J|A|C|S
COMMUNICATIONS

Published on Web 02/24/2006

Place Exchange Reactions of Alkyl Thiols on Gold Nanoparticles

Adil Kassam, Glen Bremner, Brad Clark, Gerardo Ulibarri, and R. Bruce Lennox*

Department of Chemistry and Centre for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke Street W, Montreal, QC H3A 2K6, Canada

Received October 18, 2005; E-mail: bruce.lennox@mcgill.ca

Place or ligand exchange reactions on gold nanoparticles (AuNPs) have been extensively used to create new functionalized NPs.[1] This reaction allows one to use a well characterized AuNP sample (e.g., C_6S-AuNP) as an entry point to a host of other AuNPs, with a range of functionalities. AuNPs with electrochemical,[2] fluorescent,[3] and bio-active[4] ligands have thus been prepared using *n*-alkylthiol−AuNPs as the starting materials. Not only is the introduction of new functionality to the NP important, but so is control of how many new ligands are on the Au core. In many situations, controlling the number of exchanged ligands is an important determinant of eventual properties. This control inevitably stems from an understanding of the kinetics and mechanism of the ligand exchange process. To date, kinetics studies have concluded that the ligand exchange process is associative (S_N2-like),[5,6] dissociative (S_N1-like),[7−9] or combinations thereof.[10] Each study has had to employ pairs of ligands, where one or both have a "label" appropriate to the analytical methodology used. Ligand pairs with quite different terminal groups have therefore been used (e.g., methyl/ferrocene,[6] methyl/methyl ester,[6] methyl/alcohol,[7] methyl/pyrene,[5] and methyl/TEMPO[8,9,11]).

In the related binary 2D SAM system, the terminal group is known to be an important determinant of the final SAM composition. If the terminal groups are quite different, the preparation solution often requires a large excess of one of the alkylthiols to produce, for instance, a 1:1 binary SAM.[12,13] Such a terminal group dependence is likely transferable to the nanoparticle system given the similarities between the 2D and 3D (i.e., NP or monolayer-protected cluster) SAMs.[14]

Recognizing the problem introduced by labeled alkylthiols, we have developed a GC product analysis method which allows one to study the alkylthiol-for-alkylthiol exchange reaction where the chains only differ in length. Briefly, the reactions were followed using a modified version of the published reaction-quench process.[6] However, to obtain accurate and reproducible results, the purification procedure was simplified. AuNPs were dissolved in toluene to yield 10 mg/mL solutions. These solutions were kept under an Ar atmosphere at 25 °C. Reactions were initiated by adding an appropriate quantity of alkylthiol via syringe injection. The reaction progress was tracked by removing 1 mL aliquots of solution and precipitating the NPs via introduction of 10 mL of ethanol. The AuNPs were separated from the supernatant containing free thiols via filtration with a fine glass frit. The quantity of unbound alkylthiols was determined by GC using a 5% phenyl dimethylsiloxane column and a FID detector. GC applied to this problem has a large dynamic range, excellent accuracy (±1.5%), and excellent reproducibility (±5%). Excellent run-to-run reproducibility of kinetic traces is observed when working with the same batch of AuNPs. However, some inter-batch variability is observed. This inter-batch variability does not alter the form of the kinetics fit (see below) but affects the value of the fitted parameter (the rate constant). To minimize this batch-to-batch variability, kinetics experiments were performed from samples of large (ca. 1 g in $HAuCl_4$) AuNP preparations. Particles were synthesized using the standard two-phase Brust−Schiffrin[15,16] synthesis using $Au:C_{10}SH:TOAB:NaBH_4$ in a 1:1:2.5:10 molar ratio. Nanoparticles were characterized by NMR (for free ligand), TEM (2.2 ± 0.2 nm), and TGA (18−21% organic content) analyses.

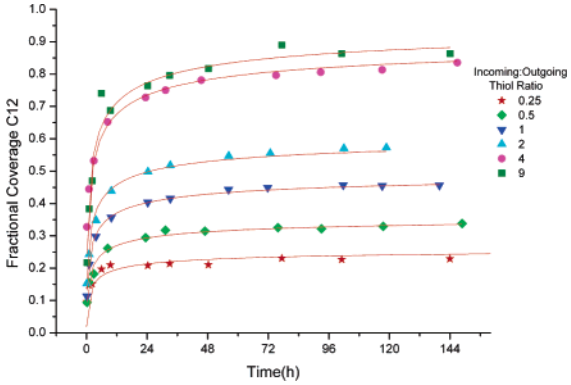

Figure 1. Time progress of reactions of $C_{12}SH$ with $C_{10}-$AuNPs at different incoming to outgoing ligand ratios. Solid lines are fits to second-order diffusion-limited Langmuir model (eq 1).

