Investigation of Electrochemical Charging Behaviors of "Naked" Gold Nanoparticles Ensembles in Aqueous Media

CHENG, Wen-Long(程文龙)   HAN, Xiao-Jun(韩晓军)   PENG, Zhang-Quan(彭章泉)
DOGN, Shao-Jun*(董绍俊)   WANG, Er-Kang*(汪尔康)
State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China

Gold nanoparticles were immobilized onto the electrode surface by simple self-assembly technique. Interestingly, the ensembles of these nanoparticles exhibit quantized charging behaviors in aqueous solution. Possible mechanism for such behaviors was proposed.

Keywords   "naked" gold nanoparticle, monolayer-protected cluster, differential capacitance, differential pulse voltammogram

Introduction

Because nanoparticles can be handled like simple molecules, the macroscale properties can be controlled via nanoscale construction. Currently, colloidal Au-derived electrodes constitute an interesting intersection between electrochemistry and nanoscale science. For example, organized architectures of nanosized particles are attracting extensive attention in diverse fields, in part, because of the fundamental importance and technological implications involved in those ordered arrays of quantum dots.[1] Controlled self-assembly of nanoparticles into nanoscale superstructures is an important objective.[2] Reports of attachments of nanoparticles[3] monolayers and multilayers to self-assembled molecular monolayers and polymer substrates have included dithiol and analogous linkers,[3a-c] polyelectrolytes,[3d] and a few examples of monolayer-protected clusters (MPCs) based on sol-gel chemistry[3e] and place-exchange reactions.[3f] Among these, MPCs have attracted particular attention due to the (sub)attofarad molecular-capacitor characteristics. Under ambient conditions, solu-

tions and surface ensembles of monodisperse MPCs exhibit quantized charging to their double layers, showing analogous features to the classical coulomb staircase.[5] However, it has to be noted that these earlier electrochemical studies are primarily confined to the MPCs,[5,3f] whereas none has been reported to "naked" gold nanoparticles (NGNs). Thus, several questions arise immediately: what a role does the protecting layer of MPCs in investigating quantized charging behaviors of nanoparticles? Is it possible to observe these charging behaviors of NGNs ensembles in aqueous media or organic media?

Experimental

Reagents and materials

The following reagents were purchased from commercial vendors and used without further purification. 1,8-Octanedithiol, $HauCl_4 \cdot 3H_2O$, trisodium citrate dihydrate, $(t\text{-}Bu)_4NCl$ and $(t\text{-}Bu)_4NClO_4$ were from Aldrich. All other reagents are of analytical grade. Solutions were prepared from ultrapure water purified with Milli-Q plus system (Millipore Co.). Its resistivity was over 18 $M\Omega \cdot cm$.

Preparation of colloid Au

All glassware used in the following procedures were cleaned in a bath of freshly prepared $HCl : HNO_3$ (3 : 1,

V: *V*) and rinsed thoroughly in H_2O prior to use. The gold colloids were prepared by the conventional citrate reduction of $HAuCl_4$ in water at near-boiling temperature.[20] Transmission electron microscopy was used to examine particle size distribution, and an average diameter of 5 nm was confirmed.
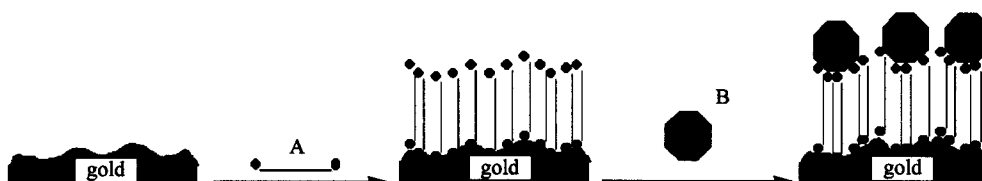
Instrument

Electrochemical experiments were carried out on the Autolab PGSTAT30 potentiostat (Utrecht, Netherlands) in a conventional one-compartment cell. The cell was hosed in a homemade Faraday cage to reduce stray electrical noise. The standard three-electrode system was used. An Ag/AgCl electrode was used as the reference electrode, a Pt foil as the counter electrode, and gold disk as the working electrode. The specimens for transmission electron spectroscope were prepared by evaporating a drop gold colloid onto a copper mesh grid and examined by a JEM-2010 high-resolution electron microscope operating at 200 kV.

