JOURNAL OF
Materials
CHEMISTRY

Shape-controlled synthesis of nanostructured gold by a protection–reduction technique

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Received 26th April 2001, Accepted 22nd October 2001
First published as an Advance Article on the web 5th December 2001

We describe a novel method to control the shape and size of Au nanoparticles using a protection–reduction technique. The remarkable feature of this method is that the reducing and protecting agents were mixed first prior to addition to the solution of $KAu(CN)_2$.The reactivity and concentration of reducing agent, the molar ratio of ascorbic acid (AA)/poly(vinylpyrrolidone) (PVP) and the redox potential of the Au complex anion have significant effects on the formation and growth of these novel nanostructures. The Au nanoparticles self-assembly into dendritic structures at molar ratios of AA/PVP > 7 while spherical and cubic nanoparticles form at ratios of AA/PVP $\leqslant 3$ and 4–6, respectively. This simple and effective method can be used for other noble metals.

Introduction

Nanoparticles of noble metals hold promise for use as advanced materials with novel electronic, optical and thermal properties as well as catalytic properties.[1,2] These properties strongly depend on the size and shape (morphology) of the metal nanoparticles. Therefore the synthesis of colloidal particles with well-controlled shape and size could be critical for these applications. Previous researches have shown that the concentration of the capping agent influences the size distribution, stability and catalytic activity of colloidal particles of noble metals and that a higher ratio of capping agent to metal tends to produce smaller Au particles.[3,4]

Shape control is an alternative tool to adjust optical properties of the materials, however, this is much more difficult to achieve. El-Sayed and coworkers[5] reported that various shapes such as tetrahedral, cubic, irregular-prismatic, icosahedral and cubo-octahedral can be obtained. A UV–reductive technique for the preparation of silver and gold nanoparticles has also been reported.[6,7] A template synthesis method is an alternate way for controlling the shape of nanoparticles. Martin and co-workers have prepared Au nanowires by electrochemically depositing Au within the pores of alumina membranes and studied their optical properties.[8]

Chemical reduction of noble metal salts in aqueous medium or organic solvents with capping agents such as ploy(vinylpyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) has been used to prepare shape-controlled noble metal nanoparticles.[9] Linear polymers and micelles are potential candidates as capping agents to control the size and shape of metal nanoparticles.[10] In most cases, capping agents such as PVP, PVA are mixed with the solutions of noble metal salts prior to adding reducing agent. This procedure leads to the change of the relative concentration of capping agent with time and therefore leads to a wide range of sizes of the resulting nanoparticles as the reaction proceeds.

Here we present a new and simple chemical protection–reduction technique for producing shape-controlled Au nanostructures at room temperature, using $KAu(CN)_2$ as the gold source and PVP as the capping agent. The reducing agent and the capping agent were mixed prior to addition to the solution of $KAu(CN)_2$. It was found that the reactivity and concentration of the reducing agent, the molar ratio of reducing agent/capping agent and the reactivity of the Au complex anion have a significant effect on the formation and growth of these novel nanostructures. This simple and effective chemical route can also be used to prepare shape-controlled nanoparticles and dendritic structures of other noble metal.

Experimental

High purity $KAu(CN)_2$ and $HAuCl_4$ were supplied by Changzhou Rare and Noble Metal Refining Factory (China). PVP (average molecular weights (M_w) of 10 000, 29 000, 40 000, 55 000 and 130 000), ascorbic acid (AA), oxalic acid and other reagents are all analytical grade (Shanghai Chemical Reagent Company). The water used was purified through a Milli-Q system. All glasswares were scrupulously cleaned with chromic acid solution and rinsed with deionized water.

A 100 mL aqueous solution of AA (0.14 mmol) and PVP at a selected molar ratio was stirred for 30 min at room temperature, and the pH of the solution was adjusted to 7.0 by 0.1 M K_2CO_3 or 0.1 M HCl.The molar ratio of AA/PVP was varied in order to change the shape and size of Au nanoparticles. The above solution was then added dropwise to a 5 ml aqueous solution of $KAu(CN)_2$ at a rate of 5 ml min^{-1} and stirred for 36 h. The reaction product was isolated by centrifugal separation and then immersed into oleic acid for later use.

