Electrochemical and Spectroscopic Studies of Nitrophenyl Moieties Immobilized on Gold Nanoparticles

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Electrochemical and spectroscopic studies of gold nanoclusters passivated by a mixed monolayer of *n*-hexanethiolates (C6S) and *p*-nitrothiophenolates (NTP) were reported. Multiple copies of NTP were incorporated into the cluster monolayers by a surface exchange reaction, where the final surface composition was determined by ^{1}H NMR, and further characterized by infrared (FTIR) study. UV−vis spectroscopic study of the exchanged particles showed a surface-plasmon (SP) band position at ca. 504 nm. The blue shift of the SP energy relative to that of the (unexchanged) hexanethiolate-protected clusters, 520 nm, was attributed, in part, to the interactions between the gold cores and the nitrophenyl functional groups. Electrochemical measurements of the cluster solutions in dried CH_2Cl_2 exhibited two (quasi-)reversible voltammetric waves within the potential range of −1.0 to −1.6 V (vs Ag/AgCl), which were ascribed to the successive single-electron-transfer processes related to the nitrophenyl moieties, with the corresponding reduction products being the anion radical and dianion, respectively. In addition, in the potential range of +1.0 to −0.8 V, multiple reversible voltammetric waves were observed, which were interpreted based on the quantized capacitance charging of nanoparticle double layer. The peak spacings were found to decrease slightly compared to those without NTP exchange, corresponding to a small increase of the particle capacitance due to the more polar NTP ligands.

Introduction

Extensive research efforts have been devoted to the design, synthesis, and characterization of novel nanoscale materials, motivated, in part, by the unique properties associated with these material dimensions that are comparable to the electronic mean-free path, the so-called quantum-size effects, and the diverse application potentialities of using these materials as the structural basis for nanofabrications.[1,2] As a relatively new member of the rapidly growing nanoparticle family, mercapto-monolayer-passivated gold nanoclusters (MPCs), since the first report by Schiffrin et al,[3] have attracted particular interest. Unlike conventional colloidal particles,[2] these nanoparticles demonstrate great stability in both solution and dry forms.[4−8] In addition, electrochemical studies indicate that gold MPCs behave as diffusive nanoelectrodes in solutions, where part of the current measured is due to the charging of the MPC double layer capacitance;[9] in particular, in solutions of MPCs with relatively narrow core size dispersity, multiple reversible voltammetric waves can be observed, the so-called electrochemical ensemble Coulomb staircase charging, which were ascribed to the discrete electron charging of the MPC double layers.[10,11]

These characteristics are likely to play an important role in the MPC applications as the building blocks for the fabrications of electronic nanocircuits/nanodevices. Therefore, it is of fundamental as well as technological importance to explore new avenues toward the manipulations of nanoparticle structures and properties. Of the approaches employed, surface exchange or couple reactions are most commonly used to achieve further functionalization of the MPC molecules.[7,8] In particular, by surface-exchange reactions, various functional moieties can be incorporated into the MPC protecting monolayers where the final surface concentrations can be readily controlled by, for instance, the initial feeding ratio of the reactants, and be characterized by a variety of analytical techniques.[7,8] Different aspects of the particle properties can be anticipated to be affected by the introduction of new functional groups. For instance, particle double layer capacitance will increase with the addition of more polar ligands in the protecting monolayer, which should be

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manifested in the electrochemical quantized charging; particle optical responses might also be varied due to the enhanced electronic interactions between the functional groups and the metal cores as well as between neighboring monolayer ligands.

On the other hand, for electroactive functional groups that are attached to the particles, unique electrochemical behaviors can be studied,[9] as the particles in solutions serve as mobile carriers so that the functional moieties can be deemed as free molecules. In addition, as the particles spin rapidly and freely in solutions, the electrochemical responses measured reflect the collective contributions of all individual functional moieties residing on the same particle cores, leading to potential applications as multielectron-transfer reagents/mediators.

