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Langmuir monolayers of gold nanoparticles: from ohmic to rectifying charge transfer

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Abstract

The lateral electrical/electronic conductivity of alkanethiolate-protected gold nanoparticles was evaluated at the air/water interface by using the Langmuir method. For particles with short protecting monolayers (C4Au and C5Au), the current–voltage profiles exhibited ohmic behaviors with conductivity several orders of magnitude smaller than that of bulk gold. The conductivity is found to decrease exponentially with increasing interparticle spacing. This is interpreted on the basis of electron tunneling/hopping between neighboring particles where the tunneling coefficient (β) is found around $0.5\,\text{Å}^{-1}$. With longer alkyl protecting layers (C6 and above), the nanoparticle monolayers demonstrated rectifying charge-transfer characters. This transition from ohmic to diode-like responses can be attributable to the nanocomposite structure of the particle molecules, where the chemical nature of the core and the protecting monolayers, along with the interparticle environment and ordering, are found to play an important role in regulating the electrical/electronic properties of the nanoassemblies.
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1. Introduction

It has been rather well documented that nanosized particle molecules exhibit unique electrical/electronic properties that differ significantly from those of the constituent atoms and bulk materials [1]. For metal nanoparticles passivated by an organic monolayer, the resulting electrical properties can be tailored by the combined effects of the conductive metal cores as well as the insulating organic shells; and the collective properties of their organized assemblies are found to be determined by the size, shape, specific environmental fluctuation as well as interparticle interactions [2]. For instance, Heath and co-workers [3] studied

the electrical characteristics of a Langmuir monolayer of alkanethiolate-protected silver (AgSR) nanoparticles (diameter 2.7 nm) at the air/water interface by examining the corresponding linear and nonlinear ($\chi^{(2)}$) optical responses and observed a transition from insulators to conductors when the interparticle spacing was squeezed from 12 to ~5 Å. Using scanning electrochemical microscopy (SECM), Bard and coworkers [4] observed a similar metal/insulator transition of AgSR nanoparticles at the air/water interface by monitoring the feedback of the current responses at varied surface pressures. Nanoparticle electronic conductivity properties have also been probed more directly by measuring the current–potential responses of their Langmuir–Blodgett thin films [5,6] as well as dropcast thick films [7,8] deposited onto electrode surfaces. Interestingly, in these studies, typically only

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ohmic behaviors were found with linear I–V profiles; however, when the particle core size was sufficiently small, nonlinear responses might be observed, which was ascribed to the Coulomb blockade effects. In these studies, the energetics as well as kinetics of the associated charge-transfer processes were evaluated, for instance, by virtue of their temperature dependence.
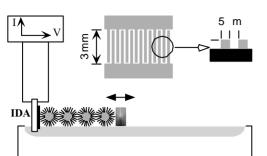
Langmuir monolayers of nanoparticles offer distinct advantages over dropcast thick films in that the interparticle structure can be well defined by the precise mechanical compression at the air/water interface (and hence the interparticle spacing). Also by carrying out the measurements directly at the air/water interface, one can maintain the structural integrity of the nanoparticle monolayers, thus providing a more unambiguous correlation between the particle structures and properties [2,3]. This is in contrast to substrate-supported Langmuir–Blodgett thin films which typically lack long-term stability [3]. So far, a large amount of work has been carried out with Ag nanoparticles [2–5], partly because of the relative ease of obtaining highly monodisperse and stable Ag nanoparticles. Only a small number of studies have been reported on the electronic conductivity of gold nanoparticle monolayers on the water surface. For instance, Majda and coworkers [9] used a microband electrode to directly measure the I–V response of a monolayer of alkanethiolate-passivated gold nanoparticles at the air/water interface. However, they observed conventional ohmic characters with only negligible electronic conductivity even at the most compressed state of the nanoparticle monolayers. This might be because the particles used in their study were quite polydisperse in size and shape and consequently long-range order was not formed, as it has been found previously that disordered close-packed nanoparticle assemblies exhibit insulating characters due to Anderson-type disordering [2].