The resulting pale green colloidal dispersion of Au nanoparticles is stable for several months at room temperature. The disappearance of $[Au(CN)_2]^-$ ions and the formation of Au nanoparticles were monitored by UV–Vis spectra recorded on a Shimadzu UV-2201 recording spectrophotometer. Transmission electron microscopy (TEM) and selected area electron diffraction (ED) images of Au nanoparticles were taken with a Hitachi model H-600A-2 TEM, using an accelerating voltage of 100 kV. Samples for TEM and ED were prepared by placing a drop of the colloidal dispersion of Au nanoparticles onto a carbon-coated copper grid and dried at room temperature. X-Ray powder diffraction (XRD) patterns of the products were determined on a D/MAX-RA rotating anode X-ray

DOI: 10.1039/b103767f

diffractometer with high-intensity Cu-Kα radiation ($\lambda = 0.151478$ nm) and a graphite monochrometer at a scanning rate of 0.02 s^{-1} in 2θ ranging from 30 to 85°.

Results and discussion

The reaction taking place at a ratio of AA/PVP = 2 : 1 is a representative example. The solution of $KAu(CN)_2$ is colorless with a peak at 245 nm in UV–vis spectrum due to the ligand-to-metal charge-transfer transition of the $[Au(CN)_2]^-$ ions. The CT peak at 245 nm decreases gradually as the reaction proceeds and disappears completely after reacting for 36 hr, indicating that the $[Au(CN)_2]^-$ ions are completely reduced. The reaction can be described by eqn. (1):

$$2\,KAu(CN)_2 + C_6H_6O_4(OH)_2 \rightarrow Au^0 + C_6H_6O_6 + 2\,KCN + 2\,HCN \qquad (1)$$

The color of the solution turns light yellow then pale green and the absorption bands shift gradually from the ultraviolet to the visible region, indicating that the Au nanoparticles are gradually formed. A broad peak at 530 nm appears after reaction for 8 h, and increases as the reaction proceeds. TEM images show the absence of any particles being formed for reaction times of less than 8 h while the sizes of the Au nanoparticles formed after reaction for 36 and 40 h are almost the same.

The formation process of the Au nanoparticles is as follows: there is an equilibrium in solution ($Au(CN)_2^- \rightleftharpoons Au^+ + 2CN^-$) and though the dissociation constant is quite low, as the reduction reaction of Au^+ proceeds, the $Au(CN)_2^-$ gradually dissociates to give Au^+ until the $Au(CN)_2^-$ has reacted completely. The resulting Au atoms diffuse, aggregate and nucleate to form nanoparticles surrounded with PVP, which coordinates to the Au nanoparticles *via* N and O atoms. Changing the surface covering PVP ratio to Au nanoparticles may change the growth rates of the different crystal faces, therefore, may change the reulting shape of the Au nanoparticles.

It has been proved that the reactivity and concentration of reducing agents have a significant effect on the size of metal nanoparticles.[11] A serious of Au nanoparticles were synthesized using various reducing agents (AA, oxalic acid and hydrazine) at ratios of reducing agent/PVP ranging from 10 : 1 to 1 : 1 reacting with 0.007 mM $[Au(CN)_2]^-$ aqueous solution for 36 h. Fig. 1 shows the TEM images of Au nanoparticles obtained by using various reducing agents with different concentrations. From Fig. 1, it is seen that both the size and monodispersity are dependent on the reducing ability of the reducing agent.

