

Electroactive gold nanoparticles protected by 4-ferrocene thiophenol monolayer

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Abstract

Numerous reports have focused on ferrocene-terminated electroactive self-assembled monolayers (SAMs) on a flat Au surface but only a few on ferrocene SAMs on Au colloid. In this paper, we employ 4-ferrocene thiophenol as a novel capping agent to produce electroactive gold nanoparticles in consideration of the peculiar π -conjugated structure. Transmission electron microscopy shows the narrow-dispersed gold core with an average core diameter of ca. 2.5 nm. UV/vis spectra examine the π -conjugated structure of 4-ferrocene thiophenol and surface plasmon absorbance of the indicated gold nanoparticles. X-ray photoelectron spectroscopy reveals electronic properties of the Au core and thiol ligands. Electrochemical measurement shows that the oxidation peak current is proportional to the scan rate, indicating the electrode process is controlled by adsorbed layer reaction. The formal potential of the Fc-MPCs is compared with that of free ferrocene in MeCN solution and the Fc-SAMs. The shifts are attributed to the phenyl moiety in the 4-ferrocene thiophenol and dielectric constant of the solvation environment.

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1. Introduction

Metal nanoparticles are the focus of chemists and physicists due to their interesting size-dependent optical, electronic, and physical properties. Ever since the first report of Brust et al. [1], great attention has been paid to the monolayer-protected metal clusters (MPCs) [2,3] for they are quite air-stable and can be repeatedly isolated from and redissolved in nonpolar organic solvents, which may lead to great application potentialities in fields such as nanodevices, biosensors, and molecule catalysts.

Ferrocene is a prototypical redox group that has been frequently incorporated at the terminal site of alkanethiol-derivatized self-assembled monolayers (SAMs) on various electrodes [4,5]. Murray and co-workers [6] reported gold nanoparticles protected by *n*-octanethiolates and ω -functionalized ferrocenyl octanethiolates mixed monolayers. In their experiment, the ferrocene moiety was place-exchanged onto the C₈SH-MPCs. Chen [7] fabricated

ω -ferrocenated gold nanoparticles thin films by using the Langmuir–Blodgett technique. Labande [8] synthesized gold nanoparticles containing a mixture of alkanethiolate and amidoferrocenylalkylthiol ligands as new redox sensors for H₂PO₄⁻ and HSO₄⁻. Herein we aim to synthesize gold nanoparticles capped by 4-ferrocene thiophenol ligand (abbreviated as Fc-MPCs). An aromatic moiety and an electroactive ferrocene moiety are contained in one molecule. Compared with alkanethiolate-MPCs [2] and thiophenol-MPCs [3], the peculiar π -electron conjugated structure of the monolayer may have some significant effects on the clusters and thus more prospective applications in future nanodevices.

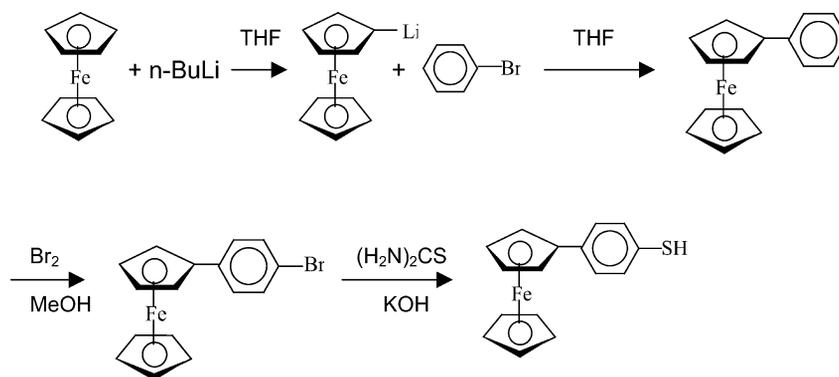
2. Experimental

2.1. Chemicals

HAuCl₄·4H₂O (99%), NaBH₄ (A.R.), toluene (A.R., distilled), ethanol (A.R.), acetone (A.R.), and acetonitrile (A.R.) were used as received. Tetraoctylammonium bromide was purchased from Aldrich. Tetrabutylammonium

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Scheme 1. Synthesis procedure of the 4-ferrocene thiophenol.

perchlorate and 1-propanethiol were purchased from Acros. Water was purified with a Milli-Q (18.3 M Ω) water system.

