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Submicrometre scale single-crystalline gold plates of nanometre thickness: synthesis through a nucleobase process and growth mechanism

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Abstract
Synthesis of submicrometre scale single-crystalline gold plates of nanometre thickness in the presence of nucleobase guanine through chemical reduction of $HAuCl_4$ was investigated. The elemental composition of the as-prepared gold nanoplates was estimated using energy-dispersive x-ray spectroscopy. The as-prepared gold plates were composed of essentially (111) lattice planes, as revealed by both x-ray diffraction (XRD) and transmission electron microscopy (TEM) results. It was found that the molar ratio of $HAuCl_4$ to guanine played a very important role in the formation of gold nanoplates. Gold nanoplates could be produced at a molar ratio of $[HAuCl_4]/[\text{guanine}] = 50:1$ while only smaller gold spherical nanoparticles were obtained at molar ratios of $[HAuCl_4]/[\text{guanine}] \leqslant 20:1$. A possible growth mechanism of the as-prepared gold nanoplates is proposed and discussed. The results and conclusion presented in this work may be valuable for our further understanding of the roles of precursor ligands in the control of nanoparticles aggregation states and the preparation of shape-controlled nanoparticles.

S Supplementary data are available from stacks.iop.org/Nano/18/295603

1. Introduction

Noble metal nanoparticles, such as gold, silver and platinum, have received considerable attention in recent years due to both their fundamental and technological interest and importance [1–6]. Among these, a lot of research has been focused on gold nanoparticles due to their important applications in catalysis [7], bioanalysis [8], nonlinear optics [9], capillary electrophoresis [10], molecular recognition [11] and supramolecular chemistry [12]. These applications are heavily dependent on their size and shape [13, 14]. As a result, increasing attention has been paid to the fabrication of size- or shape-controlled metal nanomaterials and there is considerable interest in developing new methods for their synthesis. Even molecular dynamics study has been employed to investigate the morphological formation of metal nanoparticles [4].

Many methods have been well developed to prepare spherical gold nanostructures [15]; however, the production of metal nanostructures with a high degree shape control is still a challenge for materials scientists and there is therefore considerable interest in developing new approaches for fabricating shape-controlled nanoparticles. So far gold nanostructures with various morphologies have been synthesized, including

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nanocubes [16], branched nanocrystals [17] and hexagonally shaped nanoparticles [18]. The fabrication of planar gold nanostructures such as nanodiscs and nanoplates has also been developed recently [19–22]. The mechanism of the formation of planar gold nanostructures has been investigated, indicating that capping reagents such as surfactants, polymers, biomacromolecules and coordinating ligands play a very important role in the preparation of such nanostructures [14, 19–22]. It is supposed that the adsorption of capping agents on the (111) lattice plane of face-centred cubic (fcc) gold nanoplates could lower the surface tension and stabilize the plates [23]. So far as we know, very few papers have reported on the synthesis of gold nanoplates in the absence of capping agents [21, 24, 25]; these found that the ratio of reducing reagents to gold salts played an important factor in determining the morphology of the gold products. Our research group has previously reported a wet-chemical route for the preparation of micrometre-sized hexagonal single-crystalline gold nanoplates by the reduction of $HAuCl_4$ with *ortho*-phenylenediamine in aqueous media at room temperature and ambient pressure [24]. We found that the quantity of *ortho*-phenylenediamine in the solution was the key to producing gold nanoplates. In this work we report the preparation of submicrometre scale single-crystalline gold plates of nanometre thickness in the presence of nucleobase guanine through a capping agent-free process.

Interactions between nucleic acids (including DNA, RNA, oligonucleotides and nucleobases) and metals [26–30] have been extensively studied due to their significant importance in bioinorganic chemistry [31], biological detection [32], materials science [27, 33] and bionanotechnology [34]. Much research has been focused on nucleic acid–gold interactions such as DNA-templated gold nanoparticle assembly [35] and biological detection [32, 36]. Recently, the interactions of nucleobases binding on the gold surface have also been studied theoretically and experimentally [37, 38], suggesting that guanine assumed neither a flat nor a perpendicular but a tilted orientation on the gold support.

