incident on an adsorbed molecule and chemical effect.[13] For noble metals, the enhancement effect is primarily due to the electromagnetic effect.[13c] The predominance of the bands corresponding to the in plane vibration implies significant contribution of the electromagnetic effect for the enhacement.[13d]

The electrochemical oxidation of NADH in aqueous solution has attracted considerable interest in the development of amperometric biosensors for the detection of biomolecules, which react with NAD$^+$ to produce NADH in physiological pH. To examine the electrocatalytic actvity, nMGs were self-assembled on an −SH functionalized sol−gel-derived 3-D network (Supporting Information) according to our previous report.[7a] The nMGs self-assembled electrode shows an inverted V shape voltammogram for the oxidation of NADH at −0.05 V (Supporting Information). Remarkable decrease in the overpotential (900 mV) and significant increase in the peak current with respect to the bulk Au electrode have been observed at this electrode, indicating that nMGs efficiently catalyze the oxidation of NADH. The special inverted V shape of the voltammogram implies that the oxidation process involves surface bound species. Note that the onset potential for the oxidation of NADH is −0.45 V, showing the excellent electrocatalytic activity of nMGs. As nMGs show excellent electrocatalytic response with a significant decrease in the overpotential in the absence of any additional redox mediator, it could find application in the development of electrochemical biosensors.

In conclusion, we have demonstrated a simple approach for the synthesis of single crystalline Au particle with special morphology and shape. The nanostructured Au particle is fluorescent and shows pronounced SERS and electrocatalytic activity. The SERS and electrocatalytic activity have been examined using biologically important 2-thiouracil and NADH, respectively. As our nanoparticle exhibits a longitudinal surface plasmon band in the NIR region, it can be used in infrared absorbing optical coatings. Because the nMGs are fluorescent both in the colloidal and in the solid state, it may be used in biological systems. This fluorescent nature of nMGs may be exploited for practical application by immobilizing the biological molecules that have affinity for Au. Further works to identify the oxidation products of HIAA and to investigate their spectral properties are progressing.

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Supporting Information Available: Experimental methods and results as indicated in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Graham, D.; Faulds, K.; Smith, W. E. *Chem. Commun.* **2006**, 4363. (b) Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Chem. Rev.* **1999**, *99*, 2957.

(11) (a) Cooper, D. S. *N. Engl. J. Med.* **2005**, *352*, 905. (b) Lindsay, R. H.; Romine, C. J.; Wong, M. Y. *Arch. Biochem. Biophys.* **1968**, *126*, 812. (c) Yu, M. Y. W.; Sedlak, J.; Lindsay, R. H. *Arch. Biochem. Biophys.* **1973**, *155*, 111.

(12) (a) Aguiar, H. B.; Sant'Ana, A. C.; Temperini, M. L. A.; Corio, P.; Cunha, F. *Vibrational Spectrosc.* **2006**, *40*, 127. (b) Joy, V. T.; Srinivasan, T. K. K. *J. Raman Spectrosc.* **2001**, *32*, 785. (c) Rostkowska, H.; Szczepaniak, K.; Nowak, M. J.; Leszczynski, J.; KuBulat, K.; Person, W. B. *J. Am. Chem. Soc.* **1990**, *112*, 2147.

(13) (a) Jiang, J.; Bosnick, K.; Maillard, M.; Brus, L. *J. Phys. Chem. B* **2003**, *107*, 9964. (b) Xu, H. X.; Bjerneld, E. J.; KallM.; Borjesson, L. *Phys. Rev. Lett.* **1999**, *83*, 4357. (c) Baldwin, J. A.; Vlckova, B.; Andrews, M. P.; Butler, I. S. *Langmuir* **1997**, *13*, 3744. (d) Wang, T.; Zheng, R.; Hu, X.; Zhang, L.; Dong, S. *J. Phys. Chem. B* **2006**, *110*, 14179.