4-Ferrocene thiophenol was synthesized according to the literature [9]. In brief, ferrocene initially reacted with butyl lithium and then was treated with bromobenzene to lead to the formation of phenyl-substituted ferrocene. Further bromination of a phenyl ring at the *para* position and conversion of the bromide substituent gave rise to thiol product (Scheme 1), which is characterized by ^1H NMR and EI-MS. ^1H NMR (deuterated DMSO): 7.546 (2H, Ar-H*), 7.487 (2H, Ar-H*), 4.787 (2H, C₅H₄*), 4.358 (2H, C₅H₄*), 4.004 (5H, C₅H₅*), 3.328 (1H, SH*). EI-MS: $m/e = 293.1$ (M⁺).

2.2. Synthesis of the Fc-MPCs

The nanoparticles were synthesized following a standard procedure. Toluene solution (4 mM) of tetraoctylammonium bromide was added to a vigorously stirred 0.5 mM aqueous solution of tetrachloronic acid. The aqueous phase was quickly clear and the organic phase became orange-brown, indicating the AuCl_4^- was transferred into it. The organic phase was isolated and 1 mM toluene solution of 4-ferrocene thiophenol was added. The resulting solution was stirred for 20 min and the orange-brown solution turned pale-yellow. Then, 5 mM aqueous solution of sodium borohydride was added and the organic phase turned dark immediately. The mixture was stirred overnight and the organic phase was isolated. Toluene solvent was removed on a rotatory evaporator. The black product was washed with an excess amount of water, ethanol, and acetone to remove excess thiol, disulfide, and tetraoctylammonium bromide. All these reactions were carried out at room temperature.

2.3. Fabrication of the Fc-SAMs on a gold electrode

The 4-ferrocene thiophenol SAMs were prepared by dipping a bare gold electrode in toluene solution of 2:1 (molar ratio) 1-propanethiol and 4-ferrocene thiophenol for 24 h.

2.4. Instrumental

Initial transmission electron microscopy (TEM) was taken with a JEOL-JEM-2010 transmission electron microscope operating at 200 kV (JEOL, Japan). Samples for TEM were prepared by casting one drop of cluster solution (ca. 1 mg/5 ml) onto a standard carbon-coated (200–300 Å) formvar film on a copper grid (230 mesh). Core size distributions for at least 100 individual clusters were obtained using Scion Image Beta 4.02 (downloaded from www.scioncop.com).

The ^1H NMR spectrum of the 4-ferrocene thiophenol in deuterium DMSO solution was collected at a 400-MHz NMR spectrometer (Bruker, Swiss) and the chemical shifts were internally referenced to 2.5 ppm of deuterium DMSO. The electron impact ionization mass (EI-MS) measurement of the 4-ferrocene thiophenol (methanol solvent) was recorded on Finnigan MAT LCQ using 70-eV electron ionization. The acceleration voltage was 5 kV and the mass range was selected from 100 to 550.

The UV/vis spectra of free ferrocene, 4-ferrocene thiophenol, and the Fc-MPCs were acquired with a Cary-500 UV-vis-NIR spectrophotometer (VARIAN, USA). X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB MK II spectrometer (VG Scientific, UK) employing a monochromatic $\text{MgK}\alpha$ X-ray source ($h\nu = 1253.6$ eV). Peak positions were internally referenced to the C(1s) peak at 284.6 eV.

All voltammetric measurements were carried out on a CHI 832 electrochemical station (CHI Inc., USA) with a traditional three-electrode cell. For the Fc-MPCs, electrodes were a 0.05-cm² glassy carbon disk working electrode, an Ag/AgCl reference electrode, and a Pt coil counter electrode, while for the Fc-SAMs the working electrode was the SAMs modified gold electrode. The glassy carbon electrode and gold electrode were polished with 1-, 0.3-, and 0.05- μm alumina polishing compounds consecutively, rinsed with excess water and ethanol, and briefly sonicated prior to each experiment. For the Fc-MPCs, the electrolyte was 0.1 M Bu_4NClO_4 in a mixed solvent of (2:1 volume ratio) toluene and acetonitrile containing ca. 1 mg/10 ml of MPCs (purged

with highly pure N₂ for at least 15 min before measurement). The electrolyte for the Fc-SAMs was 0.1 M acetonitrile solution of Bu₄NClO₄.