Though much attention has been paid to the synthesis of shape-controlled metallic nanoparticles using reductive methods [13, 14, 16–22], no reports have so far dealt with the preparation of gold plates in the presence of nucleobase guanine through chemical reduction of $HAuCl_4$. In this work we found that a mixture of $HAuCl_4$ and guanine with a molar ratio of 50:1 could produce submicrometre scale gold plates with nanometre thickness. The as-prepared gold plates were composed of essentially (111) lattice planes, as revealed by both XRD and TEM results. The role of molar ratio of guanine to $HAuCl_4$ in the formation of gold nanoplates was investigated using transmission electron microscopy, indicating that the quantity of guanine was the key to yielding the gold plates. It was supposed that submicrometre scale gold nanoplates were evolved from the smaller spherical gold nanoparticles when guanine was inadequate. We also propose the driving force for the formation of the gold plates from the smaller gold nanoparticles.

2. Experimental section

2.1. Chemicals

Guanine and chloroauric acid ($HAuCl_4$) were purchased from Shanghai Chemical Reagent Company (Shanghai, China). All reagents were of analytical grade and were used as-received without further purification. The water used throughout all experiments was purified by a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 transmission electron microscope operated at an accelerating voltage of 200 kV. The samples for TEM characterization were prepared by placing a drop of colloidal solution on a carbon-coated copper grid and drying it at room temperature. Scanning electron microscopy (SEM) measurements were made using a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV, equipped with a Phoenix energy dispersive x-ray analyser (EDAX). The x-ray diffraction (XRD) pattern was collected on a D/Max 2500 V/PC x-ray diffractometer using Cu (40 kV, 200 mA) radiation. Analysis of the x-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII (UK) using Mg as the exciting source.

2.3. Preparation of gold nanoplates

The gold nanoplates were prepared according to the following procedure (sample 1): first, 0.2 ml guanine aqueous solution (10 mM) was added to 10 ml water. 3.4 ml $HAuCl_4$ aqueous solution (29.4 mM) with a 1:50 molar ratio of guanine to $HAuCl_4$ was then introduced into the resulting solution under rigorous stirring at room temperature.

To examine the influence of the molar ratio of guanine to $HAuCl_4$ on the gold nanoplates thus formed, we varied the amount of $HAuCl_4$ used, under otherwise identical conditions used for preparing sample 1.

3. Results and discussion

3.1. Preparation and characterization of gold nanoplates

The formation of the gold nanoplates was confirmed by TEM observations. Figure 1(a) shows a typical TEM image of the as-prepared gold nanoplates, indicating that the products had an irregular plate-like shape. Figure 1(b) shows the higher magnification TEM image, and one can see that the size distribution of the as-prepared nanoplates is very wide, varying from 200 to 600 nm with an average size of about 350 nm. Most of the gold plates assumed a flat orientation on the TEM Cu grid (figure 1(b)). However, a few plates assumed a perpendicular orientation on the TEM Cu grid as the arrows in figure 1(b) indicate. The thickness of the gold nanoplates was estimated to be about 60 ± 10 nm from these perpendicular plates on the TEM Cu grid. Figure 1(c) shows the SEM image of the gold plates, indicating that the thickness of the plates was about 64 nm, which was consistent with the TEM results. Further careful examination of figures 1(b) and (c) revealed that some 5–7 nm spherical gold particles were obtained as by-products (also see figure 5(a)). These spherical particles will be discussed in detail later in this paper along with the growth mechanism of the gold nanoplates.

