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Ionic liquid-assisted synthesis of thorned gold plates comprising three-branched nanotip arrays†

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Hierarchically structured, thorned gold plates comprising regular, three-branched nanotip arrays were synthesized by a facile, one-pot reduction process in mixed solvents of the ionic liquid [BMIM][PF$_6$] and formamide without additives.

Gold nanostructures have attracted significant research interest because of their unique physical, chemical, and biocompatible properties, as well as promising applications.[1] Since the intrinsic properties and relevant applications of gold nanostructures are largely determined by their size and shape, there has been remarkable progress over the past decade in the shape-controlled synthesis of gold nanocrystals.[2] In particular, gold nanoparticles with sharp tips (*e.g.*, rods/wires,[3] triangles,[4] and stars/dendrites[5]) are attracting increasing interest since they can sustain large electromagnetic fields at their ends, vertices, or tip apexes upon excitation with light of appropriate energy, which makes them promising candidates for applications in ultrasensitive detection based on surface enhanced spectroscopies.[6–8] It is notable that the seeded growth method was recently employed for the fabrication of dendritic gold nanostructures with a fractal architecture[9] and thorned nanowires comprising sharp tips.[7] However, it remains a challenge to realize the facile synthesis of hierarchical gold structures comprising regular nanotip arrays.

Surface-enhanced Raman scattering (SERS) is a sensitive analytic technique and powerful tool for fundamental studies of surface species, and hence considerable efforts have been devoted to the controlled fabrication of novel plasmonic nanostructures as highly sensitive, robust, and reproducible SERS substrates.[10] Particularly, planar nanotip arrays with high tip density are appealing SERS substrates as the sharp tips and the small gaps between adjacent tips can significantly enhance the local electromagnetic fields, leading to high SERS enhancement. In this regard, various energy- or time-consuming procedures, such as Ar$^+$-ion irradiation,[11] electron beam lithography,[12] nanoimprint lithography,[13] as well as nanosphere lithography,[14] were developed for preparing gold nanotip arrays. It would be desirable to explore efficient wet chemical routes towards the controlled growth of planar gold nanotip arrays. Recently, ionic liquids have shown great potential in the solution-phase preparation of tailored inorganic nanostructures.[15] We fabricated hierarchical, three-fold symmetrical, gold dendrites by the reaction between a Zn plate and a solution of HAuCl$_4$ in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]).[16] Herein, we report a facile, one-pot synthesis of novel hierarchically ordered, thorned gold plates comprising three-branched nanotip arrays by the reduction of HAuCl$_4$ in mixed solvents of [BMIM][PF$_6$] and formamide without additives.

The synthesis of the thorned gold plates with three-branched nanotips was achieved simply by reducing HAuCl$_4$ in mixed [BMIM][PF$_6$]/formamide solvents where formamide acted as both a reducing agent and a cosolvent. In a typical synthesis, 500 μL of [BMIM][PF$_6$] containing 10 mM HAuCl$_4$ was mixed with 500 μL formamide in a plastic tube at room temperature to give a yellowish HAuCl$_4$ solution (5 mM), which was then kept in an oven at 95 °C and held for ~24 h. The resulting precipitate was washed with acetone thoroughly and characterized by scanning electron microscopy (SEM, Hitachi S4800, 15 kV), transmission electron microscopy (TEM, FEI Tecnai F30, 300 kV), and powder X-ray diffraction (XRD, Rigaku Dmax-2000, Cu-Kα).

Fig. 1 shows representative SEM images of the gold product obtained after 24 h of aging at 95 °C in mixed [BMIM][PF$_6$]/formamide solvents with a volume ratio of 1 : 1. As shown in Fig. 1a, the product consists of hexagonal plates typically about 2–4 μm in width and 500–600 nm in thickness together with some relatively smaller particles. The related XRD and energy-dispersive X-ray spectroscopy (EDS) characterizations show that the product is pure gold crystals of the cubic structure (Fig. S1, ESI†). Fig. 1b shows an enlarged SEM image of the gold plates, which suggests that the well-defined hexagonal plates show thorned surfaces comprising densely aligned nanotips on both the top and bottom planes. A high-magnification top-view clearly shows dense arrays of three-branched nanotips standing vertically on the top surface of the gold plate (Fig. 1c), while a high-magnification side-view suggests that the three-branched nanotips actually adopt a cone-like shape exhibiting sharp tip apexes (Fig. 1d). Each

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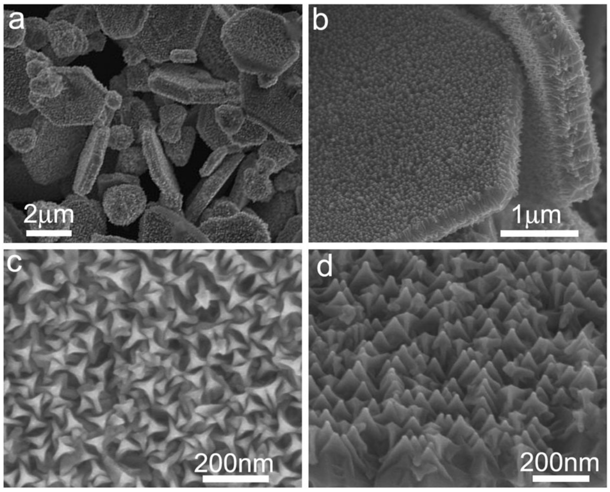