Results and discussion

In order to understand the electron-transfer chemistry involved in these surface-confined NGNs, self-assembling technique was employed to construct NGNs monolayer and these ensembles were used to investigate electrochemical charging events of NGNs. In the present paper, several electrolytes were selected to investigate the electrochemical behaviors involved in NGNs in order to understand the role of electrolyte ions in charging process of nanoparticles. The experimental results demonstrate that Cl^- ions can rectify electrochemical effect signals[5b] of NGNs surface ensembles both in aqueous solution and organic solution. These may be attributed to stronger ion-binding interaction or specific adsorption between Cl^- anions and NGNs.

The protocol for the NGNs self-assembling process is shown in Scheme 1. 1,8-Octanedithiol was self-assembled on gold surface firstly, and then NGNs were anchored on the top of the monolayer. The NGNs with the average core size of ~ 5 nm were synthesized by reduction of $HAuCl_4$ of citric acid at nearly boiling tempreture,[6] and then tannic acid was added to stabilize the as-prepared colloid. Monodisperse particles were confirmed by TEM as shown in Fig. 1. The typical incubation time for the self-assembling of NGNs onto 1,8-octanedithiol self-assembling monolayer was about 24 h, and the electrode was then rinsed with copious water purified with Milli-Q system (18.4 $M\Omega \cdot cm$) to remove the loosely bound NGNs and dried gently under nitrogen atmosphere before being transferred to an electrolyte solution for electrochemical measurements.

Fig. 1 TEM micrograph of gold nanoparticles and the corresponding electron diffraction ring pattern.

Scheme 1 Cartoon reactions for anchoring NGNs to a gold electrode surface

"A" stands for 1,8-octanedithiol, and "B" stands for naked gold nanoparticle.

Fig. 2 shows differential capacitance (by AC voltammetry) of the NGNs anchored electrode in aqueous and toluene/CH_3CN (2:1, $V:V$) solutions, respectively. It can be seen that they show different behaviors in different solvents and also different behaviors in the same solvents with different electrolytes. Chen et al.[5b] demonstrated previously that a simple ion-binding can be utilized as the molecular triggers for the rectification of single-electron transistors. Here, Cl^- anions might also play this kind of roles. Obviously Cl^- ion increases electrochemical effect signals of NGNs both in aqueous solution and toluene/CH_3CN (2:1, $V:V$) solvents. Besides, more well-defined quantized charging behaviors (Fig. 2A, top line) were found in KCl aqueous solution, whereas weak charging peaks (Fig. 2A, down line) in KNO_3 aqueous solution. The electrochemical effect signal in (t-Bu)$_4$NCl electrolyte (Fig. 2B, top line) is also stronger than that in (t-Bu)$_4$ClO$_4$ electrolyte (Fig. 2B, down line). DPV measurements exhibit the same results as differential capacitance, demonstrating a general rule rather than an accidental event. The specific adsorption of Cl^- ions on gold nanoparticles or stronger ion-binding interaction may account for this. Besides, better charging peaks were found in aqueous media (Fig. 2A) than in organic media (Fig. 2B). Why do the quantized charging behaviors of NGNs differ from that of MPCs? In most of previous reports for MPCs, well-defined quantized charging behaviors were observed only in organic media;[5a,c,d,e,g,h] whereas in aqueous solutions, only featureless responses or ill-defined charging peaks were found. In organic solvent, as per unit electrode surface area, $C_{MPC} > C_{El}$[3f,5b], (C_{MPC} is the capacitance of the anchored MPCs ensembles, and C_{El} the charging capacitance of the electrode surface), the overall electrode double-layer capacitance was mainly governed by the adsorbed particles and resulted in current measured reflected the collective quantized charging of individual surface-immobilized MPCs. Whereas in aqueous solutions $C_{MPC} \ll C_{El}$,[3f,5b] the double-layer charging is mainly through the "naked" electrode surface, showing classical features of electrode double layers. In contrast, the case for NGNs ensembles was found to be the other way round. Citric acid-tannic acid is loosely bound to surface of gold core, Cl^- ions can displace these adsorbing molecules and bind to gold core. Therefore, surface-confined gold nanoparticles in the present system are "naked" to electrolytes in fact. It seems that alkanethiol molecules have been "stripped off MPCs and immobilized

