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# Synthesis of Single-Crystal Gold Nanosheets of Large Size in Ionic Liquids

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Large-size single-crystal gold nanosheets have been successfully prepared by microwave heating of  $\text{HAuCl}_4$  in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, without any additional template agent. Transmission electron microscopy (TEM), electron diffraction (ED), scanning electron microscopy (SEM), and X-ray powder diffraction (XRD) were used to characterize the resultant gold nanosheets. It was demonstrated that the ionic liquid could act as template agent for the formation of gold nanosheets. The present synthesis route is very simple and fast. It can be expected that the method can be extended to the fabrication of other metal nanosheets in ionic liquids.

## Introduction

In the past decade, many studies have been concentrated on one-dimensional nanostructures such as nanorods, nanowires, and nanotubes because of their novel properties and potential applications as components and interconnects in nanodevices.<sup>1</sup> Recently, nanosheets have attracted much attention because they offer new possibilities for both fundamental studies and technological applications.<sup>2</sup> However, nanosheets have not been widely studied for the lack of knowledge on their synthesis.<sup>1a</sup> Among the studied nanomaterials, gold nanostructures have received much attention because of their potential applications in fabricating nanoscale electronic, optical, and magnetic devices and in the areas of catalysis, biochemistry, and so forth.<sup>3</sup> Two-dimensional gold nanosheets are of particular interest because of their potential applications in the areas of electrochemistry and producing new nanodevices.<sup>3a,3e,4</sup> Lee et al.<sup>5a</sup> and Chen et al.<sup>5b</sup> prepared gold sheets of about 10  $\mu\text{m}$  by thermal reduction of  $\text{HAuCl}_4$  in the bulk phase or liquid crystals of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer. Dong et al.<sup>5c,5d</sup> and Sastry et al.<sup>5e</sup> prepared gold sheets of about 1  $\mu\text{m}$  by aspartate or *ortho*-phenylenediamine reduction of  $\text{HAuCl}_4$  and by biological method, respectively.

Room-temperature ionic liquids (ILs) are attractive environmentally benign solvents for organic chemical reactions, separations, and electrochemical applications.<sup>6</sup> The advantages of ILs in inorganic synthetic processes have been gradually realized and have received more and more attention. Some nanostructured materials, such as gold nanoparticles, mesoporous materials, hollow microspheres,  $\text{CuCl}$  nanosheetlets,  $\text{CoPt}$  nanorods, nanocrystalline metals, and nanoporous platinum, have been prepared in ILs.<sup>7</sup> The ILs have high fluidity, low melting temperature, high boiling temperature and thermal stability, nonflammability, and very low vapor pressure.<sup>8</sup> Moreover, there are large positive ions with high polarizability in ILs, which makes ILs very good solvents for absorbing microwaves. Therefore, the use of microwave heating in ILs for the synthesis of inorganic nanomaterials has some advantages over other solvents.<sup>8a</sup> Zhu et al.<sup>8b</sup> successfully synthesized single-crystal Tellurium nanowires using the method of microwave heating in

ILs in the presence of polymer surfactant of poly(vinylpyrrolidone) (PVP).

