

# Electrochemical preparation of platinum nanothorn assemblies with high surface enhanced Raman scattering activity†

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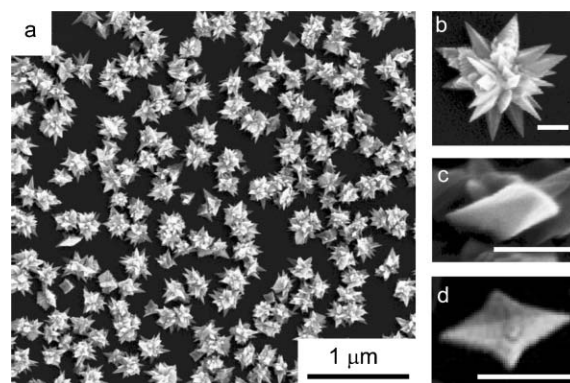
**Platinum nanothorn assemblies with sharp tips and edges were prepared, which exhibit high surface enhanced Raman scattering (SERS) activity and yield an enhancement factor as high as 2000 for adsorbed pyridine.**

Transition metal nanomaterials have attracted extensive attention due to their unique optical, electrical, magnetic, catalytic properties, as well as their important technological applications.<sup>1,2</sup> Since their physical and chemical properties can be finely tuned by means of their shape,<sup>3</sup> metal nanostructures with a wide variety of morphologies, such as spheres, cubes, rods, wires, prisms, and multipods, have been synthesized.<sup>4</sup> Surface enhanced Raman spectroscopy, highly associated with surface morphologies, is a powerful analytical tool for determining chemical information of molecules adsorbed on roughened surfaces of metals, usually coinage metals such as silver, gold and copper.<sup>5,6</sup> Unfortunately, SERS studies of transition metals, the most extensively used catalytic materials, are severely hindered by their weak enhancement. In recent years, Tian and co-workers have successfully extended the SERS study to transition metal surfaces by the special electrochemical pretreatment procedures.<sup>7,8</sup> The search for high SERS active substrates of transition metals is still invaluable. Theoretical investigations have predicted that nanoparticles with sharp tips may exhibit especially high SERS activity, since the local value of  $|E|^2$  at the tips can be as high as 500 times of the applied field.<sup>9</sup> So shape-controlled synthesis of nanoparticles with sharp edges or tips can certainly throw light on the SERS studies of transition metals. Xia and coworkers have synthesized rhodium multipods and palladium nanoplates with sharp edges or tips, and found that these nanomaterials can serve as active SERS substrates.<sup>10,11</sup> As for SERS studies of platinum nanoparticles, efforts are focused on spherical nanoparticles and their agglomerates,<sup>12</sup> there are only a few reports concerning platinum nanoparticles with sharp edges or tips.<sup>13</sup> Herein, we report a facile preparation of platinum nanothorn assemblies with sharp tips and edges by a square wave potential electrodeposition routine. In comparison with smooth platinum nanoparticles, the platinum nanothorn assemblies exhibit considerably higher SERS activity.

Electrochemical preparation of the platinum nanothorn assemblies was carried out in a standard three-electrode cell with a PAR 263A potentiostat, a platinum foil counter electrode and a saturated calomel electrode (SCE) at room temperature. All the

potentials were quoted *versus* the SCE scale. In a typical procedure, platinum nanothorn assemblies were electrodeposited on glassy carbon (GC,  $\varnothing = 6$  mm) substrate in 2 mM  $K_2PtCl_6 + 0.5$  M  $H_2SO_4$  solution by square wave potential between  $-0.20$  V and  $0.80$  V at  $10$  Hz for  $20$  min. The resultant electrode is denoted as  $Pt_{nm}/GC$ . The real area of the  $Pt_{nm}/GC$  was evaluated from the electric charge of hydrogen adsorption/desorption on the assumption of  $210 \mu C cm^{-2}$ ,<sup>14</sup> and surface roughness factor ( $R$ ) was  $5.7$ . Raman spectra of pyridine (Py) adsorbed on  $Pt_{nm}/GC$  were collected using a confocal microprobe Raman system (LabRam I from Dilor, France) at excitation line of  $632.8$  nm.<sup>15</sup>

Fig. 1a shows a typical scanning electron microscopy (SEM, LEO1530) image of the  $Pt_{nm}/GC$ . It is clearly seen that platinum nanothorn assemblies are homogeneously dispersed on the GC substrate, and their diameter ranges from  $200$  to  $350$  nm. The particle density at the surface is measured about  $1.5 \times 10^9 cm^{-2}$ . A high magnification SEM image of a platinum nanoparticle is shown in Fig. 1b, which illustrates clearly that the platinum nanoparticle is built up by tens of nanothorns radiating out from the center of the assembly. The length and base width of the nanothorns are in the range of  $80$ – $160$  and  $40$ – $80$  nm, respectively. The side face of the nanothorn is not smooth, and several sharp edges appear. The detailed morphology of the nanothorn has been further examined by high magnification SEM images taken from different directions. Fig. 1c shows a side view of a nanothorn, indicating a tetragonal pyramid-like shape. A typical top view (Fig. 1d) of a nanothorn shows a rhombic projection with slightly curved side. The above results indicate that the nanothorn is a rhombic pyramid with four curved side faces.