onto electrode surface", the nanoparticles are "bare" and the electrode surface dresses in "clothes" (this is an imaginary process to illustrate the difference between our systems and previous reports[5] as shown in Scheme 2). Therefore, C_{dl}(double layer capacitance) is predominantly determined by C_{NGNs}(the capacitance of the anchored NGNs ensembles) in aqueous solution, and determined by alkanethiol modified electrode surface charging capacitance in organic solution, then well-defined charging peaks were obtained only in aqueous media for NGNs ensembles. Although the assembling process in Scheme 2 is imaginary, it fits the experiment results observed for NGNs very well.
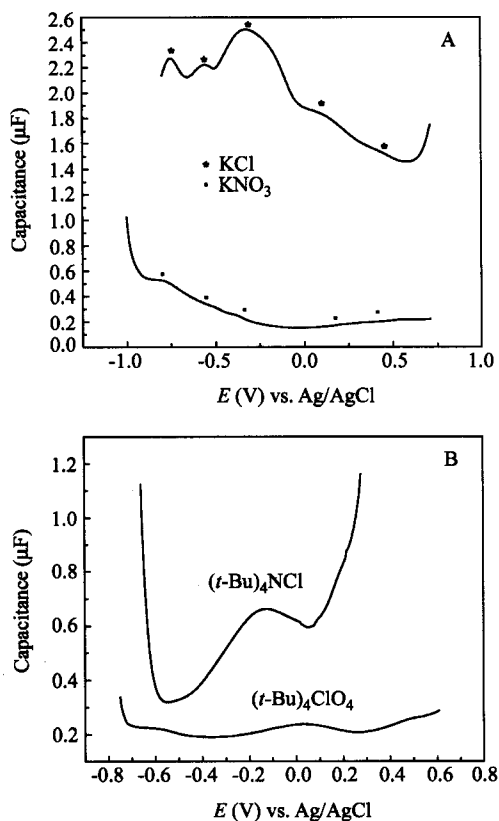

Fig. 2 Differential capacitance of a gold electrode modified with NGNs monolayer. AC frequency is 1 Hz, amplitude 50 mV, and step potential 5 mV. (A) The supporting electrolyte solutions were aqueous 0.1 mol/L KNO_3(top line) and 0.1 mol/L KCl (down line), respectively. Charging peaks are marked with asterisks and dots. (B) The supporting electrolyte solutions were 0.1 mol/L (t-Bu)$_4$NCl (top line) and 0.1 mol/L (t-Bu)$_4$NClO$_4$ (down line) in toluene/CH_3CN (2:1, $V:V$), respectively.

Scheme 2　An imaginary molecular re-construction process, which may explain the different quantized capacitance charging behaviors between NGNs and MPCs

Stripped and assembling
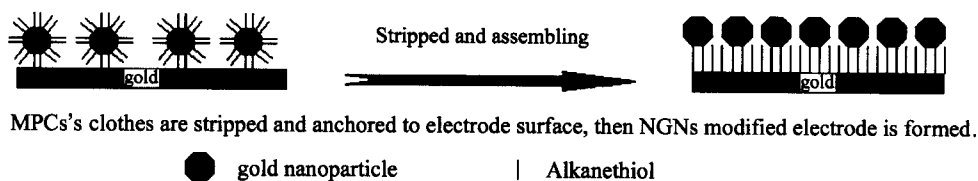
MPCs's clothes are stripped and anchored to electrode surface, then NGNs modified electrode is formed.

● gold nanoparticle　　　　　　| Alkanethiol

It has been found that the binding of electrolyte ions to an electroactive species leads to the shifting of the formal potentials with electrolyte concentrations:[7]

$$E_f = E^{0'} + (RT/n_a F)\ln(K_2/K_1) - [(p - q)RT/n_a F]\ln[Cl^-] \qquad (1)$$

Where E_f is the measured formal potential, $E^{0'}$ the formal potential in the absence of ion binding, n_a the effective number of electron transfer, K_1 and q (K_2 and p) the e-quilibirium constant and the number of Cl^- ions bound to the reduced (oxidized) forms of NGNs, respectively, and other parameters have their usual significance. Differential capacitance (Fig. 2) and DPV measurements both show the variation of the formal potentials of charging peaks observed in KCl and KNO_3 aqueous solutions. It can be seen that charging peaks in KCl aqueous solution shift cathodically about 50 mV relative to KNO_3 aqueous solution because of Cl^- ions binding or specific interaction with NGNs. Interestingly, such potential-shifting behavior of Cl^- ions adsorbed on nanoparticles was also seen in the studies of adsorption-mediated electrochemical sensing of halides on Au(111)/Ag(upd),[12] where the native Ag stripping peak at 535 mV versus Ag^+/Ag was replaced by a stripping peak at 615 mV that can be assigned to the formation of Au(111)/Ag(upd)-Cl.

