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Directing the Assembly of Gold Nanoparticles with Two-Dimensional Molecular Networks

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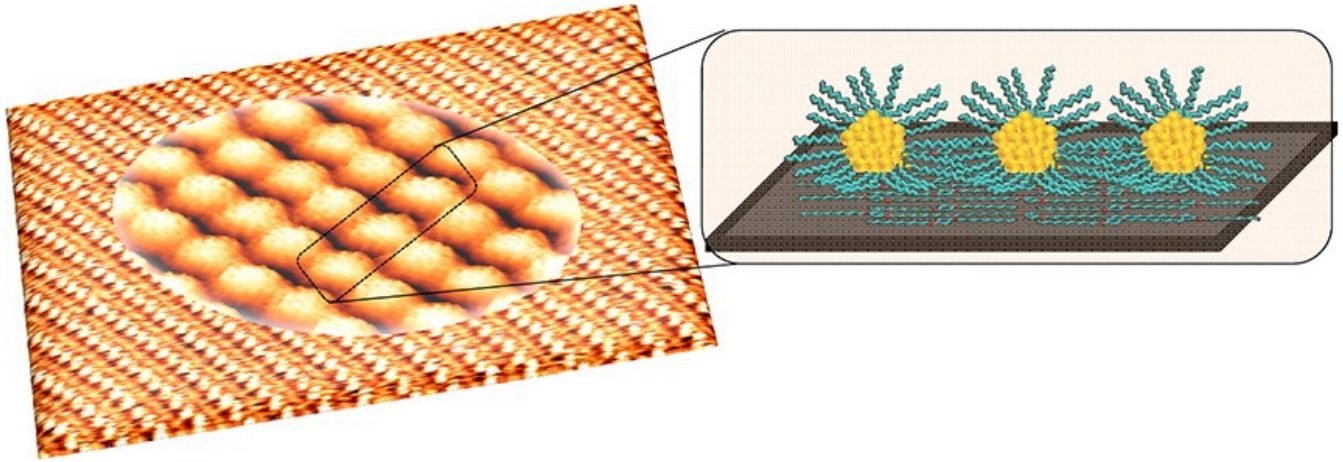
2014, 8, 2214-2222.



05-04-2014

Atanu Ghosh

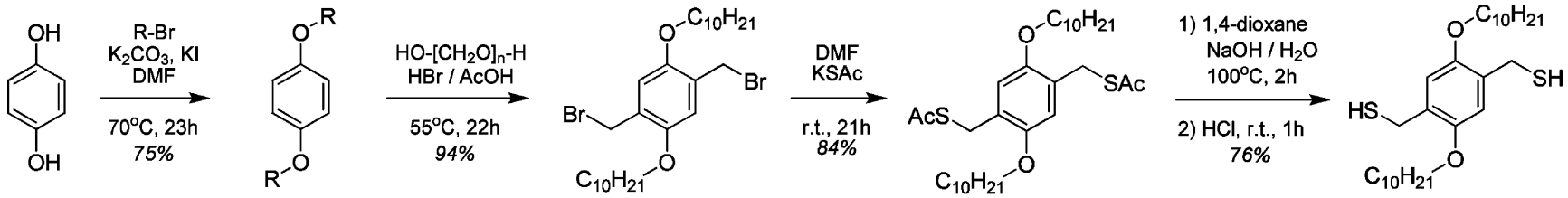
In this paper:

1. Lamellar patterns have been prepared from the adsorption of p-dialkoxybenzene derivatives on HOPG.

2. Assembly of thiol capped Au nanoparticle has been prepared using the above made template.

3. STM characterization at the liquid solid interface reveals the periodic arrangement of AuNP on top of the self-assembled molecular network (SAMN), spanning hundreds of nanometers.

4. The templating effect is based on van der Waals interactions of the alkyl chains of the SAMN and AuNP, and the assembly efficiency is greatest when these chains are of similar length.