3. Results and discussion

3.1. TEM

Figure 1 gives the TEM image of the Fc-MPCs and core size distribution. In the present study, the average core diameter of gold nanoparticles was ca. 2.5 nm. The number of gold atoms (n) in each cluster can be calculated in Eq. (1),

$$n = \frac{\rho(4/3\pi r^3)}{M_{\text{Au}}/N}, \quad (1)$$

where ρ is the density of gold, r is the radius of the gold cluster, M_{Au} is the atomic weight of gold, and N is Avogadro's number. In this experiment, each cluster contained 490 gold atoms. Assuming the core shape as a truncated octahedral, a brief calculation indicated that about 150 Au atoms were on the surface of the clusters and 80 Fc ligands in each cluster [2,10]. The calculated coverage (100% × thiolate per surface Au atom) was 53% in the present study, which was much larger than the 33% on a flat Au surface, reflecting the combination of a large proportion of edge and corner atoms on the particles and their high radius of curvature [2].

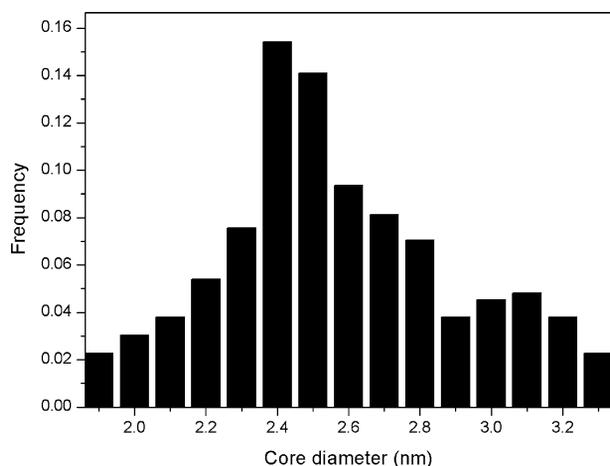
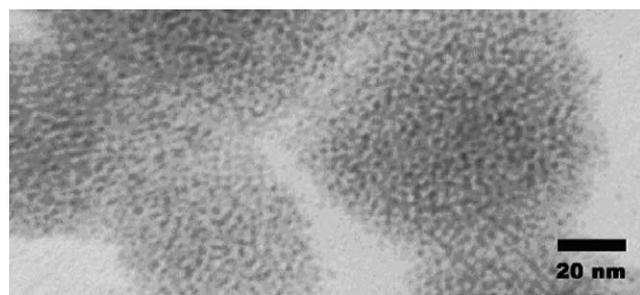


Fig. 1. TEM image of the Fc-MPCs and core size distribution.

3.2. UV/vis

The optical absorption in the UV/vis spectra of gold MPCs is a manifestation of the electronic structures of the metallic particles. That is attributed to a resonance in the collective motion of the conduction electrons in the response to an incident electromagnetic field and is called the localized surface plasmon resonance (SPR) [11].

Figure 2 shows the UV/vis spectra of free ferrocene, 4-ferrocene thiophenol, and the indicated 4-ferrocene thiophenol-capped gold nanoparticles. Free ferrocene showed a strong absorbance at 440 nm in Fig. 2a, while in Fig. 2b the absorbance of 4-ferrocene thiophenol appeared at 448 nm and the red shift was due to the conjugated structure. In Fig. 2c, the surface plasmon absorbance of the Fc-MPCs appeared at 522 nm, which was in agreement with that of alkanethiolate-MPCs (516–522 nm)². Thiophenol-MPCs [3] (ca. 6.5 nm) exhibited the SP band at 579 nm and the red shift was attributed to the aggregation of gold core. However, we argued that the conjugated structure of phenyl should also be considered. The π -conjugated structure may decrease the electron cloud density of the phenol group; hence, free electrons may hop from Au to thiophenol to decrease the free electron density of Au, resulting in the red shift of SP absorbance. In this case, the absence of red shift can be interpreted that ferrocene is an electron donor, therefore increasing the density of the electron cloud of the phenyl group, which prevents free electron hopping from gold to phenyl.