The larger electrochemical responses of NGNs in KCl motivated us to investigate the electron-transfer kinetics of NGNs and detailed quantized capacitance charging behaviors. Fig. 3 shows cyclic voltammograms of NGNs between -1.0 and 0.5 V. Several well-defined redox couples can be seen clearly. In order to evaluate the reversibility of such redox process, various scan rates were taken. Inset of Fig. 3 shows sweep rate dependence of peak potentials (for clarity, only the charging peak between 0.2 and 0.4 V is shown). The peak currents vary
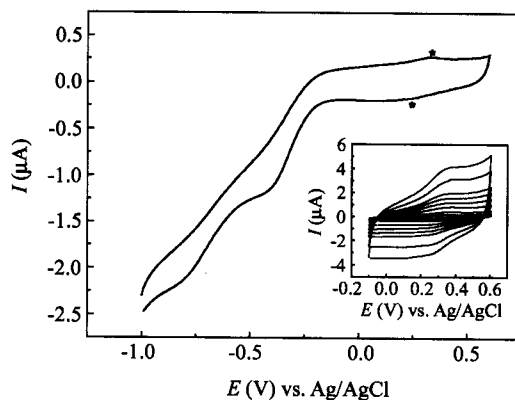

Fig. 3　Cyclic voltammograms of a gold electrode modified with NGNs monolayer. Scan rate was 50 mV/s. The supporting electrolyte was 0.1 mol/L KCl aqueous solution. Inset: cyclic voltammograms with scan rates from 50 to 100, 200, 400, 600, 800, 1000, 1500, 2000 mV/s (only charging peaks between 0.2 and 0.4 V were shown).

linearly with potential scan rates (not shown), as expected for a surface-localized redox electrochemistry. In addition, electron-transfer rate constant k can be estimated from the fitting parameters of the AC impedance spectra[8-11] as well:

$$K = 1/2\, C_{NGN} R_{CT} \qquad (2)$$

where C_{NGN} is the capacitance of NGNs ensembles, R_{CT} the electron-transfer resistance. From Fig. 4, one can reach a value of k about 0.57 s^{-1}.

It has been shown[5c] that the formal potential of a quantized capacitance charging peak in which the charge state changes from z to $z - 1$ is:

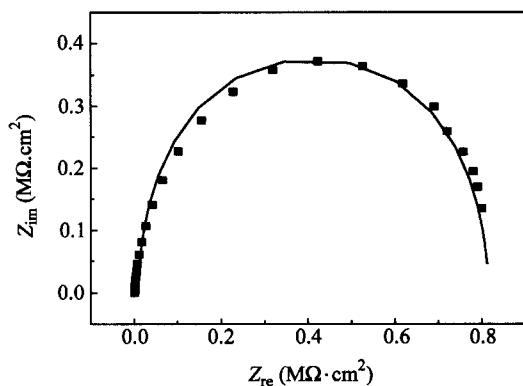$$E^0_{z,z-1} = E_{pzc} + (z - 1/2)e/C_{clu} \qquad (3)$$

Fig. 4 AC impedance plots of the experimental results (black squares) and the simulation (solid lines) of the gold electrode modified with a NGNs monolayer. The sweep frequency was from 1000 kHz to 0.01 Hz, and amplitude 50 mV. The supporting electrolyte was 0.1 mol/L KCl aqueous solution.
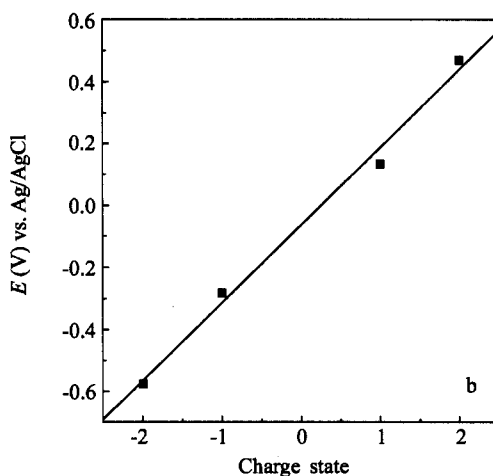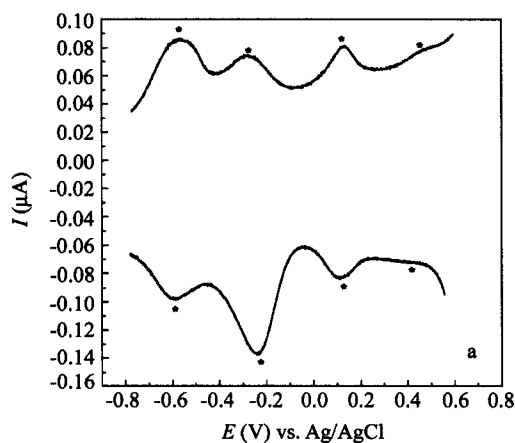
Where E_{pzc} is the zero charge potential ($i.e.$ $z = 0$) of the cluster, and z is signed such that $z > 0$ and $z < 0$ correspond to core "oxidation" and "reduction", respectively. C_{clu} is the MPC capacitance, e the electronic charge, and $E^0_{z,z-1}$ the formal potential of the $z/(z-1)$ charge state "couple". Eq. (3) dictates a linear relationship between the formal potentials and the charge states of MPCs (termed "z-plot") if C_{clu} is independent of electrode potential, and from the slope and the intercept one can evaluate C_{clu} and E_{pzc}, respectively.