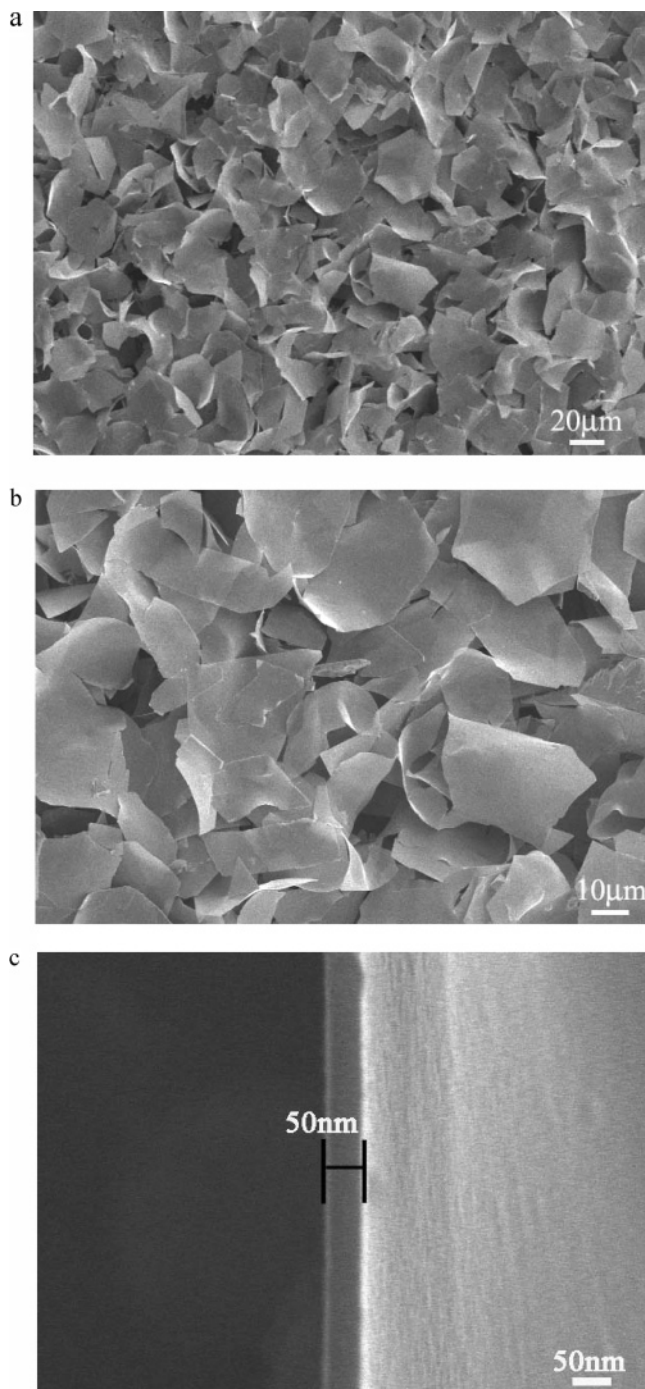
Recently, Tsuji et al.<sup>4c</sup> prepared gold nanoplates in ethylene glycol with the aid of polymer surfactant (PVP) by the microwave method, and the size of the nanosheets was less than 100 nm. The surfactant additives usually make the synthetic procedure and related operations complex. In some cases, it is difficult to avoid the surfactant contamination in the recovered products. In addition, large-size gold nanosheets will bring gold into new applications. Therefore, it is desirable to develop methods to synthesize large-size gold nanosheets without any surfactant additives. In this work, we demonstrate a novel route to prepare gold nanosheets with very large size by directly microwave heating of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{bmimBF}_4$ ). This route has some unique advantages. For example, a template agent is not required, the process is fast and simple, and the size of the nanosheets prepared by this method can be much larger than those reported by other methods.<sup>5</sup> Such large-size nanosheets may open new uses of gold in different areas. In addition, this method opens new possibilities for materials synthesis that have not been previously accessible.

## Experimental Section

1-Methylimidazole (99% in purity) was used as received from ACROS ORGANICS. 1-Chlorobutane and ethanol were supplied by Beijing Chemical Reagent Factory and were all A. R. grade. The ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{bmimBF}_4$ ) and 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{bmimPF}_6$ ), were synthesized according to the procedures in the literature.<sup>9</sup> The ILs were dried under vacuum at 40 °C until the weight remained constant with drying time. They were characterized with IR and  $^1\text{H}$  NMR.

To synthesize the nanosheets, a suitable amount of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was dissolved into 1 mL of IL in a 10-mL tube. Then, the tube with the mixture was heated in a microwave oven (Galanze WD700) for a desired time. The actual power selected for all the experiments was 126 W. The mixture was allowed to cool to room temperature naturally. The final mixture was diluted with ethanol and the products were recovered by centrifuging. The product was then washed with water and ethanol several times. X-ray diffraction analysis of the samples

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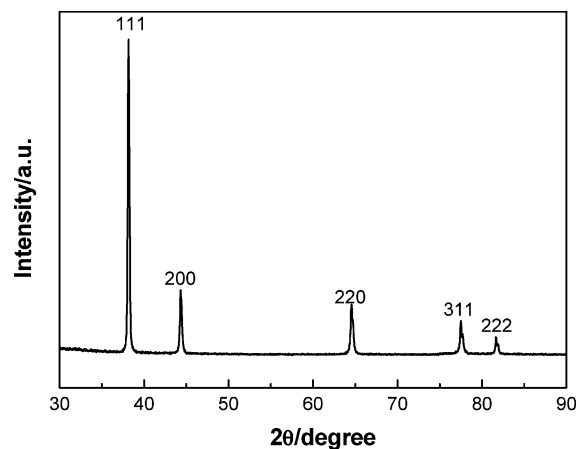


**Figure 1.** SEM images of the gold nanosheets prepared via microwave heating of 50 mg  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1 mL of  $\text{bmimBF}_4$  for 10 min. (a) Low magnification, (b) high magnification, and (c) closer SEM image of the gold sheets.