The elemental composition of the as-prepared gold nanoplates was estimated using energy-dispersive x-ray

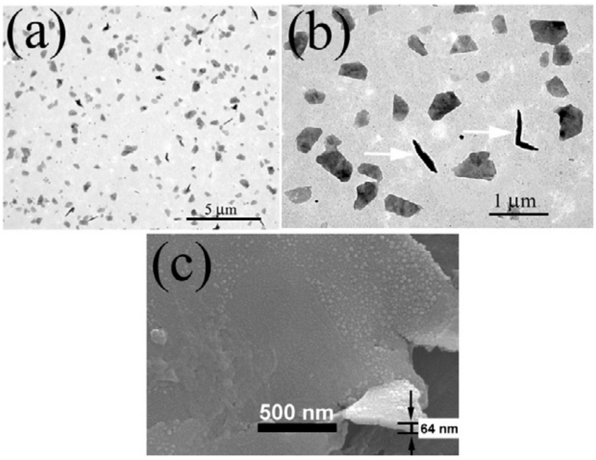

Figure 1. Typical TEM image (a) of the as-prepared gold nanoplates. (b) A higher TEM magnification image of panel (a). (c) A higher SEM magnification image of the as-prepared gold nanoplates indicating that the thickness of the gold plates is about 60 ± 10 nm.

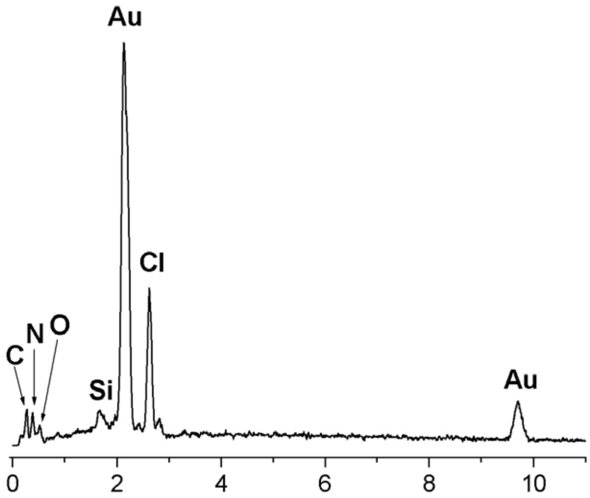

Figure 2. Energy-dispersed spectrum (EDS) of the as-prepared gold nanoplates coated on a silicon wafer.

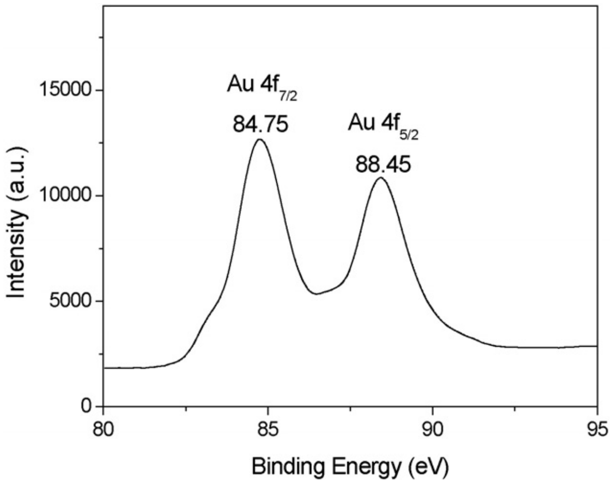

Figure 3. XPS spectrum of Au 4f of the as-prepared gold nanoplates deposited on the silicon wafer.

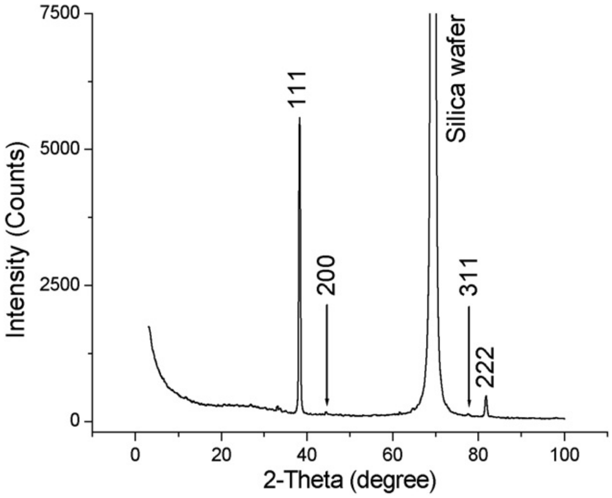

Figure 4. XRD pattern of the as-prepared gold nanoplates deposited on a silicon wafer.