Fig. 1 SEM images of thorned gold plates with three-branched nanotips obtained after 24 h of aging at 95 °C in mixed [BMIM][PF$_6$]/formamide solvents with a volume ratio of 1 : 1.

nanotip has three side branches perpendicular to the plate surface with a threefold symmetry, and each side branch approximately corresponds to a right-angled triangle less than 20 nm in thickness, ∼50 nm in base side width, and 70–80 nm in height. The three-branched gold nanotips with a threefold symmetry are reminiscent of the threefold symmetrical gold dendrites obtained in [BMIM][PF$_6$],[16] indicating that each plate is a single crystal with the flat (111) crystal face and each nanotip perpendicular to the plate face is a single crystal oriented along the [111] direction with the three side branches parallel to the $(1\bar{1}0)$, $(01\bar{1})$, and $(10\bar{1})$ planes, respectively.

The gold products obtained at earlier stages of the formation of the thorned gold plates with three-branched nanotips were examined by SEM and TEM, and the results are shown in Fig. 2. After 5 h of reaction, hexagonal gold plates typically about 2–4 μm in width and less than 100 nm in thickness were formed together with some small particles (Fig. 2a). The top surface of the plate was somewhat rugged showing some visible wrinkles (Fig. 2b). Fig. 2c presents a typical TEM image and the related electron diffraction (ED) pattern of a single plate, which shows that the hexagonal plate is a single crystal with the top face of the (111) crystal plane and with the six edges perpendicular to the $\langle 110\rangle$ directions, which is consistent with the crystal orientation of the final hexagonal thorned plates. When the reaction time was prolonged to 12 h, the hexagonal plates became considerably thicker with pristine nanotips appearing on the surface (Fig. 2d). This result suggests a two-step growth process for the thorned gold plates, namely, relatively flat, hexagonal gold plates with the top (111) plane formed first, which was followed by the vertical growth of the [111]-oriented gold nanotips with three side branches parallel to the {110} planes on the top surfaces of the gold plates. The formation of the [111]-oriented nanotips with a threefold symmetry could result from the kinetically controlled growth process under nonequilibrium conditions with a moderate driving force,[17] similar to the formation of hierarchical [111]-oriented gold dendrites in [BMIM][PF$_6$].[16]

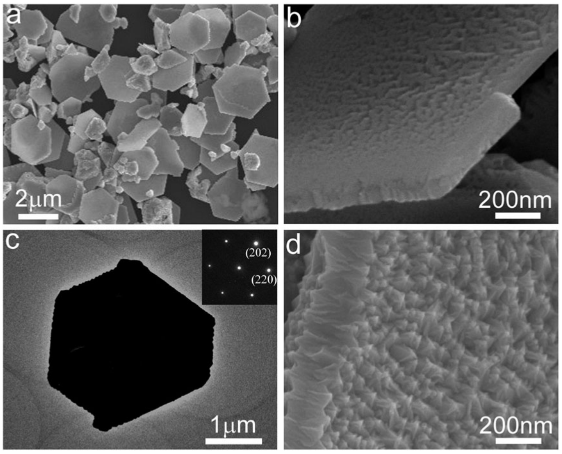

Fig. 2 SEM (a,b,d) and TEM (c) images of gold plates obtained after different aging times: (a–c) 5 h, (d) 12 h. Inset shows the related ED pattern.

It was found that an appropriate mixing ratio of [BMIM][PF$_6$] and formamide in the solution was essential to the formation of the well-defined, thorned gold plates. As shown in Fig. 3a, when the [BMIM][PF$_6$]/formamide volume ratio was decreased from 1 : 1 to 3 : 7, only thorned gold microparticles with some irregular tips were obtained. If the [BMIM][PF$_6$]/formamide ratio was increased from 1 : 1 to 7 : 3, gold plates with mildly rugged surfaces were obtained under otherwise similar conditions (Fig. 3b). Here formamide played the roles of both reducing agent and cosolvent whereas [BMIM][PF$_6$] acted mainly as an inert viscous medium. The relative concentration of the ionic liquid can considerably influence the ion diffusivity and reaction rate in the solution. At a low [BMIM][PF$_6$]/formamide ratio of 3 : 7, the reaction occurred rather fast and the driving force would be pretty high, resulting in thorned gold microparticles, whereas at a high [BMIM][PF$_6$]/formamide ratio of 7 : 3, the reaction took place quite slowly, resulting in gold plates with mildly rugged surfaces. When the [BMIM][PF$_6$]/formamide ratio was kept at 1 : 1, a delicate balance between the diffusion rate and the reaction rate or a moderate driving force was achieved, leading to appropriate nonequilibrium conditions for the growth of hierarchical sharp gold nanotips with a three-fold symmetry.[16] The significantly lowered ion diffusivity and reaction rate owing to the presence of ionic liquid could prevent uncontrolled overgrowth of gold crystals.