The shape and size of the Au nanoparticles are influenced by the molar ratio of AA/PVP. The capping polymer PVP apparently stabilizes the Au nanoparticles by preventing them from aggregating. Fig. 2 shows TEM images of Au nanoparticles synthesized at various molar ratios of AA/PVP (AA = 1.4 mM) after reaction for 36 h. As the ratio of AA/PVP increases, the shape of the nanoparticles changes from spherical to cubic. Increasing the AA/PVP ratio (AA = 1.4 mM unvaried) means that the concentration of PVP is reduced and more surface area of the nanoparticles is exposed to the solvent. This is favorable to growth of some suitable crystal faces and leads to shaped nanoparticles. When the ratio of AA/PVP is in the range 7–10, the Au nanoparticles assemble themselves in a dendrite structure shown in Fig. 3. The corresponding electron diffraction (ED) patterns reveal that the Au nanoparticles are single crystals, which was also confirmed by the corresponding XRD diffraction pattern (Fig. 4), and the dendrites assemble into a polycrystalline structure (Fig. 3d). This large, new supramolecular structure

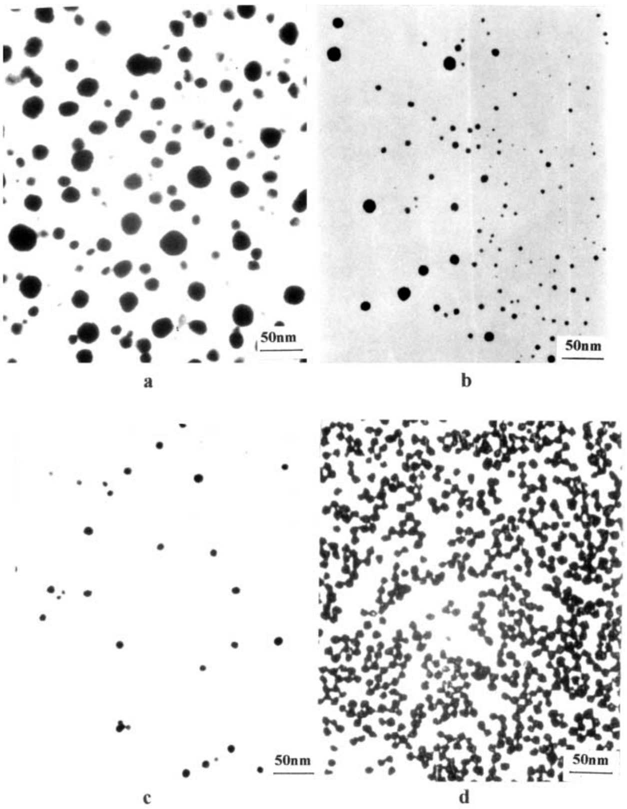


Fig. 1 TEM images of Au nanoparticles obtained using different reducing agents and different concentrations. (a) hydrazine = 1.4 mmol, $KAu(CN)_2$ = 0.007 mmol, hydrazine/PVP = 2; (b) oxalic acid = 1.4 mmol, $KAu(CN)_2$ = 0.007 mmol, oxalic acid/PVP = 2; (c) AA = 1.4 mmol, $KAu(CN)_2$ = 0.007 mmol, AA/PVP = 2; (d) AA = 4.2 mmol, $KAu(CN)_2$ = 0.007 mmol, AA/PVP = 2.