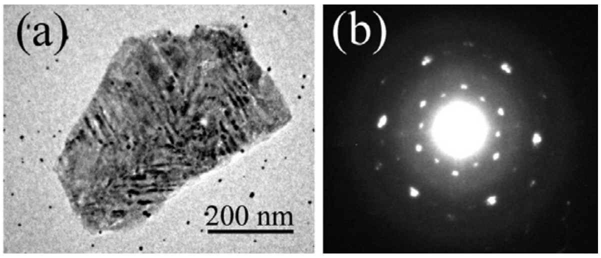

Figure 5. Typical TEM image (a) and the corresponding selected area electron diffraction (SAED) pattern (b) of a single gold nanoplate lying flat on a TEM grid.

spectroscopy. As shown in figure 2, peaks of Au, Cl, C, N and O elements are observed (the Si peak originated from the silicon wafer substrate), indicating that guanine was actually on the surface of the gold nanoplates. To further confirm the formation of the gold nanoplates, XPS was used to examine the change in the oxidation states for Au after the reduction reaction had occurred. The XPS spectrum of the as-prepared gold nanoplates shows two peaks centred at binding energies of 84.75 and 88.45 eV, which can be assigned to the Au $4f_{7/2}$ peak and the Au $4f_{5/2}$ peak respectively, confirming the formation of metallic Au (figure 3) [39].

The crystalline nature of the as-prepared gold nanoplates was characterized by the corresponding XRD pattern. The two sharp peaks at ~38.26° and 81.74° as shown in figure 4 can be assigned to diffraction peaks of the (111) and (222) lattice planes of face-centred-cubic (fcc) gold crystal, respectively, indicating that the as-prepared gold nanoplates were composed of pure crystalline gold (the peak at about $2\theta = 69.36°$ originated from the silicon wafer substrate) [24, 25]. The (111) diffraction peak showed the overwhelming intensity in the pattern, which implies that the as-prepared gold nanoplates were primarily dominated by the Au(111) facets [40, 41].

Figure 5 shows a typical TEM image (figure 5(a)) of a single gold nanoplate as well as the related selected area

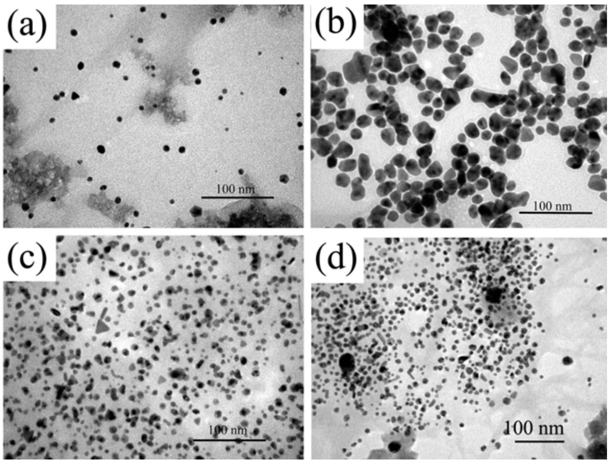

Figure 6. TEM images of gold particles obtained at a molar ratio of of guanine to $HAuCl_4$ of 1:1 (a), 1:4 (b), 1:8 (c) and 1:20 (d).

electron diffraction (SAED) pattern (figure 5(b)) obtained by focusing the electron beam on the nanoplate lying flat on the TEM Cu grid. The hexagonal symmetry diffraction spot pattern of the SAED pattern reveals that the nanoplate is a single crystal with a preferential growth direction along the Au(111) plane [24, 25]. The SAED result, along with the above-mentioned XRD data (figure 4), confirmed the formation of single-crystalline gold nanoplates.