A seed-mediated growth experiment was designed to grow nanotip arrays on smooth gold sheets with larger surface areas. Firstly, smooth gold sheets with the top (111) faces, which were typically tens of micrometres across and tens of nanometres thick (Fig. S2a,b, ESI†), were fabricated through a polyol process following the literature.[18] Secondly, a growth

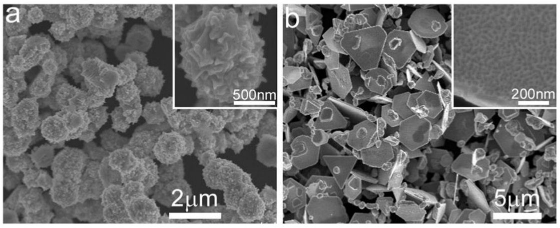

Fig. 3 SEM images of gold products obtained at different [BMIM][PF$_6$]/formamide volume ratios: (a) 3 : 7, (b) 7 : 3. Insets show the enlarged images.

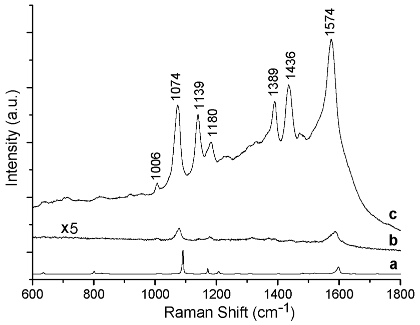

Fig. 4 Raman spectrum of solid PATP (a) and SERS spectra of PATP adsorbed on a smooth gold sheet (b) and a thorned gold plate (c).

solution was prepared by aging the [BMIM][PF_6]/formamide solution containing 5 mM $HAuCl_4$ at 95 °C for 2.5 h, which was a colorless solution due to the reduction of Au(III) to Au(I). Then, ~1 mg of smooth gold sheets were introduced into 1 mL of the [BMIM][PF_6]/formamide growth solution as the seeds for gold deposition at 95 °C. After 2.5 h of growth, all the added gold sheets exhibited rugged surfaces (Fig. S2c, ESI†). When the growth time was increased to 24 h, almost all the gold sheets grew considerably thicker and comprised densely aligned nanotip arrays, and the appearance of well-defined three-branched nanotips was evident (Fig. S2d, ESI†). This result not only testified to the proposed two-step growth mechanism for the thorned gold plates, but also demonstrated the potential application of this approach in the fabrication of regular three-branched nanotip arrays in a large area.

The interesting hierarchical structure of the thorned gold plates makes them attractive for use as an active SERS substrate. *p*-Aminothiophenol (PATP) is an increasingly important probe molecule in SERS;[19,20] hence the SERS sensitivity of the obtained thorned Au plates comprising three-branched nanotip arrays was investigated using PATP as a probe molecule and using the smooth Au sheets as a reference sample (See ESI† for measurement method). The Raman spectra of PATP solid and the PATP molecules adsorbed on the two SERS substrates excited with the 633 nm laser line are presented in Fig. 4. The SERS spectrum of the PATP molecules adsorbed on the thorned Au plate exhibits the bands at 1006, 1074, and 1180 cm^{-1} attributed to a_1 modes, the bands at 1139, 1389, and 1436 cm^{-1} assigned to b_2 modes, and the band at 1574 cm^{-1} formed by both a_1 and b_2 modes.[19] Generally, the a_1 modes of PATP are predominantly enhanced through the electromagnetic (EM) effect whereas the b_2 modes are predominantly enhanced through the chemical or charge-transfer (CT) effect; however, it was recently pointed out that the "b_2 modes" peaks could result from laser-induced chemical transformation of PATP.[20] Obviously, the SERS intensity on a thorned plate gains remarkably larger enhancement than that on a smooth Au sheet. Particularly, the SERS intensities of the peaks at 1074 and 1574 cm^{-1} for the thorned Au plate are about 35 and 74 times stronger than those for a smooth Au sheet, respectively, while the exposed surface area for the thorned Au plate was estimated to be just 2–3 times that for a smooth Au sheet. This large enhancement in Raman scattering on the thorned gold plate may be ascribed to the giant local electromagnetic fields at the apexes of densely arrayed nanotips and the small gaps between adjacent nanotips as well as adjacent side branches.

In conclusion, the facile, one-pot synthesis of unique thorned gold plates comprising three-branched nanotip arrays, which exhibited enhanced SERS response, was achieved by the reduction of $HAuCl_4$ in mixed solvents of [BMIM][PF_6] and formamide without additives. This work may open new avenues towards large-area, hierarchical plasmonic structures with unusual patterns and useful properties.

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