In this paper, we report on the electrochemical and spectroscopic studies of gold nanoclusters protected by a mixed monolayer of *n*-hexanethiolates (C6S) and *p*-nitrothiophenolates (NTP), where multiple copies of NTP were exchanged into the C6SAu MPC monolayer and the final surface concentration was controlled by the initial feeding ratio of NTP/C6S. Such effects of the incorporation of NTP on MPC as quantized capacitance charging, optical responses, as well as the electrochemical reactions of the NTP moieties will be discussed.

Experimental Section

Chemicals. Tetrahydrofuran (THF, Fisher), *p*-nitrothiophenol (NTP, Aldrich), and *n*-hexanethiol (C6SH, 96%, ACROS) were all used as received. Tetra-*n*-butylammonium perchlorate (TBAP, ACROS) was dried at 40 °C under reduced pressure overnight prior to use. Methylene chloride (CH$_2$Cl$_2$, Fisher) was freshly distilled in the presence of CaH$_2$. Water was supplied from a Barnstead Nanopure water system (18.3 MΩ).

Nanoparticle Synthesis. Hexanethiolate-protected gold nanoparticles (C6SAu MPCs) were synthesized using a literature procedure[3-5] where the synthetic solution was kept at 0 °C with a 3-fold molar excess of thiols over gold (C6S/Au = 3:1), hence the resulting particles were denoted as C6SAu (0 °C, 3×). After removal of excessive reactants and reaction side products, the particles were characterized with ^{1}H NMR where no sharp features were observed, indicating the samples were spectroscopically clean. The nanoparticles were then partially fractionated[12] with mixed solvents of toluene and ethanol (1:2 v/v), and the resulting fraction was found to consist of roughly 145 Au atoms of the core and 53 C6S chains of the monolayer.[4b,12]

Multiple copies of NTP were then incorporated into the particle monolayers by a surface exchange reaction.[7,8] In a typical reaction, 113 mg of the fractionated C6Au MPCs and 13 mg NTP (initial ratio of NTP/C6S ≈ 1:2) were codissolved in 30 mL THF under constant stirring for 1 week. The solvent was then removed at reduced pressure and the sample was rinsed thoroughly with ethanol to remove excessive NTP and displaced C6S molecules. The resulting monolayer composition was then characterized by first I$_2$ desorption of the particle monolayers and then measurements of ^{1}H NMR (Varian 300) where it was found that *on average* there were ca. 13 NTP molecules per cluster, or 25% exchange.

Spectroscopies. UV−vis study was carried out with a Unicam ATI spectrometer, with a resolution of 2 nm. The cluster solution concentration was typically 1 mg/10 mL in THF. The surface plasmon band position was determined by the 2nd-order derivative of the absorption spectra by using a commercial program (VISION).

Infrared study was performed with a Nicolet 960 FTIR spectrometer. A thick film of samples was prepared on a KBr plate by drop casting the corresponding solutions in CH$_2$Cl$_2$, which was then further dried in a nitrogen stream. Spectra were acquired from 100 scans with a resolution of 4 cm^{-1} and corrected from background.

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Electrochemistry. Electrochemical study was carried out with a BAS 100B/W Electrochemical Workstation. A gold disk electrode (area 0.022 cm²) that was sealed in a glass tubing was used as the working electrode, a platinum coil as the counter electrode, and a Ag/AgCl electrode as the reference electrode. Prior to use, the gold electrode was polished with suspended 0.05 μm alumina (Buehler), followed by extensive rinsing with dilute H$_2$SO$_4$, Nanopure water, ethanol, and acetone, consecutively. The cluster solutions were degassed with CH$_2$Cl$_2$-saturated nitrogen for at least 30 min prior to electrochemical measurements and blanketed with a N$_2$ atmosphere during the entire experimental process.

Results and Discussion

In this section, we start with the description of the electrochemical behaviors of gold nanoclusters passivated by a mixed monolayer of *n*-hexanethiolates (C6S) and *p*-nitrothiophenolates (NTP) that were obtained from a surface exchange reaction (denoted as C6NTP−MPC), including the effect of exchanged NTP on the particle electrochemical ensemble Coulomb staircase charging and the redox chemistry associated with the NTP moieties, followed by the results of spectroscopic studies.