As for NGNs in our system, C_{clu} is the doule-layer capacitance of NGN, and other symbols have the same significance as mentioned above. From Fig. 5, it can be seen that there exists also a linear relationship between the formal potentials and charge states. From the regression line, we estimate that C_{NGN} is about 0.68 aF as estimated from Fig. 5b (1 aF = 10^{-18} F). The differential capacitance experiments also give the similar results, which proves that differential capacitance also can be used to characterize these quantized capacitance charging behaviors of nanoparticles ensembles like DPV. However, it seems that these experimental results contradict with the concentric sphere capacitance model.[5e] A capacitor with conducting spherical metal core separated by a dielectric of thickness d and static dielectric constant ε has a capacitance given by[5e]

$$C_{CLU} = 4\pi\varepsilon_0\varepsilon (r/d)(r + d) \tag{4}$$

Fig. 5 (a) Differential pulse voltammograms of a gold electrode modified with NGNs monolayer. The DC potential scan rate is 10 mV/s and pulse amplitude 10 mV. The supporting electrolyte was 0.1 mol/L KCl aqueous solution (charging peaks are marked with asterisks). (b) Plot of charging formal potentials versus NGN charging states (z-plot). Data were obtained from DPV measurements. Lines shown are linear regression.

Where C_{CLU} is the cluster capacitance, ε_0 the permittivity of free space, ε the dielectric constant of solvent, r the radius of the core, and d the thickness of electric double-layer of the core. Assuming the electrochemical interface of NGN is an ideal capacitor, the average double-layer thickness of NGN is 1.5 nm.[9] By this model, 5 nm of NGN has a capacitance of about 57 aF, which is much larger than that of 0.68 aF estimated by the experimental results. Several reasons may account for this:

(1) The anchored NGNs are half "naked" and half protected because of the roughness of electrode surface (Scheme 1). Therefore, the "naked" surface of NGNs is smaller than ideal concentric sphere capacitor because of

sulfur-gold binding interactions, and the real capacitance of NGN is much smaller 57 aF (1,8-octanedithiol protected gold nanoparticle with a metal core of 5 nm gives a capacitance of about 2.4 aF by concentric capacitance model).

(2) The NGNs are not naked in fact, but protected by citrate acid and tannic acid. Therefore, the real dielectric constant of protecting layer of nanoparticle is much smaller than water dielectric constant,[13] and the calculated capacitance of gold nanoparticle should much smaller than 57 aF.

(3) Quantized charging behaviors of NGNs may not be a single-electron oxidation (or reduction) process, but a multiple-electron oxidation (or reduction) process. At that condition, the effective cluster capacitance should be evaluated by $\Delta V = ne/C_{CLU}$ rather than $\Delta V = e/C_{CLU}$, and therefore larger value of ΔV was observed when $n \geqslant 2$ (for example, for two-electron oxidized process, C_{CLU} was 1.36 aF estimated by the present experiment results). Of course, this speculation needs still additional proofs from other experimental methods, which is being designed at present.

(4) The discrepancy can be traced to ε used. The value of 80 employed for the dielectric constant of water assumes that the molecules are free to rotate and so re-orient on changing the applied field. The water molecules on the surface of nanoparticles will not be able to change orientation at all, therefore, the dielectric constant of adsorbed water is much less than 80 ($\varepsilon \leqslant 6$).