Figure 1 presents the time progress of reactions of $C_{12}SH$ with $C_{10}Au-$NP, where the (incoming ligand):(outgoing ligand) ratio ranges from 9:1 to 1:4. The reaction proceeds in a progressive, rather than discontinuous (e.g., bi- or multiphasic) manner over 100 h, and reaches a limiting value corresponding to the ligand ratio of the experiment. An excellent fit is obtained when the entire time course data are applied to a second order Langmuir diffusion-limited rate equation:[17,18]

$$\Theta(t) = \frac{Ak\sqrt{t}}{1 + k\sqrt{t}} \qquad (1)$$

A number of alternative kinetics models, including other Langmuir, first-order, and second-order models, yield either inappropriate or lesser quality fits than those to eq 1 (see Supporting Information). It is significant that the exchange/adsorption kinetics of thiols to 2D gold surfaces also adhere to simple[19,20] or diffusion-limited[21−23] Langmuir kinetics.

The values of the extent of reaction at infinite time correspond to a K_{eq} value of 0.97 ± 0.09 (Table 1). The robustness of the Langmuir kinetics fit is readily visualized in a plot where the kinetic data are normalized to one curve (Figure 2). The reaction is described by a *single* rate constant, 0.0137 ± 0.0006 ($s^{-1/2}$), and the reaction rate is independent in incoming ligand concentration (i.e., zero-order). The incoming ligand concentration only affects the extent of reaction. The rate decrease with time[6] reflects the approach to equilibrium rather than a changing rate constant.

The implications of a $K_{eq} \approx 1$ are clear. Under the reaction conditions used ($C_{12}SH$ and $C_{10}S-$AuNP, 25 °C, toluene as a

10.1021/ja057091q CCC: $33.50

Table 1. Summary of Alkylthiol Place Exchange Reactions ($C_{12}SH$ with $C_{10}Au-NP$)

incoming $C_{12}SH$: outgoing $C_{10}SH$ thiol ratio	final coverage of incoming thiol ($C_{12}SH$)[a]	predicted final coverage[b]	yield
0.27	0.23	0.21	1.08
0.49	0.34	0.33	1.00
1.06	0.46	0.52	0.88
2.12	0.57	0.68	0.84
3.95	0.84	0.80	1.05
9.56	0.86	0.91	0.95
		mean	0.97 ± 0.09

[a] Calculated from the last experimental point obtained in each reaction. [b] Final predicted coverage of the incoming $C_{12}SH$, if the replacement occurs with a 1:1 stoichiometry.

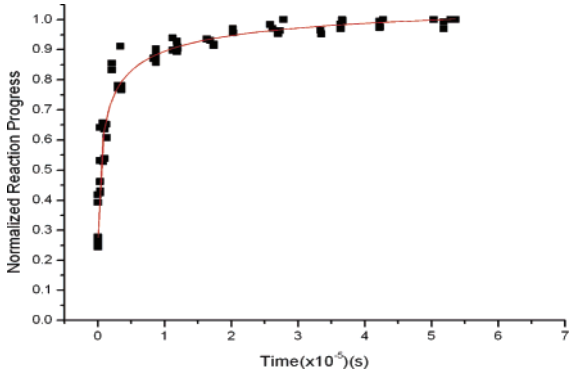

Figure 2. Normalized reaction progress for data in Figure 1. Solid line is fitted to a second-order diffusion-limited Langmuir model (eq 1). Fitting values: $A = 1.10 \pm 0.01$, $k = 0.0137 \pm 0.008$, $r^2 = 0.96$.

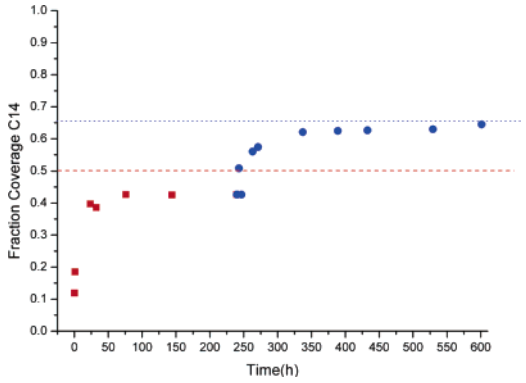

Figure 3. Place exchange reaction of C_{10}AuNP with $C_{14}SH$. After 250 h, a second equivalent of $C_{14}SH$ was added.

solvent), there is no discernible discrimination between an outgoing ligand rebinding to the NP surface and an incoming ligand binding to the NP surface. The chemical nature of the outgoing and incoming species has been postulated as being a thiyl radical,[24] thiolate,[10] or disulfide.[9] The kinetics as presented here do not, however, provide insight into these mechanistic details.