In this report, using highly monodisperse gold nanoparticles (2 nm in diameter) and alkyl spacers of varied chainlengths (C4 to C10), we carefully examine the charge-transfer chemistry of their Langmuir monolayers at the air/water interface. Interestingly, rectified electron-transfer is generally observed even at relatively low electrode potentials for nanoparticles passivated with an alkanethiolate monolayer longer than hexanethiolate (C6); whereas for shorter chainlengths (e.g. C4 and C5), their behaviors are far more

sensitive to the interparticle distance, exhibiting linear ohmic behaviors with higher conductivity at more compressed states. The overall results demonstrate a transition of the particle monolayer (lateral) conductivity from that characteristic of semiconductors (rectified charging) to that of conductors (linear or ohmic). This transition is interpreted by the variation of interparticle electronic coupling interactions which can be manipulated by the interparticle separation as well as dielectric properties. The disparity of this research from previous studies [9] might be, at least in part, ascribed to the ordered structure of the particle monolayers originating from the low dispersity of their size and shape [2].

2. Experimental section

In a typical experiment, alkanethiolate-protected gold (C_nAu with n denoting the number of carbon of the alkyl chains) nanoparticles were synthesized by the Brust protocol [10]. The particle size dispersity was then reduced by the fractional precipitation method [11]. These different fractions of particles were then thermally annealed by refluxing in toluene for 4–8 h, [12] resulting in highly monodisperse particle core size and spherical shape of the particle molecules. The particle core sizes were determined by transmission electron microscopic (TEM, Hitachi H7100 at 100 kV operation voltage) measurements [12]. One fractionated batch of Au particles exhibited a diameter of 2 nm with less than 10% dispersity. These particles were used in the subsequent conductivity measurements. Experimentally, the particles were first dissolved in hexane at a concentration of 1 mg/ml (corresponding to roughly 14 μM), and a typical aliquot of 150 μl was spread dropwise by a Hamilton microliter syringe onto the water (>18 MΩ) subphase surface of a Langmuir–Blodgett trough (NIMA 611D) which was equipped with a Welhelmy plate as the surface-pressure sensor. At least 20 min was allowed for solvent evaporation and between compression cycles. The typical compression speed was 20 cm^2/min (corresponding approximately to 1.6 nm^2 per particle per min).

The corresponding electrical conductivity was then examined by applying a dc potential bias to the two leads of a gold interdigitated array (IDA) electrode

Scheme 1. Schematic setup of the electrical conductivity measurements of nanoparticle Langmuir monolayers. Inset shows the dimensions of the interdigitatd array (IDA) electrode.

(ABTECH Scientific) which was aligned vertically at the air|water interface (Scheme 1) and measuring the resulting current responses at ambient temperature with a slow potential scan rate of 10 mV/s (BAS 100 BW Electrochemical Workstation). The IDA electrodes consist of 25 pairs of gold fingers ($L \times W \times H = 3\,mm \times 5\,\mu m \times 5\,\mu m$) with a 5 μm gap between neighboring fingers (Scheme 1 inset), which were deposited on a silicon substrate surface. The electrode was first incubated in an ethanolic solution of 1 mM

n-butanethiol for one hour to render the gold finger surfaces hydrophobic and thus enhance contact between the electrode and the particles, prior to being positioned perpendicularly at the air/water interface for the conductivity measurements (Scheme 1).

3. Results and discussion

A representative surface pressure (π)–area (A) isotherm is shown in Fig. 1 for *n*-butanethiolate-protected gold (C4Au) nanoparticles, similar to those observed previously [13]. One can see that when the area is greater than 6.8 nm² per particle, the surface pressure is practically zero, indicating a (two-dimensional) gas-like state of the nanoparticle molecules; whereas at smaller areas, the surface pressure starts to increase sharply. This take-off area of 6.8 nm² per particle corresponds to a center-to-center interparticle distance of 2.8 nm (by assuming a hexagonal close-packed structure, [13] Fig. 1 inset). One might note that the physical diameter of the nanoparticle molecules (D) is ∼3.0 nm, which equals to the particle core size (2 nm) plus two fully extended butanethiolate chains (0.51 nm each calculated by
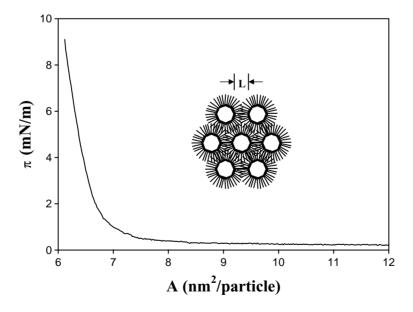

Fig. 1. Surface pressure (π)–area (A) isotherm of the Langmuir monolayer of *n*-butanethiolate-protected gold (C4Au) nanoparticles (diameter 2 nm). Inset shows the schematic particle assemblies on the water surface (L denotes the edge-to-edge distance between neighboring particles).