R = $C_{10}H_{21}$: PhC10
$C_{18}H_{37}$: PhC18

PhC10-Br

PhC10-SAc

PhC10-SH

Published in: Mohamed A. Mezour; Iryna I. Perepichka; Jun Zhu; R. Bruce Lennox; Dmitrii F. Perepichka; *ACS Nano* **2014,** 8, 2214-2222.
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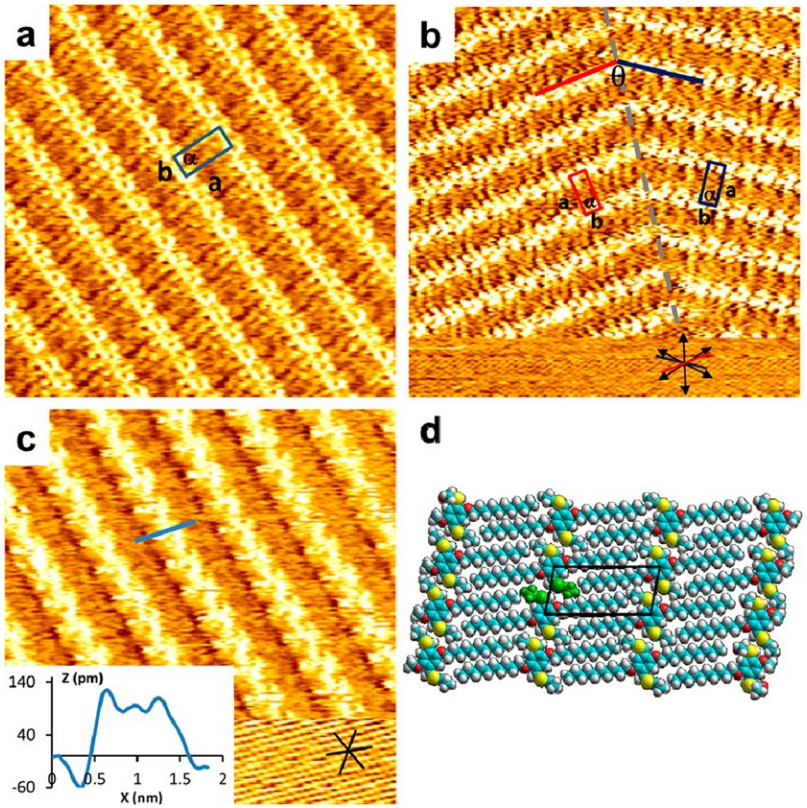

(a) Representative STM image (14 × 14 nm2; *V*b = 700 mV, *I*t = 0.2 nA) of PhC10-SAc showing the unit cell: *a* = 2.1 ± 0.1 nm; *b* = 1.0 ± 0.1 nm, α = 86 ± 1°. (b) STM image (21 × 21 nm2) showing two domains of PhC10-SAc (*V*b = 1373 mV, *I*t = 0.2 nA) simultaneously resolved with the underlying HOPG (*V*b = 50 mV, *I*t = 0.2 nA). The black arrows indicate the main crystallographic axes of graphite ⟨−1100⟩. The red and blue lines indicate the lamellar directions. (c) Smaller scale STM image (12 × 12 nm2; *V*b = 700 mV, *I*t = 0.09 nA (for SAMN) and *V*b = 25 mV, *I*t = 0.09 nA for HOPG) reveals out-of-plane substituents in the benzene ring (inset: cross-sectional profile corresponding to blue line). (d) Molecular mechanics model of the 2D packing of PhC10-SAc on a graphene sheet; optimized unit cell parameters: *a* = 2.1 nm; *b* = 0.93 nm, α = 81°. The green color identifies the upright position of the acetylthiol group.