Effects of Polar Dopants on MPC Double-Layer Charging. In solutions of MPCs with narrow core-size dispersity, electrochemical measurements exhibited multiple reversible voltammetric waves which were attributed to the quantized charging of the MPC double layers.[10,11] It has been found that these represent consecutive single-electron transfer processes with the potential spacings (ΔV) between neighboring charging peaks directly dependent upon the MPC capacitance (C$_{MPC}$), $\Delta V = e/C_{MPC}$, and $C_{MPC} = 4\pi\epsilon\epsilon_0(r/d)(r + d)$, where *e* is the electronic charge, ϵ is the monolayer dielectric constant, and *r* and *d* are the core radius and monolayer thickness.[10] Hence, one can see that C_{MPC} is sensitive to the particle core size, monolayer thickness, and dielectric properties.[10,11]

The surface exchange reaction provides a handy route toward the controlled tethering of MPC monolayer structures and properties. For instance, the introduction of rigid and polar molecules might affect the monolayer packing and the monolayer dielectric. Therefore, by introducing the more polar NTP molecules into the C6SAu MPC protecting monolayers, it is anticipated that the MPC capacitance will be varied, demonstrated by the potential spacing of the charging features. Figures 1 and 2 show the cyclic (A, CV) and differential pulse voltammograms (B, DPV) of the fractionated C6SAu MPC without and with NTP exchange in CH$_2$Cl$_2$ containing 0.1 M TBAP, where one can see that without NTP exchange, the usual features of electrochemical Coulomb staircase charging can be observed within the wide potential range of −1.8 to +1.0 V, better resolved by DPV (Figure 1). With multiple copies of NTP exchanged into the C6SAu MPC monolayers, the Coulomb staircase charging features, within the potential range of −0.8 to +0.4 V, appear to be also quite well-defined (Figure 2, right panels). However, there appears to be a slight difference of the potential separations between neighboring charging peaks in the presence and absence of NTP. The peak spacing was found to be about 0.22 V for C6NTP particles (Figure 2B, right panel), and the corresponding MPC capacitance $C_{MPC} = 0.73$ aF. For comparison, the same batch of MPCs without NTP exchange exhibited a peak spacing of about 0.26 V (Figure 1), corresponding to MPC capacitance of about 0.61 aF (here it should be noted that the C6SAu MPCs studied here were only partially fractionated, therefore the MPC capacitance is somewhat greater than that evaluated from monodisperse 145-Au core particles reported previously[10]). Assuming that the monolayer thickness was effectively
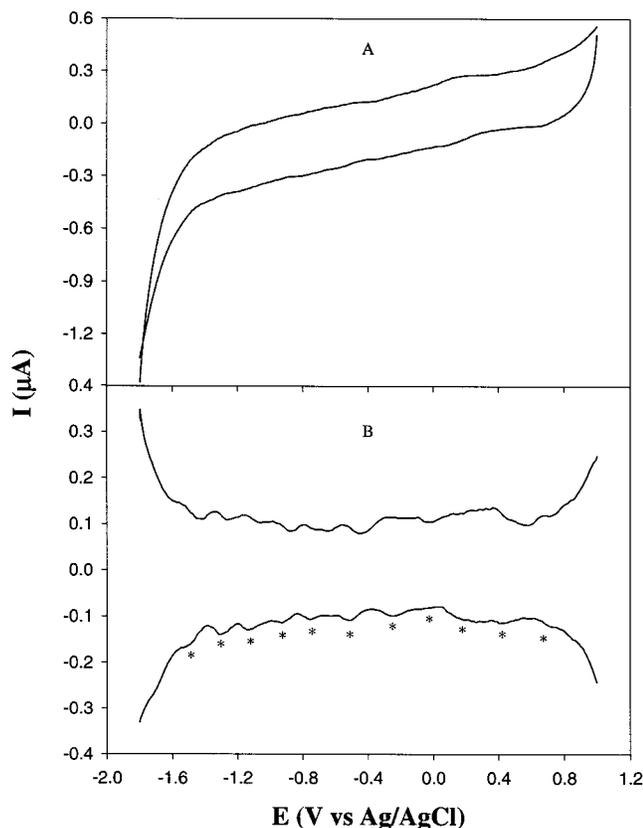
Figure 1. Cyclic (A, CV) and differential pulse voltammograms (B, DPV) of C6Au nanoparticles ca. 10 μM in CH$_2$Cl$_2$ containing 0.1 M TBAP. (A). Potential sweep rates 100 mV/s; (B). Sweep rate 10 mV/s, pulse amplitude 50 mV, pulse width 50 ms, sample width 17 ms, pulse period 200 ms. Charging peaks are identified with asterisks.
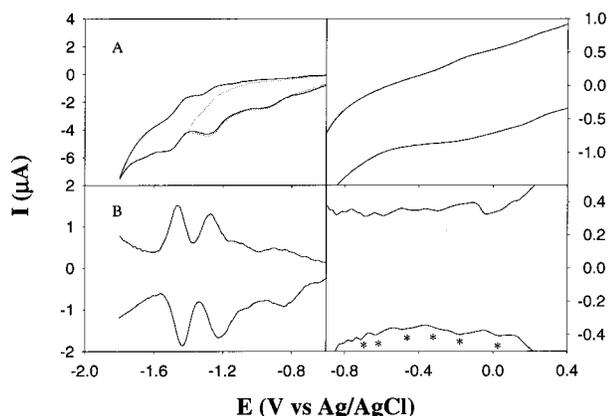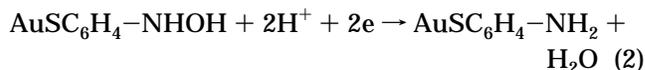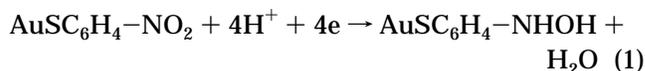