Hyperchem®). This indicates at this surface area intercalation of the protecting alkanethiolate ligands starts to occur.

Fig. 2A shows the *I–V* responses of a monolayer of C4Au nanoparticles at varied interparticle spacings (edge-to-edge spacing (*L*) shown as figure legends; Fig. 1 inset) at the air|water interface. One can see that, in comparison to the control experiment in the absence of the nanoparticle monolayers ("blank"), the currents measured are substantially greater, and increase with decreasing interparticle spacings (corresponding to an increasing degree of ligand intercalation; vide ante). In general, the voltammetric profiles behave linearly, indicating ohmic characters.
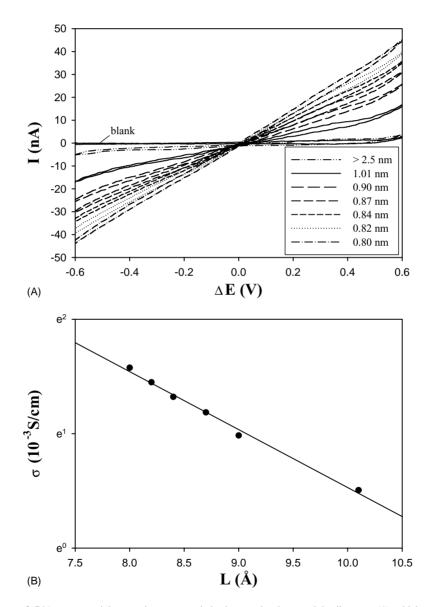

Fig. 2. (A) *I–V* curves of C4Au nanoparticle monolayers at varied edge-to-edge interparticle distances (*L*) which were shown in figure legends. Potential scan rates 10 mV/s. (B) Variation of electronic conductivity with the interparticle spacings. Symbols are experimental data and line is the linear regression.

This seems to indicate strong coupling between neighboring particles due to the close proximity of the particle molecules. The conductivity evaluated from the slope is of the order of 10^{-3} S/cm (Fig. 2B) which is about eight orders of magnitude smaller than that for bulk gold (4.43×10^5 S/cm at ambient temperature [14]). Nonetheless, the result is comparable to those of (micrometer) thick films [7,8,15] of gold nanoparticles of similar core sizes and protecting alkanethiolate monolayers (the conductivity was found to range from 10^{-3} to 10^{-9} S/cm with the chainlengths of the alkanethiolate protecting layers increasing from C4 to C16 with similar core size). In other studies using silver nanoparticles [3,5], the electrical conductivity is found to be on the order of 10^{-6} to 10^{-7} S/cm. All these experimental observations suggest semiconductor electrical characteristics of the nanoparticle materials due to their nanoscale organic/inorganic composite structures. In addition, the conductivity decreases exponentially with increasing interparticle distance (Fig. 2B), with a decay coefficient (β) of about 0.5 Å^{-1}. It should be noted that the electronic conductivity of a nanoparticle molecule is governed by at least two factors, the cores and the protecting monolayers, which are reflected by the effects of Coulomb blockade and electron tunneling, respectively [8a]. In the present case, the bandgap structure of the particle molecules is anticipated to be rather insignificant due to the relatively large particle core size; [11b] thus, the collective responses of nanoparticle assemblies are interpreted on the basis of electron tunneling between neighboring particles, [7,8] where the β value reflects the dependency of the (interparticle) electron transfer on the tunneling barriers.