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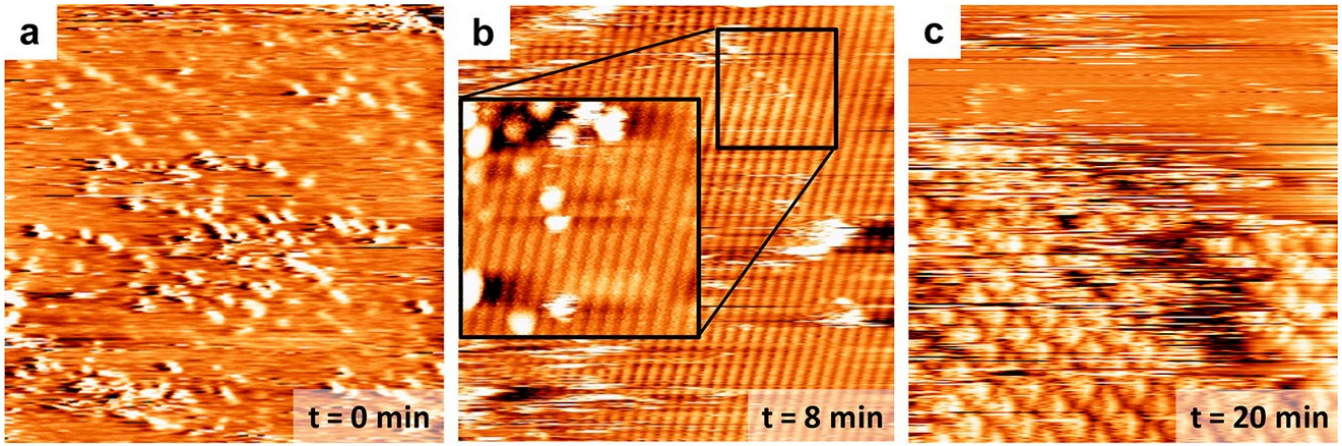

STM images of AuNP-C12SH assembly on top of HOPG before and after adding PhC10-SAc. (a) Representative STM image (130 × 130 nm2; *V*b = 800 mV, *I*t = 0.1 nA) of AuNP-C12SH at tetradecane/HOPG. (b, c) STM images (80 × 80 nm2 and 50 × 50 nm2; *V*b = 800 mV, *I*t = 0.08 nA) of AuNPs at the tetradecane/PhC10-SAc/HOPG interface after 8 and 20 min of time scanning, respectively.

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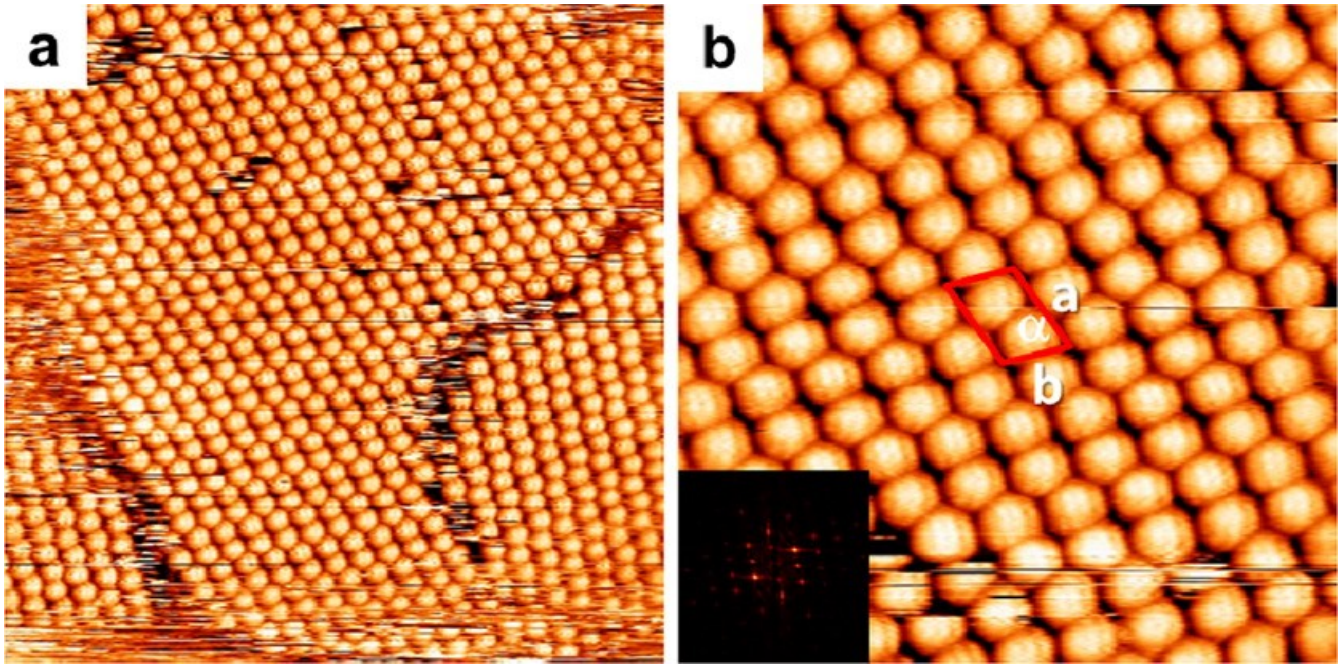