Figure 2. Cyclic (A, left panel, CV) and differential pulse voltammograms (B, right panel, DPV) of C6NTP−Au nanoparticles ca. 14 μM in dried CH$_2$Cl$_2$ containing 0.1 M TBAP at a gold electrode (0.022 cm^2). (A). Potential sweep rates 100 mV/s; (B). Sweep rate 10 mV/s, pulse amplitude 40 mV, pulse width 50 ms, sample width 17 ms, pulse period 200 ms. Charging peaks are identified with asterisks.

unchanged, this variation of MPC capacitance reflects roughly a 20% increase of the monolayer dielectric constant after NTP exchange.

When more NTP molecules were introduced into the MPC monolayers by increasing the initial ratios of NTP/C6S for the exchange reactions, for instance, 50% or even 100% exchange, only featureless responses were found (not shown). This is consistent with previous theoretical

simulations which showed that, with the increase of MPC capacitance (C_{MPC}), the detection of small ΔV became difficult.[10c]

Electrochemistry of the Nitrophenyl Moiety. The electrochemistry of *p*-nitrothiophenol has been mostly confined to self-assembled monolayers on (flat) electrode surfaces.[13] The emergence of soluble nanoparticles provides a mobile basis where the NTP molecules can be incorporated into the 3-dimensional monolayers, allowing one to probe the electron-transfer characteristics in the solution phase. It should be noted that the electrochemical reaction mechanism of nitrophenyl derivatives, in general, is rather complicated.[13,14] The reaction pathways have been found to be dependent upon a variety of factors, including the specific substituents on the aromatic ring, electrolyte ions, solvent media, acidic impurities, as well as physical state of the nitrophenyl derivatives, i.e., adsorbed on the electrode surface or in the bulk solution.[14] Previous electrochemical studies of NTP monolayers adsorbed on gold electrode surfaces have established that the redox chemistry associated with the nitro moiety typically involves two *irreversible* reduction processes and the exact reaction mechanism is very sensitive to the solvent media.[13] For instance, in acidic aqueous media, it has been found that the reduction of surface-immobilized NTP is rather complex, where typically the nitro moieties undergo a 6-e reduction process to form −NH$_2$.[13,14] The reaction process can be summarized into two steps below