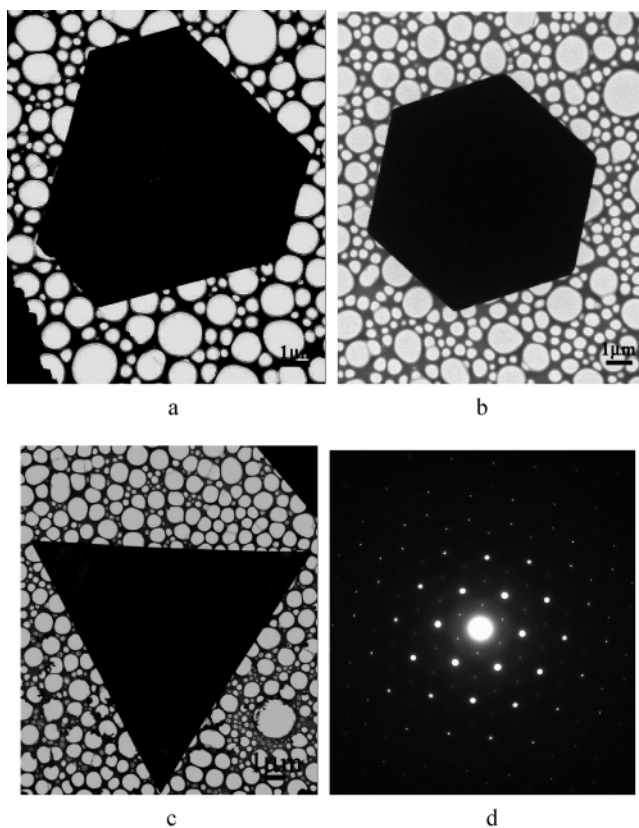
was carried out using an X-ray diffractometer (XRD, Model D/MAX2500, Rigaku) with  $\text{Cu K}\alpha$  radiation. The morphology of the as-prepared products was characterized by scanning electron microscopy (SEM, Hitachi-530) and transmission electron microscopy (TEM, JEOL-2010, operating voltage of 200 kV).

### Results and Discussion

Figure 1a shows the SEM image of the products obtained via microwave heating of 50 mg  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1 mL of  $\text{bmimBF}_4$  for 10 min. It can be seen that large-scale gold nanosheets with a size larger than  $30 \mu\text{m}$  in length are formed,



**Figure 2.** X-ray diffraction pattern of the product prepared via microwave heating 50 mg of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1 mL of  $\text{bmimBF}_4$  solution for 10 min.



**Figure 3.** Typical TEM images and ED patterns of the gold nanosheets prepared via microwave heating 50 mg of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1 mL  $\text{bmimBF}_4$  for 10 min.

which are much larger than those of the gold nanosheets reported in the literature (maximum  $10 \mu\text{m}$ ).<sup>5</sup> From the SEM images (Figure 1a, 1b), it can be observed that the products are mainly gold sheets with irregular shapes. Some gold sheets with regular (triangle or hexagon) shapes can also be observed in the products. From Figure 1b, it is seen that some gold sheets are fractured. The fracture of sheets might occur in the washing process because their size was very large. The thickness of the gold nanosheets was estimated from the closer SEM image. Figure 3c shows a typical closer SEM image of a single gold nanosheet. It can be known from the figure that the thickness of the gold nanosheets was about 50 nm. We also examined the thickness of some other gold nanosheets, and the results



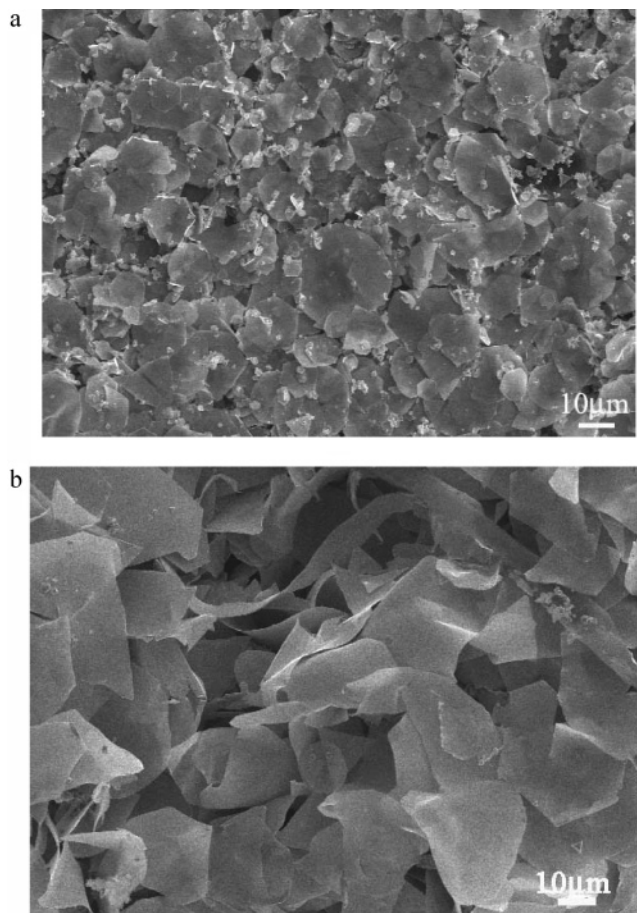
showed that thickness of all the nanosheets examined was about 50 nm. It also can be observed that the gold sheets have a trend to curve, which may result from their large size. After a heating time of 10 min, the temperature of the mixture measured by a thermometer was about 210 °C. However, we believe that the temperature in the solution was not locally uniform during the reaction.