3.2. Growth mechanism of the as-prepared gold nanoplates

To investigate the growth mechanism of gold nanoplates, the influence of the molar ratio of guanine to $HAuCl_4$ on the formation of gold nanoplates was investigated by varying the amount of guanine used (figure 6). At a 1:1 molar ratio of guanine to $HAuCl_4$, polydisperse gold nanoparticles with a mean diameter of 9 nm were obtained (figure 6(a)). As for a 1:4 and 1:8 molar ratio of guanine to $HAuCl_4$, we obtained products consisting of polydisperse irregularly shape gold nanoparticles with mean diameters of 15 and 8 nm, respectively (figures 6(b) and (c)). A 1:20 molar ratio gave products mainly containing polydisperse spherical particles with a mean diameter of 7 nm and a small fraction of larger fused particles (about 30 nm) (figure 6(d)). However, submicrometre scale gold nanoplates could be obtained with a 1:50 molar ratio of guanine to $HAuCl_4$ as mentioned above (figures 1 and 5). The above experimental results clearly suggest that the quantity of guanine plays a vital role in the formation of gold nanoplates.

As mentioned above, at a 1:50 molar ratio of guanine to $HAuCl_4$ smaller spherical gold nanoparticles with a diameter of 5–7 nm were obtained as well as the submicrometre scale gold nanoplates (figures 1 and 5(a)). Interestingly, the size of these gold nanoparticles at a 1:50 molar ratio of guanine to $HAuCl_4$ approximated to the size of gold nanoparticles obtained at molar ratios of $HAuCl_4$ to guanine $\leqslant$ 20:1. Also the as-prepared gold nanoplates could be destroyed by a heating treatment (see supplementary information available at stacks.iop.org/Nano/18/295603). These results might imply that the smaller gold nanoparticles could evolve into submicrometre scale gold nanoplates when guanine is inadequate (figure 7).

So, what is the driving force for the formation of nanoplates from smaller nanoparticles precursors? The redox reaction between $HAuCl_4$ and guanine occurs according to the equation (1):

$$[AuCl_4]^- + \text{Guanine} \rightarrow Au^0 + 4Cl^- + \text{Guanine}_{ox}. \qquad (1)$$

The two relevant half reactions are:

$$[AuCl_4]^- + 3e \rightarrow Au^0 + 4Cl^- \qquad (2)$$

$$\text{Guanine} - e \rightarrow \text{Guanine}_{ox}. \qquad (3)$$

The standard reduction potential of $[AuCl_4]^-$ is +1.002 V (versus NHE), which is higher than that of guanine (+0.889 V versus NHE) [40, 42–46][1]. For the net reaction 1, a $\Delta G_{\text{redox}} = -32.71\ \text{kJ mol}^{-1}$ is calculated. Therefore, the reduction of $HAuCl_4$ with guanine is favoured thermodynamically.

Meanwhile, guanine can adsorb on the gold surface in a complex manner [47], and the net stabilization due to coordination of guanine base with the gold surface has been evaluated theoretically to be about $\Delta G_{\text{coordination}} = -351.54\ \text{kJ mol}^{-1}$ (equation (4)) [38]:

$$Au^0 + \text{Guanine} \rightarrow [\text{Au–Guanine}]_{\text{coordination}}. \qquad (4)$$

Since $|\Delta G_{\text{coordination}}| > |\Delta G_{\text{redox}}|$, it seems reasonable that guanine can act as a capping agent for the preparation of gold nanoparticles (figure 7). It was thought that the preparation of metal nanoparticles from their salt solutions could be divided into three processes: the reduction of metal cations, nucleation and growth [48]. Once the $HAuCl_4$ was reduced into elemental gold by guanine in our system, nucleation occurred immediately. However, the growth of gold nanoparticles could be suppressed since guanine favourably bound to the gold nanoparticle surfaces in a system with ample guanine. In fact, even a 1:20 molar ratio of guanine to $HAuCl_4$ gave mainly spherical gold nanoparticles (figures 6 and 7). If the quantity of guanine further decreased to a molar ratio of 1:50 of guanine to $HAuCl_4$, gold nanoplates were obtained. In this case, there was too little guanine to stabilize the smaller gold nanoparticles, and these smaller gold nanoparticles could evolve into larger gold nanoplates (figure 7). The single-crystalline nature of the as-prepared gold nanoplates could be assigned the lowest surface energy of the (111) plane of fcc gold, which resulted in a preferential growth direction along the gold (111) plane [49].