Figure 3 provides additional evidence that the extent of reaction is determined by the molar ratio of incoming to outgoing ligand. When studying the C_{10}AuNP reaction with $C_{14}SH$, we observe that addition of a second equivalent of $C_{14}SH$ to a reaction whose conversion has already reached a limiting value results in additional conversion and a new limiting value consistent with $K_{eq} \approx 1$. This is relevant to previous work, which concluded that a complete exchange of alkylthiols is not possible for particles with greater C4 chains.[6] This conclusion leads to a complex mechanism involving multiple types of binding sites on the NP, some of which are nonexchangeable. Although the data presented here do not preclude there being an interchange of ligands on the NP surface, they also do not require that there be a population of nonexchangeable ligands. The observed $K_{eq} \approx 1$ requires a large incoming:outgoing ligand ratio (>100) to establish whether complete exchange has occurred. However, the limitations of the GC method used here preclude monitoring the kinetics for an incoming:outgoing ligand ratio >10.

In summary, we have demonstrated that the place exchange reaction between $C_{10}S-Au$ NP and $C_{12}SH$ follows Langmuir diffusion kinetics. The reaction rate notably has a zero-order dependence in the incoming ligand concentration. A $K_{eq} \approx 1$ in the C_{10}/C_{12} case is observed for the reaction performed in toluene at 25 °C. With this information in hand, the opportunities and restrictions of the place exchange reaction as a preparative reaction are now clarified.

Acknowledgment. We thank NSERC (Canada), FQRNT (Quebec), and Genome Quebec for support of this research.

Supporting Information Available: Additional figures and table. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Brust, M.; Kiely, C. J. *Colloids Surf., A* **2002**, *202*, 175−186.
(2) Hostetler, M. J.; Green, S. J.; Stokes, J. J.; Murray, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 4212−4213.
(3) Demers, L. M.; Mirkin, C. A.; Mucic, R. C.; Reynolds, R. A., III; Letsinger, R. L.; Elghanian, R.; Viswanadham, G. *Anal. Chem.* **2000**, *72*, 35−41.
(4) McIntosh, C. M.; Esposito, E. A., III; Boal, A. K.; Simard, J. M.; Martin, C. T.; Rotello, V. M. *J. Am. Chem. Soc.* **2001**, *123*, 7626−7629.
(5) Montalti, M.; Prodi, L.; Zaccheroni, N.; Baxter, R.; Teobaldi, G.; Zerbetto, F. *Langmuir* **2003**, *19*, 5172−5174.
(6) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782−3789.
(7) Song, Y.; Murray, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 7096−7102.
(8) Ionita, P.; Caragheorgheopol, A.; Gilbert, B. C.; Chechik, V. *J. Am. Chem. Soc.* **2002**, *124*, 9048−9049.
(9) Ionita, P.; Caragheorgheopol, A.; Gilbert, B. C.; Chechik, V. *Langmuir* **2004**, *20*, 11536−11544.
(10) Song, Y.; Huang, T.; Murray, R. W.*J. Am. Chem. Soc.* **2003**, *125*, 11694−11701.
(11) Chechik, V. *J. Am. Chem. Soc.* **2004**, *126*, 7780−7781.
(12) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* **1992**, *8*, 13340−13346.
(13) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M.; Deutch, J. *J. Phys. Chem.* **1994**, *98*, 563−571.
(14) Badia, A.; Lennox, R. B.; Reven, L. *Acc. Chem. Res.* **2000**, *33*, 475−481.
(15) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Chem. Commun.* **1994**, 801−802.
(16) Hostetler, M. J. W.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17−30.
(17) Where A is the final fractional coverage, Θ is the fractional surface coverage of the incoming thiol, and k is the rate constant.
(18) In these experiments, we note that the rate of reaction is proportional to the surface coverage of incoming ligand and to the solution fraction of incoming ligand, both of which scale with $(1 - \Theta(t))$. This leads to the observed second-order Langmuir kinetics. Diffusion of the active species to the surface has previously been reported to be the limiting factor in 2D exchange reactions; see ref 21.
(19) Biebuyck, H. A.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1825−1831.
(20) Schessler, H. M.; Karpovich, D. S.; Blanchard, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 9645−9651.
(21) Georgiadis, R.; Peterlinz, K. P.; Peterson, A. W. *J. Am. Chem. Soc.* **2000**, *122*, 3166−3173.
(22) Yan, D.; Saunders, J. A.; Jennings, G. K. *Langmuir* **2002**, *18*, 10202−10212.
(23) Peterlinz, K. A.; Georgiadis, R. *Langmuir* **1996**, *12*, 4731−4740.
(24) Ionita, P.; Gilbert, B. C.; Chechik, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 3720−3722.

JA057091Q