(5) The mechanism for electrical double layer formation at highly charged NGNs is very complex,[14,15] and further study is still needed.

Conclusion

To the best of our knowledge, this is the first report of electrochemical charging behaviors of surface-confined NGNs in aqueous solutions. This study demonstrates that quantized charging behaviors of NGNs with a larger core mass can be observed in appropriate experimental conditions. Besides, Cl⁻ ions can be utilized to rectify electrochemical responses of electron-transfer process associated with NGNs by simple ion-binding or specific adsorption interaction. More detailed studies are desired to further investigate the quantized charging behaviors of other metal or semiconductor NGNs and to search better binding ions utilized as triggers for the rectification of single-electron

transistors. The theoretical study of a possible mechanism of multiple-electron oxidation (or reduction) of NGNs is underway in our laboratory.

References

1 (a) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.
(b) Schmid, G.; Peschel, S.; Sawitowsdi, T. *Z. Anorg. Allg. Chem.* **1997**, *623*, 719.
(c) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690.
(d) Kiely, C. J.; Fink, C. J.; Brust, M.; Bethell, D.; Schriffrin, D. J. *Nature* **1998**, *396*, 444.

2 Schmid, G. *J. Chem. Soc., Dalton Trans.* **1998**, 1077.

3 (a) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1148.
(b) Bethell, D.; Brust, M.; Schiffrin, D. J.; Kiely, C. J. *Electroanal. Chem.* **1996**, *439*, 137.
(c) Blonder, R.; Sheeney, L.; Willner, I. *Chem. Commun.* **1998**, 1393.
(d) Liu, Y.; Wang, Y.; Claus, R. O. *Chem. Phys. Lett.* **1998**, *298*, 315.
(e) Yonezawa, T.; Matsune, H.; Kunitake, T. *Chem. Mater.* **1999**, *11*. 33.
(f) Chen, S. *J. Phys. Chem. B* **2000**, *104*, 663.

4 (a) Whetten, R. L.; Shafigullin, M. N.; Khoury, J. T.; Schaaff, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. *Acc. Chem. Res.* **1999**, *32*, 397.
(b) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

5 (a) Chen, S.; Ingram, R. S.; Hosteler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvrez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098.
(b) Chen, S. *J. Am. Chem. soc.* **2000**, *122*, 7420.
(c) Chen, S.; Murray, R. W.; Feldberg, S. W. *J. Phys. Chem. B* **1998**, *102*, 9898.
(d) Chen, S.; Murray, R. W. *J. Phys. Chem. B* **1999**, *103*, 9996.
(e) Hicks, J. F., Templeton, A. C.; Chen, S.; Sheran, K. M.; Jasti, R.; Murray, R. W.; Debord, J.; Schaaff, G.; Whetten, R. L. *Anal. Chem.* **1999**, *71*, 3703.
(f) Baum, T.; Bethell, D.; Brust, M.; Schiffrin, D. J. *Langmuir* **1999**, *15*, 866.
(g) Chen, S.; Murray, R. W. *Langmuir* **1999**, *15*, 682.
(h) Zamborini, F. P.; Hicks, J. F.; Murray, R. W. *J.*

Am. Chem. Soc. **2000**, *122*, 4514.

6   Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.

7   Sagra, T.; Maeda, H.; Yuan, Y.; Nakashima, N. *Langmuir* **1999**, *15*, 3823.

8   (a) Creager, S. E.; Wooster, T. T. *Anal. Chem.* **1998**, *70*, 4257.
     (b) Weber, K.; Hockett, L.; Creager, S. E. *J. Phys. Chem. B* **1997**, *101*, 8286.

9   Wang, Z. W.; Yi, X. Z.; Li, G. Z.; Guan, D. R.; Lou, A. J. *Chem. Phy.* **2001**, *274*, 57.

10   Li, T. T. T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**,

106, 6107.

11   Carter, M. T.; Rowe, G. K.; Richardson, J. N.; Tender, L. M.; Terrill, R. H.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 2896.

12   Michalitsch, R.; Laibinis, P. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 941.

13   Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

14   Chandra, A. *J. Mol. Struct.* **1998**, *430*, 105.

15   Aguilella, V. M.; Mafe, S.; Manzanares, J. A. *Chem. Phys. Lipids* **2000**, *105*, 225.

(E0112251   ZHAO, X. J.; DONG, H. Z.)