(a) Large-scale and (b) high-resolution STM images (100 × 100 nm2 and 40 × 40 nm2; *V*b = 700 mV, *I*t = 0.1 nA) of AuNP-C12SH at the tetradecane/PhC10-SAc-modified HOPG interface. Unit cell parameters: *a* = 6.1 ± 0.2 nm, *b* = 4.1 ± 0.1 nm, α = 67 ± 2°. Inset: FFT of image (b).

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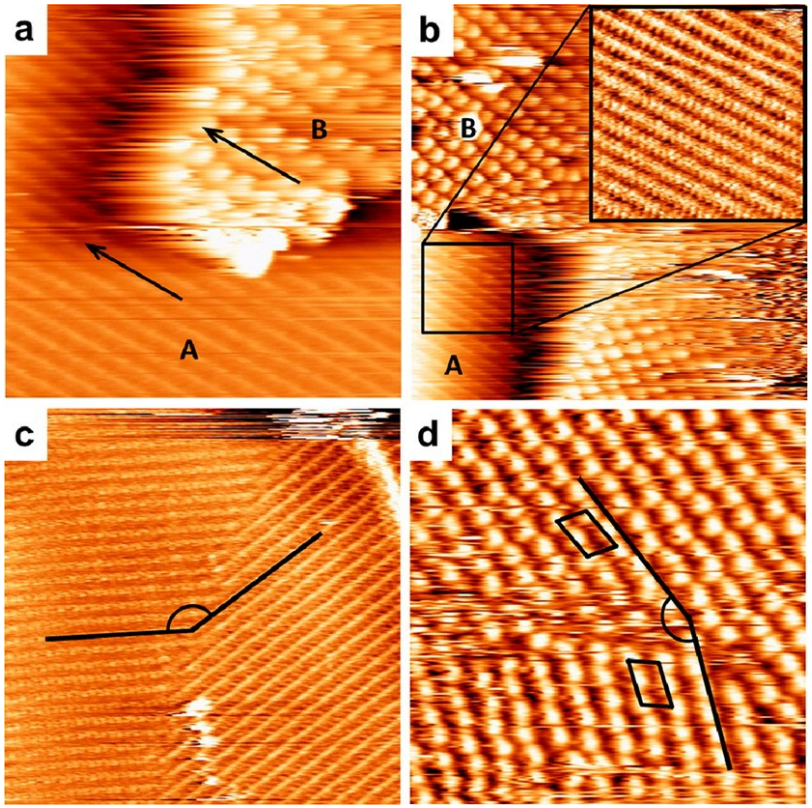

(a, b) STM images (*a*: 60 × 60 nm2, *V*b = 800 mV, *I*t = 0.1 nA; *b*: 50 × 50 nm2, *V*b = 800 mV, *I*t = 0.3 nA) showing domains of PhC10-SAc (region A) and AuNP-C12SH (region B) simultaneously. The inset in (b) corresponds to a (29 × 29 nm2) zoom of the molecular network of PhC10-SAc. The black arrows in (a) indicate a parallel orientation of the PhC10-SAc lamellae and AuNP rows. (c) STM image (52 × 52 nm2; *V*b = 800 mV, *I*t = 0.1 nA) of PhC10-SAc domains oriented at 148 ± 3°. (d) STM image (80 × 80 nm2; *V*b = 800 mV, *I*t = 0.09 nA) of AuNP domains oriented at 154 ± 4°.