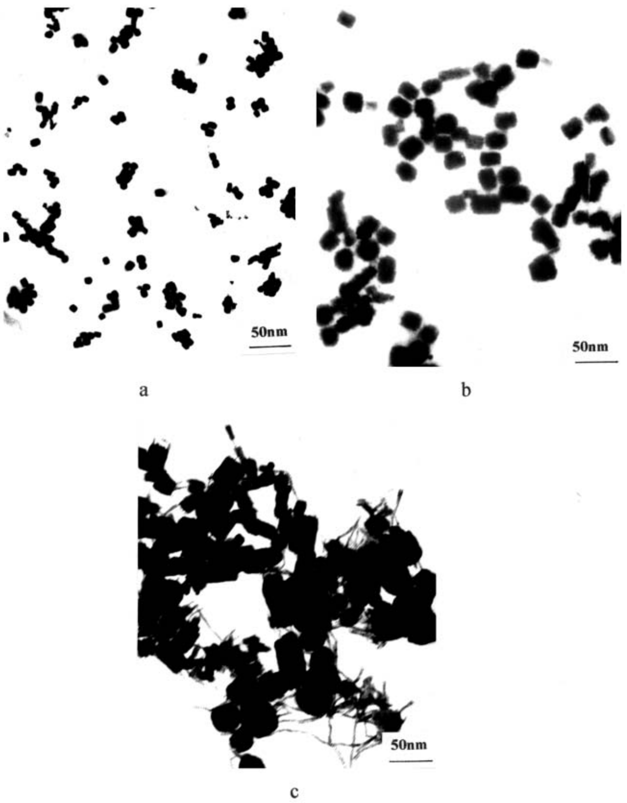
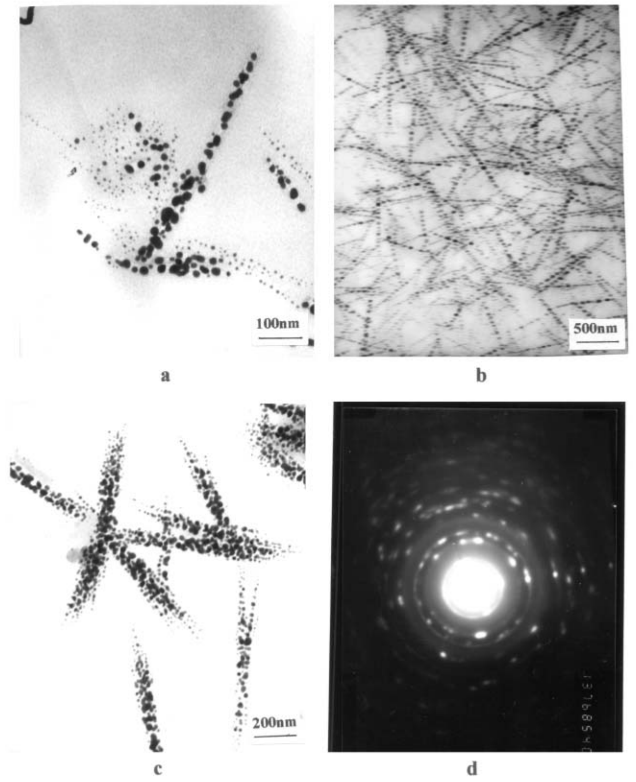


Fig. 2 TEM images of Au nanoparticles synthesized at various AA/PVP ratios (AA = 1.4 mmol, $KAu(CN)_2$ = 0.007 mmol): (a) AA/PVP = 3; (b) AA/PVP = 4; (c) AA/PVP = 5



a b c d

Fig. 3 TEM images of the Au dendrite structures synthesized at high AA/PVP ratios (AA = 1.4 mmol, $KAu(CN)_2$ = 0.007 mmol): (a) AA/PVP = 7; (b) AA/PVP = 8; (c) AA/PVP = 10; (d) ED of an Au dendrite structure.

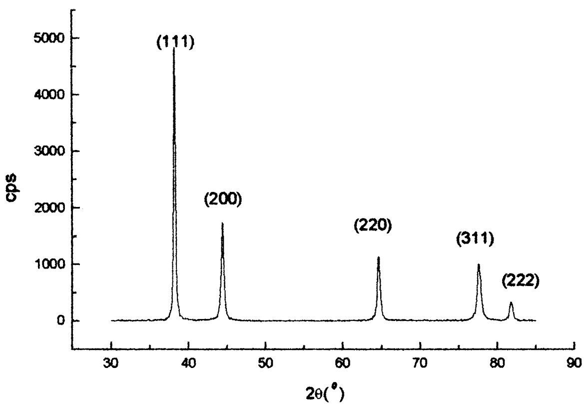
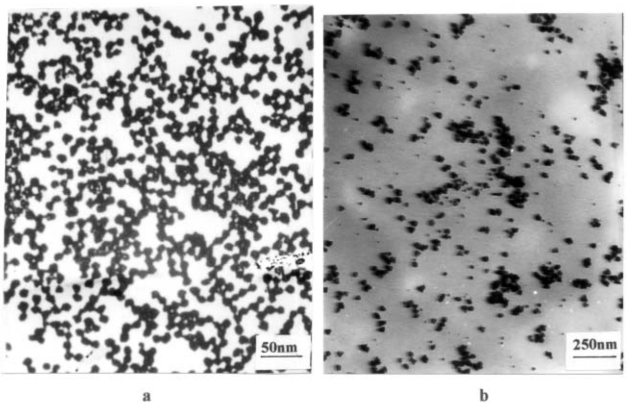