4. Conclusions

The quantity of capping agent plays a very important role in the preparation of shape-controlled nanomaterials [50, 51]. In this work synthesis of submicrometre scale single-crystalline gold plates of nanometre thickness in the presence of nucleobase guanine through chemical reduction of $HAuCl_4$ was investigated. It was found that the molar ratio of

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[1] The redox potential of guanine base has been extensively studied [44–46] indicating that the value of the redox potential varies in a wide range with different oxidation pathways. Here we took a relative negative value for our estimation (+0.889 V versus NHE [44]).

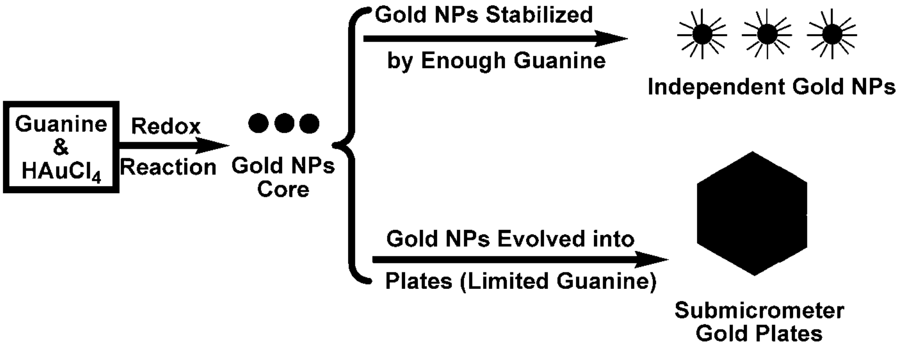

Figure 7. Reaction scheme of $HAuCl_4$ with different quantities of guanine.

$HAuCl_4$ to guanine played a key role in the formation of gold nanoplates. Ample guanine gave only spherical gold nanoparticles while quite inadequate guanine could yield gold plates. It was supposed that the submicrometre scale gold nanoplates were evolved from the smaller spherical gold nanoparticles when guanine was inadequate. The results and conclusion presented in this work may be valuable for the further understanding of the roles of precursor ligands in the preparation of shape-controlled nanoparticles.