3.3. XPS

Figure 3 shows the XPS spectra of the indicated nanoparticles. Binding energies of Au(4*f*_{7/2}) and S(2*p*) appeared at 83.4 and 162.8 eV, respectively. Brust et al. [1] observed a Au(4*f*_{7/2}) binding energy of 83.8 eV in MPCs. The Au(4*f*_{7/2}) peak value in the present study tended to bulk

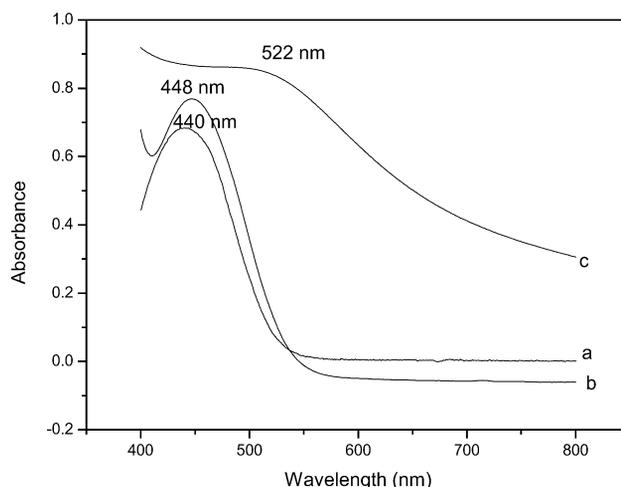


Fig. 2. UV/vis spectra of free ferrocene (a), 4-ferrocene thiophenol (b), and the Fc-MPCs (c).

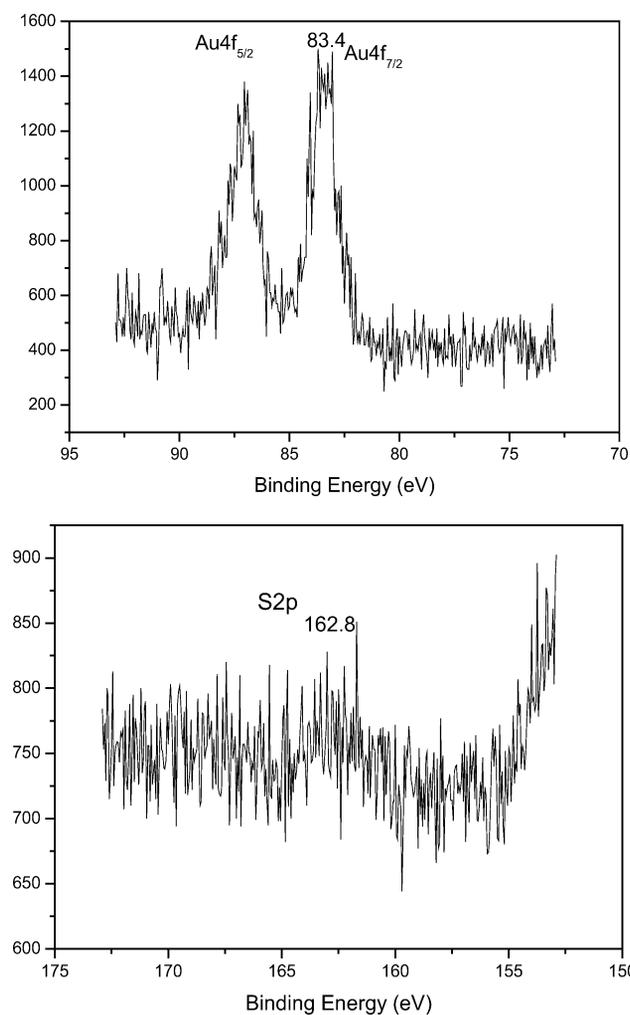


Fig. 3. XPS spectra of the Fc-MPCs showing the Au(4f_{7/2}) and S(2p) binding energies of 83.4 and 162.8 eV, respectively.

Au(0) in core with a surface layer of Au(I) [2]. Elemental S has an S(2p) binding energy of 164.2 eV [12]. The S(2p) binding energy value is 162 eV for SAMs on a flat Au surface and MPCs [13]. In this case, the S(2p) binding energy was 162.8 eV. The shift corresponded to a negative charge-bearing S absorbed to a gold core.

3.4. CVs

The Fc-MPCs could be physically absorbed onto the electrode and easily rinsed away by transfer of the electrode to fresh solvent [6,14]. Figure 4 shows an illustrative CV of the Fc-MPCs (scan rate = 50 mV/s). The single wave of CV indicates all the redox centers of gold nanoparticles appear identical. The formal potential

$$E^0 = \frac{E_{pa} + E_{pc}}{2}$$

of the Fc-MPCs was 0.5 V as the constant with scan rate (Murray's group [6] observed the formal potential of C₈SH/C₈Fc MPCs at 0.4 V) and it shifted anodically compared with 0.307 V of free ferrocene in CH₃CN solvent [15].