One can see that the present β value is somewhat smaller than that typically found for through-chain electron tunneling of saturated alkyl spacers (0.8–1.4 Å^{-1}) [16]. This might be ascribed to the cross-chain contribution in particle Langmuir monolayers due to ligand intercalation, as it has been found that through-chain tunneling is more favorable than the cross-chain (through-space) mechanism [16b]. This variation of charge-transfer mechanism might also account for the discrepancy between the present experimental results and earlier data with nanoparticle dropcast thick films ($\beta = 0.8$ Å^{-1}) [7], where particle structural inhomogeneity in solid state might give rise to unblocked paths leading to more efficient electron

transfer and hence diminish the effects of cross-chain tunneling [7].

For C5Au particles of same core size, the voltammetric responses were quite similar. Fig. 3A shows the corresponding I–V curves at varied interparticle spacings. One can see that the current scales were comparable to those with C4Au particles at similar interparticle distance (see Fig. 2A). However, one might notice that the linearity of the I–V curves was not as good as that with C4Au particles, as there appears to be a "translocation" of currents around $\Delta E = 0$ V (the overall response appears akin to a sigmoidal transition). This indicates a slight deviation from the ohmic characters, in comparison to the case with C4Au particles observed above despite the fact that the interparticle distance is quite similar. Fig. 3B depicts the variation of the particle monolayer conductivity with interparticle spacings which is again found of the order of 10^{-3} S/cm (certainly, since the I–V curves are not strictly linear, the conductivity evaluated from their linear regressions will be only an approximation). One can see that at $L < 10$ Å, the particle conductivity increases exponentially with decreasing L whereas at longer spacings, the conductivity appears to be invariant of the interparticle distance. These observations seem to suggest that the controlling mechanism for electron transfer might be different depending upon the interparticle spacing and hence degree of ligand intercalation. For instance, in the transition of Ag nanoparticles from insulators to conductors [3], the charge transfer mechanism was found to change from hopping to tunneling to metallic transport with decreasing interparticle spacings.

In addition, the observed difference in I–V responses between C4Au and C5Au particles even at similar interparticle spacings seems to suggest that the lateral electron transfer of nanoparticle monolayers is also regulated by some other factors in addition to the interparticle separation [3]. One plausible explanation may be related to the electronic coupling between adjacent particle molecules [2,3], where the interactions are also sensitive to the organic media surrounding the particle molecules (in addition to interparticle spacing), as further demonstrated below with particles protected by alkanethiolate monolayers of longer chainlegths.

For gold particles with longer alkanethiolate protecting monolayers, the voltammetric responses
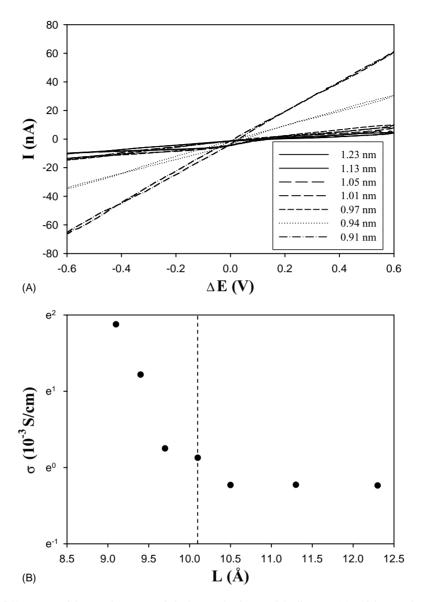
Fig. 3. *I–V* curves of C5Au nanoparticle monolayers at varied edge-to-edge interparticle distances (*L*) which were shown in figure legends. Potential scan rate 10 mV/s. (B) Variation of electronic conductivity with the interparticle spacings.

change quite drastically. Fig. 4 shows the *I–V* curves for C6Au to C10 Au particles with the interparticle spacing (*L*) roughly equal to a respective single chainlength (the corresponding chainlengths of these alkanethiolate ligands are calculated by Hyperchem®: C6, 0.78 nm; C8, 1.02 nm; C9, 1.14 nm; C10, 1.28 nm). First, one can see that the voltammetric currents are generally much smaller than those with shorter pro-