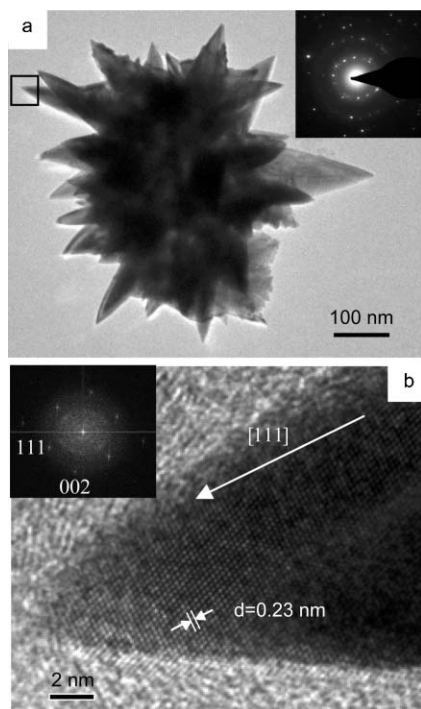
**Fig. 1** SEM images of platinum nanothorn assemblies. (a) Overview SEM image; (b) high magnification SEM image of a platinum nanothorn assembly; (c) side view of a nanothorn; (d) top view of a nanothorn. The scale bar in (b), (c), and (d) is  $100$  nm.

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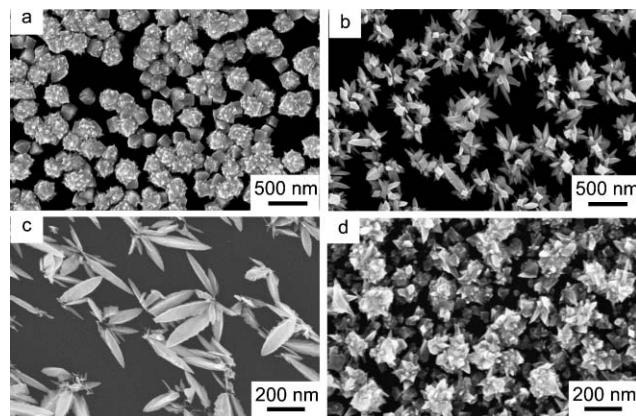
† Electronic supplementary information (ESI) available: Raman spectra of Py adsorbed on different platinum nanostructures. See DOI: 10.1039/b609164d

The crystal structure of the platinum nanothorn assembly was investigated by high resolution transmission electron microscopy (HRTEM, FEI Tecnai-F30). Fig. 2a shows the TEM image of a platinum nanothorn assembly. The inset to Fig. 2a displays the corresponding selected area electron diffraction (SAED) patterns, which can be indexed to face centered cubic (fcc) structure. It is noteworthy that several discrete bright dots instead of continuous rings appear in the SAED pattern, which indicates that the platinum nanothorn assemblies possess a high crystallinity. The HRTEM image of the tip of a nanothorn marked in Fig. 2a is displayed in Fig. 2b. The continuous fringe pattern and the corresponding fast Fourier transform (FFT) image (inset) verify the single crystalline property of the nanothorn. The lattice spacing of 0.23 nm agrees with the distance between two {111} planes of platinum. The growth direction of the nanothorns is determined to be along [111], and the radius of curvature at the tip is about 1 nm by the statistics of tens of HRTEM images. As compared with other three-dimensional platinum nanostructures reported recently,<sup>16</sup> the unique characteristic of the as-prepared platinum nanothorn assemblies is their sharp tips and edges, which are crucial for high SERS activity.

The preparation conditions for platinum nanothorn assemblies have been also optimized. It was found that both the lower ( $E_L$ ) and upper ( $E_U$ ) potential limits of the square wave are crucial for the growth of the nanothorns (Fig. 3). When  $E_L$  is above  $-0.10$  V, nanothorn can hardly be observed (Fig. 3a). On the other hand, when  $E_U$  exceeds  $1.00$  V, the tip of the nanothorn becomes obtuse and the number of nanothorns in an individual nanoparticle decreases considerably (Fig. 3b). As  $E_U$  becomes more positive, *e.g.*  $1.20$  V, only leafy nanostructures were observed (Fig. 3c).