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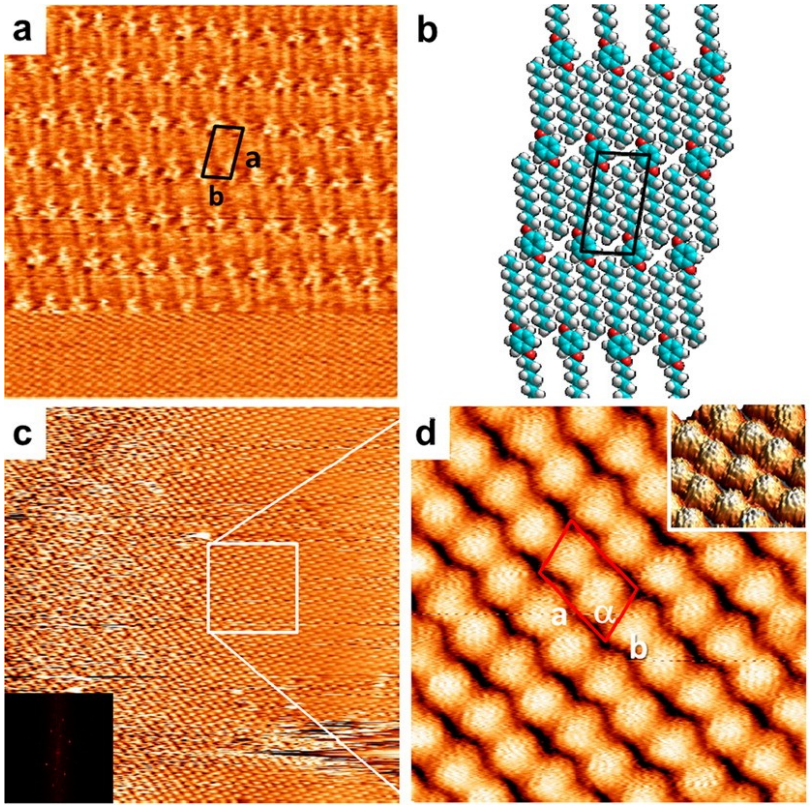

(a) Typical high-resolution STM image (13.7 × 13.7 nm2) simultaneously showing the SAMN of PhC10 molecules (*V*b = 500 mV, *I*t = 0.2 nA) and the underneath HOPG lattice (*V*b = 50 mV, *I*t = 0.2 nA). Unit cell parameters: *a* = 1.8 ± 0.2 nm, *b* = 1.00 ± 0.1 nm, α = 80 ± 2°. (b) Molecular mechanics model of the 2D packing of PhC10 on a graphene sheet, with optimized unit cell parameters: *a* = 1.78 nm, *b* = 0.91 nm, α = 83°. (c) Large-scale STM image (72.5 × 72.5 nm2, *V*b = 500 mV, *I*t = 0.1 nA) of AuNP at the tetradecane/PhC10-modified HOPG interface. Inset: Corresponding FFT image. (d) High-resolution STM image (25 × 25 nm2, *V*b = 500 mV, *I*t = 0.1 nA) showing rows of well-aligned AuNP-C12SH. Unit cell parameters: *a* = 6.1 ± 0.2 nm, *b* = 3.9 ± 0.1 nm, α = 73 ± 2°. Inset: 3D image of AuNP assembly showing the protrusions on AuNP.

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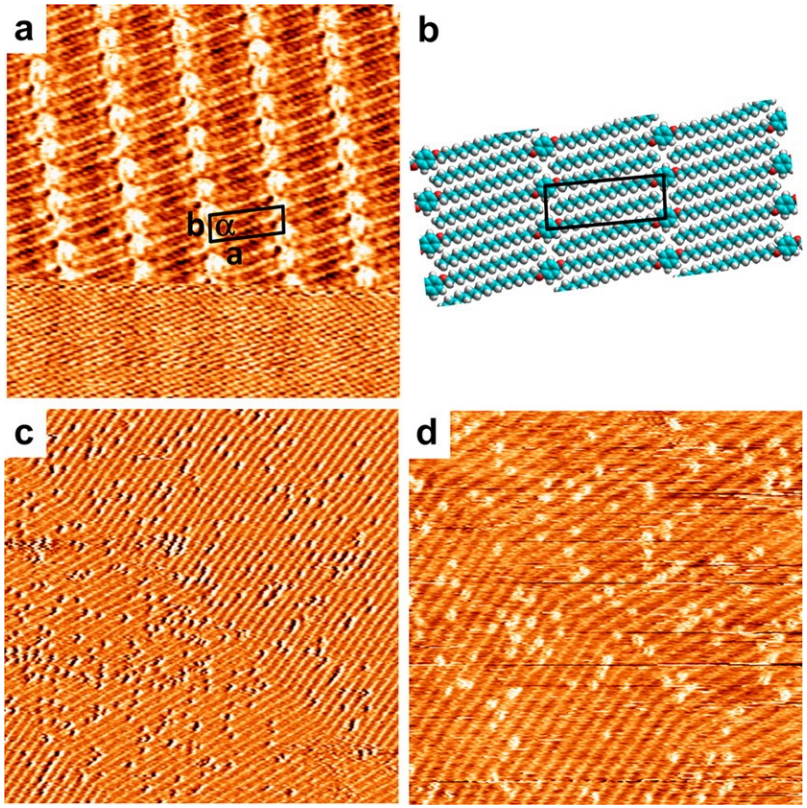