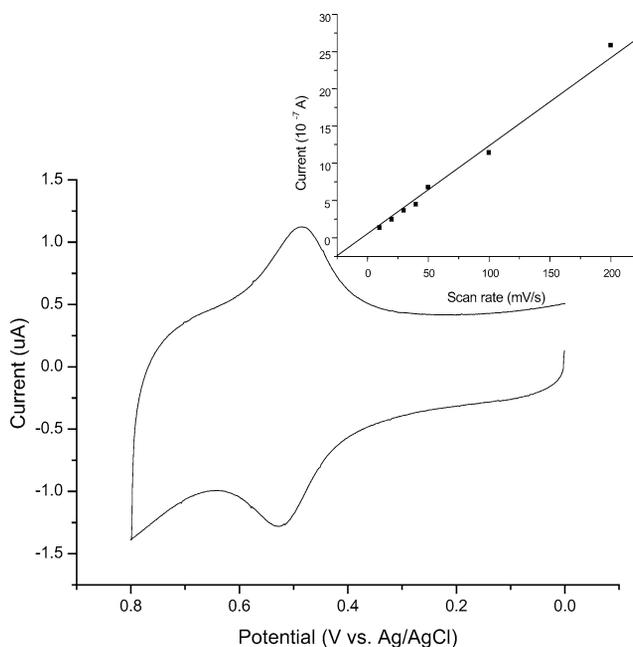


Fig. 4. Cyclic voltammogram of the Fc-MPCs at a glassy carbon electrode in (2:1 toluene:acetonitrile, volume ratio) mixed solvent. The electrolyte, 0.1 M Bu₄NClO₄. Scan rate, 50 mV/s. The inset shows the plot of the oxidation peak current (10⁻⁷ A) against the scan rate (mV/s).

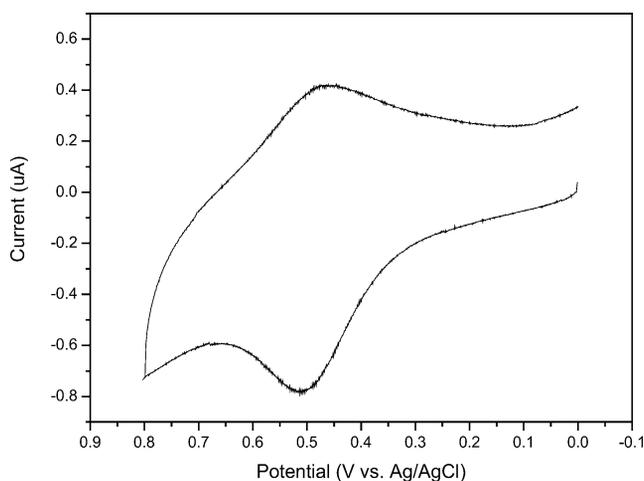


Fig. 5. Cyclic voltammogram of the Fc-SAMs at a gold electrode in acetonitrile solvent. The electrolyte, 0.1 M Bu₄NClO₄. Scan rate, 100 mV/s.

The electrochemistry behavior of the 4-ferrocene thiophenol SAMs (Fc-SAMs) was also examined and its cyclic voltammogram was shown in Fig. 5. The quasi-reversible shape indicated the CV was dictated by thermodynamic factors rather than by the rate of electron transfer [16]. The formal potential of the Fc-SAMs was 0.49 V.

SAMs on a flat gold surface with pendant ferrocenes tend to exhibit significantly more positive formal potentials than their solution analogs. This positive shift suggests that the solvation environment of the ferrocenes has a lower dielectric constant. Therefore, the similarity in the formal potential of the Fc-MPCs and the Fc-SAMs suggested an analogical solvation environment. Besides, the formal

potential shifts to substantially more positive potentials as electron-withdrawing substituents are added to the cyclopentadienyl [17]. Considering the decreased dielectric constant caused by the introduction of the phenyl ring and the π -conjugation structure, it was not surprising that the formal potential shifted more anodically compared with Murray's results. The plot of the oxidation peak current against scan rate was nicely linear as shown in the inset curve in Fig. 4, indicating that the oxidation current was dominated by the surface reaction of adsorbed Fc-MPCs.