$$\text{AuSC}_6\text{H}_4-\text{NO}_2 + 4\text{H}^+ + 4\text{e} \rightarrow \text{AuSC}_6\text{H}_4-\text{NHOH} + \text{H}_2\text{O} \quad (1)$$

$$\text{AuSC}_6\text{H}_4-\text{NHOH} + 2\text{H}^+ + 2\text{e} \rightarrow \text{AuSC}_6\text{H}_4-\text{NH}_2 + \text{H}_2\text{O} \quad (2)$$

where the formal potentials of the reduction reactions (typically within the potential range of −0.6 and −1.2 V) were found to be sensitive to solution pH, and no apparent anodic return waves were found.[13,14] In aprotic media, however, the surface-immobilized NTP exhibited only a featureless response even in a much bigger potential range (not shown), which might be ascribed to the redox potentials that are more negative than the NTP desorption potential from the gold electrode surface. This indicates that the reaction mechanism differs rather significantly in aqueous and organic media.

For nitrophenyl derivatives that are *dissolved* in aprotic solutions, typically two pairs of rather well-defined and reversible voltammetric waves can be observed, corresponding to the successive single-electron-transfer processes that involve the formation of radical anions and dianions,[14] as shown below

$$\text{aryl-NO}_2 + \text{e} \leftrightarrow \text{aryl-NO}_2^{\bullet-} \quad (3)$$

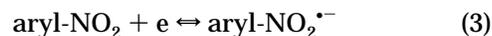$$\text{aryl-NO}_2^{\bullet-} + \text{e} \leftrightarrow \text{aryl-NO}_2^{2-} \quad (4)$$

Figure 2 (left panels) shows that, for C6NTP Au MPCs, within the potential range of −1.0 to −1.8 V, two pairs of rather well-defined voltammetric waves can be seen in the CV and DPV measurements with formal potentials of

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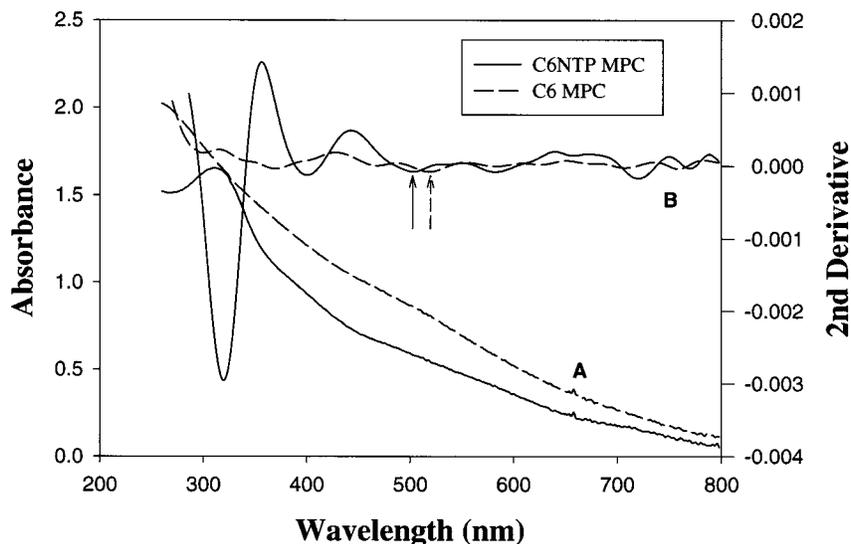
Figure 3. UV−Vis spectra (A) and the corresponding 2nd-order derivatives (B) of C6Au and C6NTP−Au nanoparticles at ca. 0.1 mg/mL in THF.