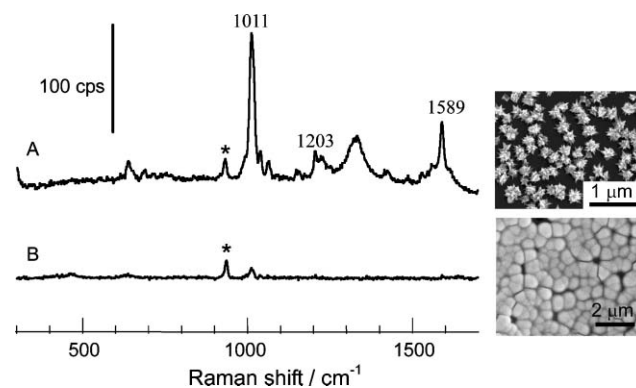
**Fig. 2** (a) TEM image of a platinum nanothorn assembly; the inset is the SAED of the nanoparticle; (b) HRTEM image of the nanothorn marked in (a), indicating the growth direction is along [111]. The inset is the corresponding FFT image.



**Fig. 3** SEM images of platinum nanostructures prepared by square wave potential routine for 20 min of deposition time: (a)  $E_L = -0.10$  V,  $E_U = 0.80$  V; (b)  $E_L = -0.20$  V,  $E_U = 1.00$  V; (c)  $E_L = -0.20$  V,  $E_U = 1.20$  V. (d) SEM image of platinum nanostructure prepared by potentiostatic deposition at  $-0.20$  V for 10 minutes.

When the electrodeposition is carried out in potentiostatic mode, *e.g.*  $-0.20$  V, the nanothorns in the resultant nanoparticles are poorly developed (Fig. 3d).

The SERS activity of the platinum nanothorn assemblies was studied and Py was selected as a probe molecule. Fig. 4 is the electrochemical Raman spectrum of Py adsorbed on the Pt<sub>nm</sub>/GC at  $-0.60$  V (curve A). As a comparison, the Raman spectrum of Py adsorbed on smooth platinum nanoparticles (the inset to Fig. 4) with a size of *ca.* 500 nm is also displayed (curve B). The smooth platinum nanoparticles were prepared by a modified method as described by Penner.<sup>17</sup> The Raman signal of the total symmetric vibration ( $\nu_1$ ,  $1011$   $\text{cm}^{-1}$ ) of Py adsorbed on the platinum nanothorn assemblies is 140 cps, while it is only about 10 cps on the smooth platinum nanoparticles. The surface enhancement factor (SEF) for the Pt<sub>nm</sub>/GC, calculated by the method described in ref. 18, is as high as 2000, which is about one order of magnitude larger than that of electrochemically roughened platinum electrodes.<sup>18</sup> To further elucidate the edge- and



**Fig. 4** Electrochemical Raman spectra of Py adsorbed on (A) platinum nanothorn assemblies and (B) smooth platinum nanoparticles deposited on GC substrate. Solution: 0.01 M Py + 0.1 M NaClO<sub>4</sub>; electrode potential:  $-0.60$  V; acquisition time: 20 s; excitation line: 632.8 nm. The band at  $932$   $\text{cm}^{-1}$  (asterisk) appearing in both spectra is from Raman scattering of ClO<sub>4</sub><sup>-</sup> ions in the bulk solution. The SEM images beside the spectra are corresponding nanostructures.

tip-effects of the Pt nanothorn assemblies on the SERS activity, Raman spectra of Py adsorbed on all the samples illustrated in Fig. 3 were also collected (see ESI†). The corresponding SEFs are around 160, 420, 220, and 300, respectively. As we expected, the SEF significantly decreases as the nanothorn becomes obtuse and the nanothorn density decreases (samples 3b to 3c), and the sample 3a provides the minimal SEF due to the absence of nanothorn structure.

It is well-known that there are three kinds of contribution to electromagnetic (EM) field enhancement of SERS: (i) the resonant excitation of surface plasmon, (ii) the lightning-rod effect, and (iii) the image dipole enhancement effect.<sup>19</sup> The EM enhancement is considered to mainly come from a geometrically defined surface plasmon resonance (SPR) at metal nanoparticles, especially for Au, Ag, Cu.<sup>9,13</sup> Although the coupling between conduction electrons and interband electronic transitions depresses the quality of the localized SPR of platinum considerably, the electromagnetic field located near high-curvature points of nanothorns (*i.e.*, the lightning-rod effect) can result in a large electric field near the sharpest surface.<sup>7,13</sup> Accordingly the lightning-rod effect may play the important role to the EM enhancement for the present platinum nanothorn assemblies. The enhancement increases remarkably with increase of the aspect ratio.<sup>20</sup> The high SERS activity of nanothorn assemblies induced by the sharp tips and edges is in good agreement with the theoretical calculation based on electromagnetic enhancement.<sup>9,13,20</sup>

In summary, platinum nanothorn assemblies with sharp tips and edges were prepared by a simple electrochemical method, and exhibit high SERS activity. The method can be readily extended to other transition metals, such as palladium, rhodium, which is in progress in our laboratory. The study is of significance in shape-controlled synthesis of metal nanoparticles, and is of importance not only in SERS application but also in electrocatalysis, sensors and fuel cells.

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