(a) High-resolution STM image (14.5 × 14.5 nm2) showing the SAMN of PhC18 molecules (*V*b = 700 mV, *I*t = 0.25 nA) and the underneath HOPG lattice (*V*b = 50 mV, *I*t = 0.25 nA) simultaneously. Unit cell parameters: *a* = 2.7 ± 0.1 nm, *b* = 1.0 ± 0.1 nm, α = 85 ± 2°. (b) Molecular mechanics model for the 2D packing of PhC18 on a graphene sheet, with optimized unit cell parameters: *a* = 2.72 nm, *b* = 0.93 nm, α = 87°. (c, d) STM images (c: 200 × 200 nm2; *V*b = 900 mV, *I*t = 0.1 nA; d: 93.5 × 93.5 nm2; *V*b = 1000 mV, *I*t = 0.5 nA) of AuNP at the tetradecane/PhC10-SAc-modified HOPG interface.

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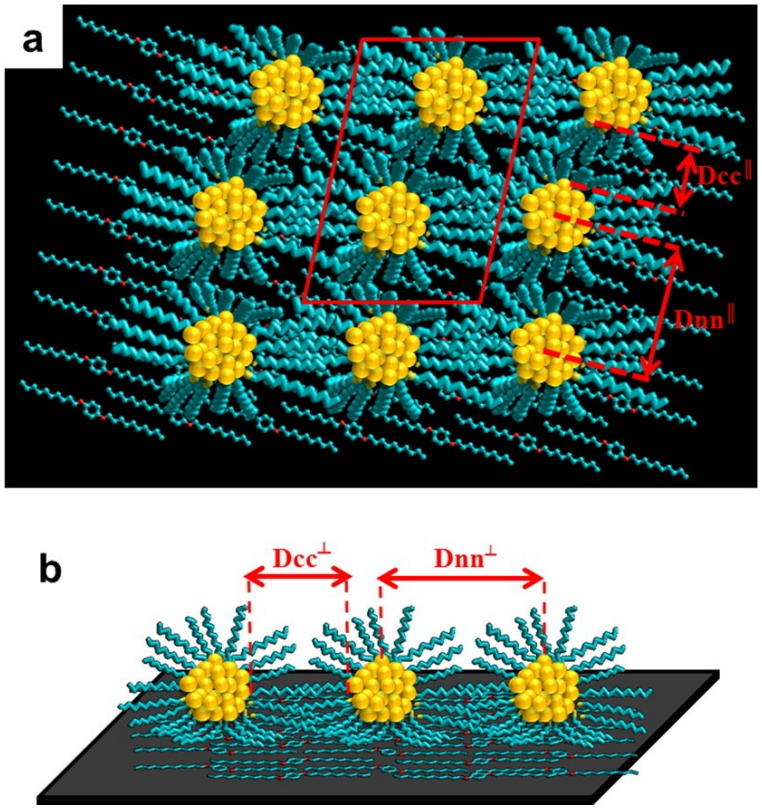

Schematic illustration of AuNP assembly on PhC10-modified HOPG from (a) top and (b) side view. *D*nn and *D*cc are the interparticle distances (center-to-center and core-to-core, respectively).