Powder X-ray diffraction (XRD) was used to characterize the phase structure of the obtained products. The XRD pattern of the product prepared via microwave heating of 50 mg  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1 mL  $\text{bmimBF}_4$  for 10 min is shown in Figure 2. Five peaks can be observed, assigned to diffraction from the (111), (200), (220), (311), and (222) planes of face-centered cubic (fcc) gold, respectively. This indicates that pure crystalline Au was formed via microwave heating the solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in  $\text{bmimBF}_4$ . From Figure 2, it can also be known that the relative diffraction intensity of either (200)/(111) or (220)/(111) is unusually lower than the corresponding conventional values (JCPDS 04-0784). This observation indicates that the resultant gold nanosheets are mainly dominated by (111) facets, and therefore their (111) planes tend to be preferentially oriented parallel to the surface of the supporting substrate in the experiment.

Transmission electron microscopy (TEM) and electron diffraction (ED) were also used to characterize the morphology and the crystallinity of the nanosheets. The results of the TEM observation are similar to those of SEM, and some gold sheets were fractured. Figure 3a–3c shows some typical TEM images of the truncated triangle, hexagon, and triangle gold nanosheets. As an example, the electron diffraction pattern obtained by focusing the electron beam onto the triangle nanosheet is shown in Figure 3d. The hexagonal symmetry of the pattern spots of the ED patterns indicates that the gold nanosheet is face-centered cubic (fcc) single-crystal growing along the (111) plane.<sup>5</sup> Similar results are obtained from nanosheets of other shapes

We also prepared gold nanosheets by changing the amount of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  dissolved in 1 mL of  $\text{bmimBF}_4$ , while other experimental conditions were the same. The SEM images of the products are shown in Figure 4a and 4b. When the amount of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was 5 mg, the size of most nanosheets was less than 20  $\mu\text{m}$ , and some nanoparticles were coexistent with the nanosheets (Figure 4a). By further increasing the amount of the  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  to 100 mg, a large quantity of larger gold nanosheets was formed (Figure 4b).

We also prepared some gold products in another ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{bmimPF}_6$ ). It was found that large-scale gold nanosheets with large size were also obtained from  $\text{bmimPF}_6$  solutions. It is known that only gold particles are formed in the traditional solvent ethylene glycol via the microwave heating of  $\text{HAuCl}_4$  without the presence of polymer surfactant (PVP).<sup>4c</sup> Thus, it can be concluded that the formation of the large-scale gold nanosheets is directly related to the special properties and structures of IL. It is known that ILs can absorb microwaves and can make the temperature increase rapidly, which saves the reaction time.<sup>8a,8b</sup> It has been reported that many ILs have ordered structures.<sup>10</sup> 1,3-Dialkyl imidazolium ILs such as  $\text{bmimBF}_4$  and  $\text{bmimPF}_6$  used in this work can form two-dimensional polymeric structure by hydrogen bonds between the cations and anions,<sup>10c</sup> and so it is reasonable to deduce that the organized structure of the IL has a template effect for the formation of Au sheets. During the microwave heating process, IL not only works as a microwave absorbent to make the temperature of the medium increase up to the reaction temperature very quickly, but also it



**Figure 4.** SEM images of the gold microsheets prepared via microwave heating of different amounts of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  dissolved in 1 mL of  $\text{bmimBF}_4$  for 10 min. (a) 5 mg and (b) 100 mg.

acts as a template agent for the growth of gold, resulting in the final formation of nanosheets. In addition, our experiments showed if the solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in  $\text{bmimBF}_4$  was heated in an electrically heated oven to 210 °C, which was the same as the final temperature in the microwave heating experiments, the gold nanosheets were not formed. In other words, the microwave heating played an important role for the formation of gold nanosheets.

## Conclusion

In summary, single-crystal gold nanosheets have been successfully prepared by microwave irradiation process in  $\text{bmimBF}_4$ . There is no additional template agent in the synthesis process, which makes the synthetic procedures and the related treating processes very simple. The present synthetic route is fast and the size of the resultant nanosheets is very large, and it is favorable to produce gold nanosheets in large scale. Because of the large size and the single-crystal characteristic of the formed gold nanosheets, we believe that they have potential applications in different areas, such as in fabricating new nanodevices, in electrochemistry, and in physics. Such a simple synthetic procedure may be a versatile approach that can be extended to the fabrication of some other metal nanosheets of different sizes.

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