tecting monolayers (see Figs. 2 and 3) and decrease with increasing chainlength. Second, the sigmoidal *I–V* curves exhibit a rectifying feature, and the nonlinearity (current translocation) is much more significant than that with C5Au particles (Fig. 3A). For instance, for C6Au particles, the current at $\Delta E < +0.2$ V is substantially larger than that at $\Delta E > +0.2$ V. Similar observations can also be found with C8Au and C9Au
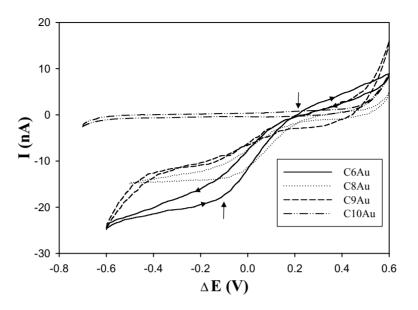
Fig. 4. *I–V* curves of varied nanoparticle monolayers with the interparticle distance (*L*) roughly equal to a single chainlength of the corresponding protecting monolayer. Potential scan rate 10 mV/s. Arrows indicate the current onsets.

particles where their turn-on bias is also found at about +0.2 V (Fig. 4). For C10 particles, the voltammetric response is somewhat different. Within the potential range of −0.6 to +0.5 V the current is essentially zero beyond which the current starts to increase rapidly, a behavior akin to Coulomb blockade. Rectifying charge transfer has also been observed previously with nanowires involving metal-semiconductor heterojunctions [17], as well as nanoparticle organized ensembles sandwiched between dissimilar cathodes and anodes [6]. In these earlier cases [6,17], the rectifying features were accounted for by the charge injection at one of the interfaces. In the present system involving symmetrical experimental setup of the IDA fingers and the nanoparticle monolayers, the observations of asymmetrical voltammetric behaviors are rather surprising. While the origin of this asymmetric *I–V* character is not clear at this point, one possible explanation is that the current step (indicated by two arrows in Fig. 4) might reflect the collective re-alignment of nanoparticle dipoles by the applied external electric field, as the particles are strongly dipole-coupled to one another [4]. This dipole re-arrangement appears to initiate at +0.2 V and results in an enhancement of the corresponding voltammetric currents, equivalent to (double-layer) capacitive charging. Additionally,

there appears to be a hysteresis of the current response (C6Au to C9Au particles, Fig. 4), which seems to imply a memory effect of the nanoparticle thin films. Again, these unique charge-transfer behaviors can be attributable to the interfacial dipole properties of the nanoparticle molecules where the alignment of the nanoparticle dipoles generated during electron transfer process might not be readily switched by the bias polarity [17,18].

From the above studies (Figs. 2–4), one can see that even at the same interparticle spacing, the *I–V* responses still vary with particles of different molecular structures, i.e. evolving from ohmic (C4Au and C5Au) to rectifying (C6Au–C10Au) characters. This indicates that the interparticle electronic coupling interactions are dependent upon not only the physical separation but also the dielectric properties between neighboring particles. At longer interparticle distances, the electronic coupling interactions between adjacent particles become weaker and the overall nanoparticle assemblies behave more like insulators (e.g. C10Au particles). Further studies of these issues are underway.

It should be noted that with nanoparticle dropcast thick films [7,8], generally only ohmic responses were observed for all these particles even within a

much larger potential regime. This was interpreted by the availability of unblocked paths for conduction between neighboring nanoparticles in solid state. This is likely to be the major source of discrepancy in the present measurements of micrometer-sized bands of nanoparticles trapped between the IDA fingers where long-range ordering was maintained. In addition, in the present study, the current plateaus (akin to limiting currents, Fig. 4) are suspected to arise from the saturated charge transfer originating from electron tunneling/hopping between neighboring particles.

4. Concluding remarks

In summary, using interdigitated arrays (IDA) electrodes at the air/water interface, lateral electronic conductivity of nanoparticle molecules can be characterized at varied surface structures of the monolayers. Overall the electrical conductivity is a few orders of magnitude smaller than that of bulk gold but comparable to that evaluated from particle dropcast thick films. Additionally, it is found that the electrical conductivity exhibits a transition from ohmic to rectifying characters with increasing chainlengths of the particle protecting monolayers. This might be ascribed to the electronic coupling between neighboring particles which is dependent upon the interparticle distance as well as dielectric properties. These studies demonstrate that the nanoparticle electronic/electrical conductivity can be manipulated by the nanoscale composite nature of the particle molecules as well as the interparticle chemical environment. More detailed studies are currently underway to examine the effects of particle core size and chemical structures on their rectifying charge-transfer properties.