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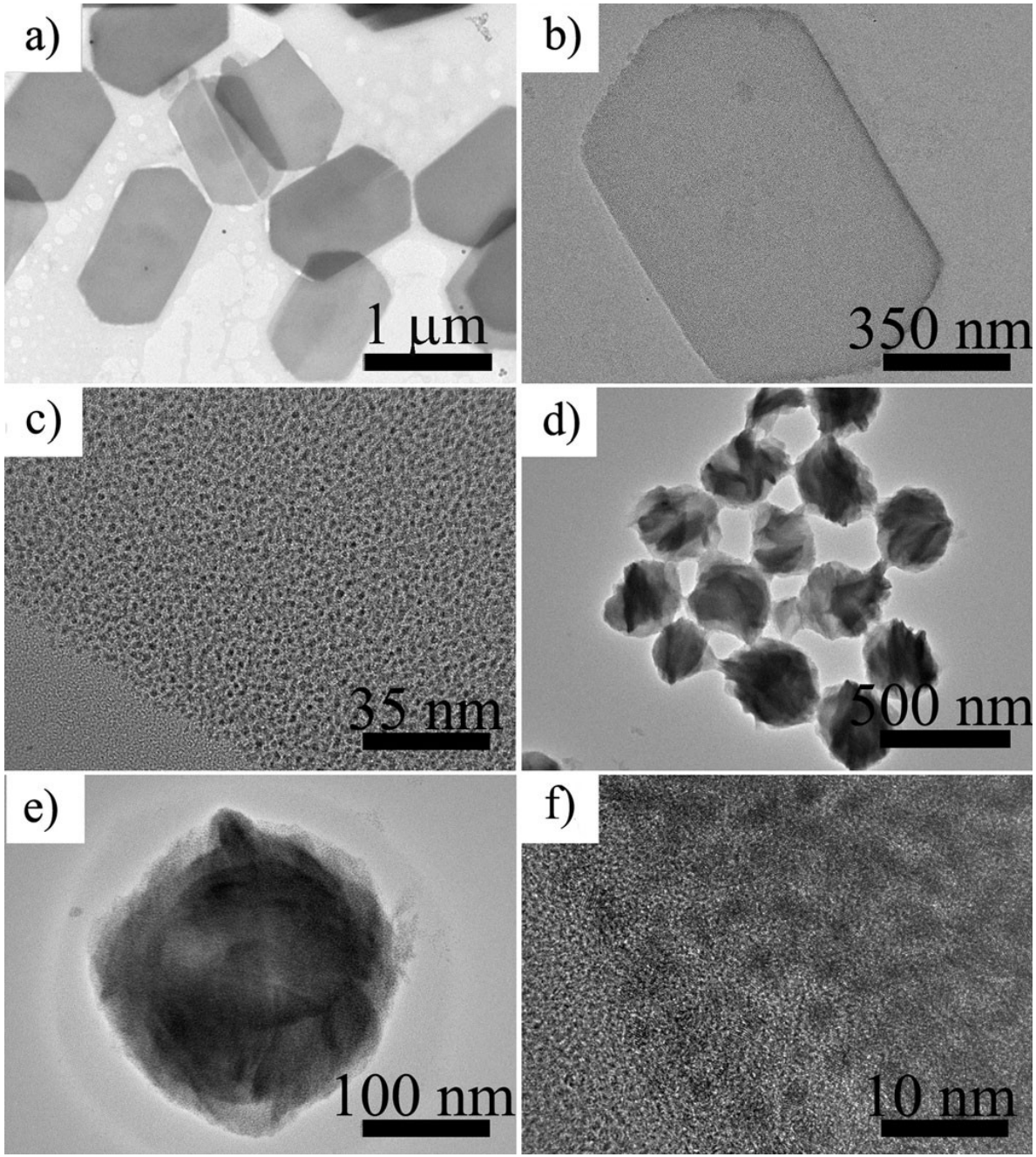

Self-Assembly of Au15 into Single-Cluster-Thick Sheets at the Interface of Two Miscible High-Boiling Solvents

Figure 3. Low (a) and high (b and c) magnification TEM images of the isolated nanosheets, produced by annealing the Au15 cluster solution at 140°C for 10 min under N2. The cluster concentration is 0.032 mmol. Low (d) and high (e and f) magnification TEM images of the nanospheres obtained by annealing the Au15 solution at 1408C for 1 h under vacuum. The cluster concentration is 0.008 mmol. The LP/ BE volume ratio is 7.5:1.

Angew. Chem. Int. Ed. 2013, 52, 9952 –9955


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