−1.25 and −1.45 V, respectively. The peak splittings (ΔE_p) are typically smaller than 40 mV and the ratios of the cathodic and anodic peak currents are close to unity, indicating that they are both (quasi-)reversible processes; whereas for C6SAu MPCs, in the same potential range, the features observed are, again, ascribed to the quantized capacitance charging (Figure 1). The electrochemical responses observed with C6NTP Au particles at the negative potential regime (−1.0 to −2.0 V) might be, therefore, ascribed to the redox behaviors of the nitrophenyl moieties (eqs 3 and 4), which, akin to ω-ferrocenated MPCs,[9] reflect the collective contributions from all the particle-bound NTP moieties. A crude wave-shape analysis based on microelectrode voltammetry (see Supporting Information) showed a slope of about 73 mV for both waves, somewhat greater than the predicted value of 59 mV. Nonetheless, it suggests that the particle-bound NTP moieties react by 13 successive 1-electron reactions. The broad wave at −0.82 V, which appears to be irreversible, might be attributed to some solution impurities (e.g., trace oxygen).

It should be noted that the above electrochemical features were observed only with dried CH_2Cl_2 that was freshly distilled in the presence of CaH_2. In the case that acidic aqueous impurities were not removed, the electrochemical responses were more complicated. For instance, CV and DPV diagrams of the same batch of particles in as-received CH_2Cl_2 and TBAP depicted a new pair of (quasi-) reversible waves at a more negative potential (−1.63 V), in addition to the two waves at −1.25 and −1.45 V and the broad cathodic wave at −0.82 V (not shown). This new wave (−1.63 V) appeared to involve a multi-electron-transfer process, which could result from side reactions caused by the presence of trace acidic impurities (see eqs 1 and 2 above).[14]

Spectroscopic Studies. Particles on the nanoscale exhibit unique optical responses within the UV−visible region, where the absorbance shows an exponential decay with decreasing photon energy (the so-called Mie scattering) onto which a surface plasmon resonance band, specific for the particle materials, is superimposed.[15] The surface plasmon energy and intensity have been found to be sensitive to a number of factors, including particle size, shape, immediate surrounding media, etc.[15] For alkanethiolate- or arenethiolate-protected gold nanoparticles (1 to 5 nm in diameter), the surface plasmon band was typically found at 520 nm, virtually independent of the monolayer structures as well as the solvent media.[4,5,11] However, by introducing electron-donating or withdrawing functional groups to the aryl moieties, it is speculated that one might be able to vary the particle electronic energy due to the enhanced electrostatic interactions between the monolayer π-electrons and the particle core 5d electrons, which can then be manifested optically. For instance, gold particles protected by a *p*-hydroxythiophenolate monolayer (530 nm) demonstrated a red shift compared to that of alkanethiolate/arenethiolate counterparts.[16] Figure 3A shows the UV−vis spectra of C6SAu and C6NTP Au particles, where a weak surface-plasmon band can be found, from the 2nd-order derivatives of the absorption spectra (Figure 3B), at ca. 520 nm for C6SAu particles while for C6NTP Au particles, at ca. 504 nm. In addition, with more NTP exchanged into the MPC monolayers, the surface plasmon band shifts to an even higher energy (shorter wavelength): when ca. 50% of the C6S ligands were displaced by NTP, the resulting MPC demonstrated a surface plasmon at 502 nm; and when at close to 100% exchange, at 498 nm (spectra not shown). It should be mentioned that the phenyl moiety alone did not appear to affect the particle dielectric property.[11] Thus, this observed blue shift is most likely due to the effect of the electron-withdrawing nitro moieties, in contrast to the electron-donating hydroxy functional groups.[16] The band at ca. 320 nm is ascribed to the transition related to the nitrophenyl functional groups.

In light of these observations, the particle electronic energy and hence the optical properties might be able to be readily manipulated by, for instance, introducing varied functional groups to the *p*-substitution of the phenyl moiety with varying electron-withdrawing/-donating strength, such as halide, carbonyl, and azide. This should be important in the sensor/device development.