Fig. 4 XRD pattern of Au nanoparticles obtained by adding a mixture of AA and PVP (AA/PVP = 3,AA = 1.4 mmol) dropwise to a solution of 0.007 mmol $KAu(CN)_2$ for a reaction tine of 36 h.

of Au nanoparticles, abbreviated DLA (diffusion-limited aggregate) represents a very wide variety of growth, in which one particle after the other is formed and then diffuses, sticking to the growing structure.

When the molar ratio of AA/PVP $\leqslant$ 3, the Au nanoparticles were well dispersed and spherical. The amount of PVP is a critical factor for forming shaped Au nanoparticles.

It is well known that flexible polymers with a low degree of polymerization have extended polymer chains, whereas those with a high degree of polymerization adopt random-coil conformations in solution. To examine the influence of the chain conformation of PVP on the shape and size of the Au nanoparticles, a serious of PVP polymers with various M_w (10 000, 29 000, 40 000, 55 000 and 130 0000) were used in the preparation of Au nanoparticles. The results show that the M_w of the PVP has little effect on the shape and size of the Au nanoparticles.



a b

Fig. 5 TEM images of Au nanoparticles reduced from different Au complex ions (AA = 1.4 mmol, AA/PVP = 2): (a) $KAu(CN)_2$ = 0.035 mmol; (b) $HAuCl_4$ = 0.035 mmol.

Fig. 5(a) and (b) show TEM images of Au nanoparticles using $HAuCl_4$ and $KAu(CN)_2$ as gold sources respectively. It can be seen that the average size of Au nanoparticles obtained from $KAu(CN)_2$ is about one-fifth that from $HAuCl_4$, and the distribution of particle size obtained from $KAu(CN)_2$ is narrower than that from $HAuCl_4$ under the same conditions. Although the stability constant of $KAu(CN)_2$ is higher than that of $HAuCl_4$, the redox potential is quite different for Au^+/Au (E^0 = 1.68 V) and Au^{3+}/Au (E^0 = 1.50 V). The monocation Au^+ more readily forms neutral gold atoms than does $Au^{3+}$and this faster reduction leads to smaller nanoparticles for $KAu(CN)_2$ as the Au source.

Conclusion

In this work, we established a method for controlling the shape and size of Au nanoparticles by using a protection–reduction technique. The reactivity and concentration of reducing agents, the molar ratio of AA/PVP and the redox potential of Au cations have significant effects on the formation and growth of these novel nanostructures. The molar ratio of AA/PVP in our experimental conditions is a crucial factor. The nanoparticles are spherical at molar ratios < 3, while they adopt cubic shapes at ratios in the range 4–6. When the molar ratio of AA/PVP is >7, the Au nanoparticles self-assemble into dendrite structures. At lower concentrations of PVP there may be insufficient polymer to cover all surfaces of the nanoparticles, which leads to favorable growth of some suitable crystal faces to form shaped nanostructures. When the ratio of AA/PVP is >7, more surface area of the nanoparticles are exposed to the solution which favours nanoparticle aggregation and assembly into dendritic structures. This simple and effective method can also be used to prepare shape-controlled nanostructures of other noble metals, such as silver and palladium.

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