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References

[1] Burda C, Chen X B, Narayanan R and El-Sayed M A 2005 *Chem. Rev.* **105** 1025–102
[2] Daniel M-C and Astruc D 2005 *Chem. Rev.* **104** 293–346
[3] Wei H, Li J, Wang Y L and Wang E K 2007 *Nanotechnology* **18** 175610
[4] Zeng Q, Jiang X, Yu A and Lu G 2007 *Nanotechnology* **18** 035708
[5] Zhang L X, Sun X P, Song Y H, Jiang X E, Dong S J and Wang E K 2006 *Langmuir* **22** 2838–43
[6] Petty J T, Zheng J, Hud N V and Dickson R M 2004 *J. Am. Chem. Soc.* **126** 5207–12
[7] Haruta M and Date M 2001 *Appl. Catal.* A **222** 427–37
[8] Jia J B, Wang B Q, Wu A G, Cheng G J, Li Z and Dong S J 2002 *Anal. Chem.* **74** 2217–223
[9] Vance F W, Lemon B I and Hupp J T 1998 *J. Phys. Chem.* B **102** 10091–3
[10] Yu C-J, Su C-L and Tseng W-L 2006 *Anal. Chem.* **78** 8004–10
[11] Kim Y, Johnson R C and Hupp J T 2001 *Nano Lett.* **1** 165–7
[12] Boal A K and Rotello V M 2000 *Langmuir* **16** 9527–32
[13] El-Sayed M A 2001 *Acc. Chem. Res.* **34** 257–64
[14] Eustis S and El-Sayed M A 2006 *Chem. Soc. Rev.* **35** 209–17
[15] Schulz J, Roucoux A and Patin H 2002 *Chem. Rev.* **102** 3757–78
[16] Sun Y and Xia Y 2002 *Science* **298** 2176–9
[17] Chen S, Wang Z L, Ballato J, Foulger S H and Carroll D L 2003 *J. Am. Chem. Soc.* **125** 16186–7
[18] Kuo C H, Chiang T F, Chen L-J and Huang M H 2004 *Langmuir* **20** 7820–4
[19] Kim J U, Cha S H, Shin K, Jho J Y and Lee J C 2004 *Adv. Mater.* **16** 459–64
[20] Shankar S S, Rai A, Ankamwar B, Singh A, Ahmad A and Sastry M 2004 *Nat. Mater.* **3** 482–8
[21] Shao Y, Jin Y D and Dong S J 2004 *Chem. Commun.* 1104–5
[22] Millstone J E, Park S, Shuford K L, Qin L, Schatz G C and Mirkin C A 2005 *J. Am. Chem. Soc.* **127** 5312–3
[23] Chen S, Fan Z and Carroll D L 2002 *J. Phys. Chem.* B **106** 10777–81
[24] Sun X P, Dong S J and Wang E K 2004 *Angew. Chem. Int. Edn* **43** 6360–3
[25] Sun X P, Dong S J and Wang E K 2005 *Langmuir* **21** 4710–2
[26] Purohit C S and Verma S 2006 *J. Am. Chem. Soc.* **128** 400–1
[27] Wei H, Li B L, Du Y, Dong S J and Wang E K 2007 *Chem. Mater.* **19** 2987–93
[28] Li Z and Mirkin C A 2005 *J. Am. Chem. Soc.* **127** 11568–9
[29] Roitzsch M and Lippert B 2004 *Inorg. Chem.* **43** 5483–5
[30] Dobrzynska D and Jerzykiewicz L B 2004 *J. Am. Chem. Soc.* **126** 11118–9
[31] Boerner L J K and Zaleski J M 2005 *Curr. Opin. Chem. Biol.* **9** 135–44
[32] Rosi N L and Mirkin C A 2005 *Chem. Rev.* **105** 1547–62
[33] Seeman N C 2003 *Nature* **421** 427–31
[34] Love J C, Estroff L A, Kriebel J K, Nuzzo R G and Whitesides G M 2005 *Chem. Rev.* **105** 1103–70
[35] Sharma J, Chhabra R, Liu Y, Ke Y and Yan H 2006 *Angew. Chem. Int. Edn* **45** 730–5
[36] Li C Z, Liu Y and Luong J H T 2005 *Anal. Chem.* **77** 478–85
[37] Pergolese B, Bonifacio A and Bigotto A 2005 *Phys. Chem. Chem. Phys.* **7** 3610–3
[38] Mohan P J, Datta A, Mallajosyula S S and Pati S K 2006 *J. Phys. Chem.* B **110** 18661–4
[39] Fabris L, Antonello S, Armelao L, Donkers R L, Polo F, Toniolo C and Maran F 2006 *J. Am. Chem. Soc.* **128** 326–36
[40] Maye M M, Zheng W, Leibowitz F L, Ly N K and Zhong C J 2000 *Langmuir* **16** 490–7
[41] Kan C X, Zhu X G and Wang G H 2006 *J. Phys. Chem.* B **110** 4651–6
[42] Zhou Y, Wang C Y, Zhu Y R and Chen Z Y 1999 *Chem. Mater.* **11** 2310–2
[43] Ferapontova E E 2004 *Electrochim. Acta* **49** 1751–9
[44] Steenken S and Jovanovic S V 1997 *J. Am. Chem. Soc.* **119** 617–8
[45] Abbaspour A and Mehrgardi M A 2004 *Anal. Chem.* **76** 5690–6
[46] Oliveira-Brett A M, Diculescu V and Piedade J A P 2002 *Bioelectrochemistry* **55** 61–2
[47] Ostblom M, Liedberg B, Demers L M and Mirkin C A 2005 *J. Phys. Chem.* B **109** 15150–60
[48] Miranda O R, Dollahon N R and Ahmadi T S 2006 *Cryst. Growth Des.* **6** 2747–53
[49] Yin Y, Erdonmez C, Aloni S and Alivisatos A P 2006 *J. Am. Chem. Soc.* **128** 12671–3
[50] Narayanaswamy A, Xu H, Pradhan N, Kim M and Peng X 2006 *J. Am. Chem. Soc.* **128** 10310–9
[51] Tang Z, Kotov N A and Giersig M 2002 *Science* **297** 237–40