Vibrational spectroscopy has been used quite extensively to investigate the structures and conformations of

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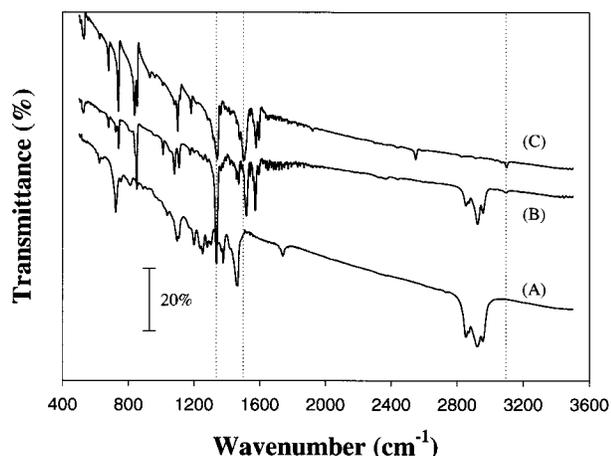(16) Chen, S. *Langmuir* **1999**, *15*, 7551.

Figure 4. FTIR spectrum of (A) C6Au MPC, (B) C6NTP−Au MPC, and (C) NTP monomers. Samples were prepared by dropcasting a thick film onto a KBr plate and dried in a nitrogen stream.

the organic monolayers on nanoparticle core surfaces.[17] The incorporation of functional moieties into the nanoparticle monolayers can, therefore, be identified by their characteristic vibrational features. Figure 4 shows the FTIR spectra of the particles before (A) and after (B) NTP exchange; also shown is the spectrum for NTP monomers (C). One can see that the characteristic bands for the nitro moiety (symmetrical stretch at 1342 cm^{-1}, and asymmetrical stretch at 1510 cm^{-1}) are quite intense in the exchanged particles. In addition, the small band at 3095 cm^{-1} indicates the presence of aromatic C−H groups. Both features reconfirm the presence of NTP moieties in the particle protecting monolayers.

Concluding Remarks

Functionalized aromatic (*p*-nitrothiophenolate) ligands were introduced into the nanoparticle protecting monolayers, which were found to have quite significant effects on various particle properties, including particle double-layer capacitance, optical and spectroscopic responses, as well as electrochemical behaviors. Electrochemical mea-

surements of the nitrophenyl moieties exhibited two (quasi-)reversible voltammetric waves involving single-electron transfer, which were found to be sensitive to the solution media. Effects of the electron-withdrawing nitro moieties on particle optical responses appeared to be consistent with earlier studies with electron-donating hydroxy groups. It is, therefore, speculated that by introducing varying functionalized aromatic groups that show different electron-withdrawing/-donating strength (e.g., X−C$_6$H$_4$−SH, X = halide, carbonyl, etc.) into the particle monolayers, one might be able to achieve molecular-level manipulation of the particle properties. This should be of great interest and importance especially in sensor/device development.

In addition, recently White *et al.*[18] showed that in the presence of an external magnetic field, nitrobenzene exhibited a significant increase of the cathodic current, which was attributed to the enhanced mass transfer resulting from the interaction between the reaction intermediates (anion radicals) and the magnetic field, the so-called electrogenerated magnetic force. Therefore, in the case of NTP-doped MPCs, similar effects are anticipated, where a different extent of surface exchange (i.e., varied surface concentration of NTP) might be differentiated in the magnetic field. On the other hand, organized assemblies of nanoparticles might be constructed by magnetic alignment.[19]

Supporting Information Available: Cyclic voltammogram of C6NTP−Au nanoparticles ca. 14 μM in dried CH$_2$Cl$_2$ containing 0.1 M TBAP at a Pt microelectrode (dia. 10 μm); sweep rate 10 mV/s. This material is available free of charge via the Internet at http://pubs.acs.org.

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