Acknowledgements

References

[1] (a) G. Schmid, Clusters and Colloids: From Theory to Applications, VCH, New York, 1994.;
(b) H. Haberland (Ed.), Clusters of Atoms and Molecules, Springer, New York, 1994.;
(c) R. Turton, The Quantum Dot: A Journey into the Future of Microelectronics, Oxford University Press, New York, 1995.

[2] F. Remacle, R.D. Levine, Chem. Phys. Chem. 2 (2001) 20, and references cited therein.

[3] G. Markovich, C.P. Collier, S.E. Henrichs, F. Remacle, R.D. Levine, J.R. Heath, Acc. Chem. Res. 32 (1999) 415, and references cited therein.

[4] B.M. Quinn, I. Prieto, S.K. Haram, A.J. Bard, J. Phys. Chem. B 105 (2001) 7474.

[5] (a) S.-H. Kim, G. Medeiros-Ribeiro, D.A.A. Ohlberg, R.S. Williams, J.R. Heath, J. Phys. Chem. B 103 (1999) 10341;
(b) J.F. Sampaio, K.C. Beverly, J.R. Heath, J. Phys. Chem. B 105 (2001) 8797.

[6] T. Cassagneau, T.E. Mallouk, J.H. Fendler, J. Am. Chem. Soc. 120 (1998) 7848.

[7] (a) W.P. Wuelfing, R.W. Murray, J. Phys. Chem. B 106 (2002) 3139;
(b) W.P. Wuelfing, S.J. Green, J.J. Pietron, D.E. Cliffel, R.W. Murray, J. Am. Chem. Soc. 122 (2000) 11465.

[8] (a) S.D. Evans, S.R. Johnson, Y.L. Cheng, T. Shen, J. Mater. Chem. 10 (2000) 183;
(b) R.C. Doty, H. Yu, C.K. Shih, B.A. Korgel, J. Phys. Chem. B 105 (2001) 8291;
(c) A.W. Snow, H. Wohltjen, Chem. Mater. 10 (1998) 947;
(d) L. Clarke, M.N. Wybourne, L.O. Brown, J.E. Hutchison, M. Yan, S.X. Cai, J.F.W. Keana, Semicond. Sci. Technol. 13 (1998) A111.

[9] W.-Y. Lee, M.J. Hostetler, R.W. Murray, M. Majda, Isr. J. Chem. 37 (1997) 213.

[10] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, J. Chem. Soc. Chem. Commun. (1994) 801.

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

[12] M.M. Maye, W. Zheng, F.L. Leibowitz, N.K. Ly, C.-J. Zhong, Langmuir 16 (2000) 490.

[13] (a) S. Chen, Adv. Mater. 12 (2000) 186;
(b) S. Chen, Langmuir 17 (2001) 2878.

[14] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 76th ed., CRC Press, New York, 1995.

[15] F.L. Leibowitz, W. Zheng, M.M. Maye, C.-J. Zhong, Anal. Chem. 71 (1999) 5076.

[16] (a) R.E. Holmlin, R. Haag, M.L. Chabinyc, R.F. Ismagilov, A.E. Cohen, A. Terfort, M.A. Rampi, G.M. Whitesides, J. Am. Chem. Soc. 123 (2001) 5075;

(b) K. Slowinski, R.V. Chamberlain, C.J. Miller, M. Majda, J. Am. Chem. Soc. 119 (1997) 11910;

(c) J.F. Smalley, S.W. Feldberg, C.E.D. Chidsey, M.R. Linford, M.D. Newton, Y. Liu, J. Phys. Chem. 99 (1995) 13141;

(d) K. Weber, L. Hockett, S.E. Creager, J. Phys. Chem. B 101 (1997) 8286.

[17] N.I. Kovtyukhova, B.R. Martin, J.K.N. Mbindyo, P.A. Smith, B. Razavi, T.S. Mayer, T.E. Mallouk, J. Phys. Chem. B 105 (2001) 8762.

[18] D. Schmeisser, O. Böhme, A. Yfantis, T. Heller, D.R. Batchelor, I. Lundstrom, A.L. Spetz, Phys. Rev. Lett. 83 (1999) 380.

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