Based on hexagonal close packing of 2.5 nm MPCs, a full coverage of MPCs monolayer should be 1.67×10^{-11} mol/cm². The absorbed ferrocene was taken to be 2.06×10^{-10} mol/cm² by integrating the charge under the oxidation wave of Fc in CV. In the present study where 80 Fc ligands were assembled onto each MPC, adsorbed MPCs can be calculated as 2.57×10^{-12} mol/cm². Therefore, the adsorption amounts to only a fraction of monolayer (ca. 15%), which was in agreement with C₈SH/C₈Fc MPCs [6].

The peak potential separation (ΔE_{peak}) of the anodic and the cathodic peaks was only 42 mV at 50 mV/s. The small ΔE_{peak} showed a fast electron transfer process of Fc-MPCs, which was caused by a multielectrons transfer from diffusion.

4. Conclusions

We synthesized 4-ferrocene thiophenol, a novel electroactive thiol with benzene moiety and ferrocene moiety, and assembled it onto gold clusters. The TEM image gave well-isolated nanoparticles with an average core diameter of ca. 2.5 nm, which corresponded to Au₄₉₀Fc₈₀. XPS revealed Au(4*f*_{7/2}) binding energy at 83.4 eV and S(2*p*) binding energy at 162.8 eV, which corresponded to mixed valence (0 and I) of gold and S (−2). The SP absorbance appeared at 522 nm in a UV/vis spectrum. Compared with thiophenol-MPCs, the lack of red shift was attributed to the electron-donating nature of ferrocene. Cyclic voltammograms revealed that the electrode reaction was controlled by the adsorbed MPCs layer. Due to a phenyl moiety linked to ferrocene, the formal potential of the Fc-MPCs shifted anodically compared with free ferrocene in solution. The

coverage of the Fc-MPCs on an electrode surface was calculated as 2.57×10^{-12} mol/cm², which was only a small fraction (15%) of monolayer.

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References

- [1] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* (1994) 801–802.
- [2] M.J. Hostetler, J.E. Wingate, C.J. Zhong, J.E. Harries, R.W. Vachet, M.R. Clark, J.D. Londono, S.J. Green, J.J. Stokes, G.D. Wignall, G.L. Glish, M.D. Porter, N.D. Evans, R.W. Murray, *Langmuir* 14 (1998) 17–30.
- [3] S.W. Chen, R.W. Murray, *Langmuir* 15 (1999) 682–689.
- [4] A. Kumar, G.M. Whitesides, *Science* 263 (1994) 60–62.
- [5] K.S. Weber, S.E. Creager, *J. Electroanal. Chem.* 485 (1998) 17–22.
- [6] S.J. Green, J.J. Stokes, M.J. Hostetler, J. Pietron, R.W. Murray, *J. Phys. Chem. B* 101 (1997) 2663–2668.
- [7] S.W. Chen, *Langmuir* 17 (2001) 6664–6668.
- [8] A. Labande, D. Astruc, *Chem. Commun.* (2000) 1007–1008.
- [9] K.S. Weber, Ph.D. dissertation, Indiana University, 1997.
- [10] R.L. Whetten, J.T. Khoury, M.M. Alvarez, S. Murthy, I. Vezmar, Z.L. Wang, P.W. Stephens, C.L. Cleveland, W.D. Luedtke, U. Landman, *Adv. Mater.* 8 (1996) 428–433.
- [11] T.R. Jensen, M.L. Duval, K.L. Kelly, A.A. Lazaride, G.C. Schatz, R.P. Van Duyne, *J. Phys. Chem. B* 103 (1999) 9846–9853.
- [12] R. Riga, J.J. Verbist, *J. Chem. Soc. Perkin Trans. 2* 10 (1983) 1545–1551.
- [13] C.D. Bain, H.A. Biebuyck, G.M. Whitesides, *Langmuir* 5 (1989) 723–727.
- [14] S.J. Green, J.J. Jeremy, J.J. Stokes, M.J. Hostetler, H. Vu, W.P. Wuelfing, R.W. Murray, *Langmuir* 14 (1998) 5612–5619.
- [15] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, New York, 1980.
- [16] H.O. Finklea, *Electroanalytical Chemistry*, Vol. 19, Marcel Dekker, New York, 1996, pp. 109–335.
- [17] T. Kondo, M. Takechi, Y. Sato, K. Uosaki, *J. Electrochem. Soc.* 381 (1995) 203–207.