Supporting Information

Stabilizing Surface Ag Adatoms into Tunable Single Atom Arrays by Terminal Alkyne Assembly

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1. Details of Density Functional Theory (DFT) Calculations

DFT calculations were performed by using the Vienna Ab Initio Simulation Package (VASP).^{1, 2} The exchange-correlation energy was calculated within the generalized gradient approximation and functional proposed by Perdew-Burke-Ernzerhof.^{3, 4} The van der Waals

dispersive correction was considered for intramolecular, intermolecular and moleculesubstrate interactions.⁵ Projector augmented wave potentials were used.^{6, 7} The valence electron count is 1, 4, and 11 for H, C and Ag, respectively. The kinetic energy cutoff was set to 400 eV. Gamma-centered k-point grids were used, with all grid spacing less than 0.021 Å⁻¹ in the reciprocal space. The optimized lattice parameter of the face-centered cubic silver was 4.140 Å. For the adsorption of molecules and Ag adatoms in the structural motif, Structures B and D, the Ag(111) surface was described by a two-atomic-layer slab with the bottom layer fixed. We also tested models with thicker Ag slab. The relative adsorption energies of single DEDM molecule absorbed on the top site versus the hollow site of Ag(111) substrate were calculated on both two-layer and three-layer Ag slabs. The models with different Ag slabs both predict the favorable adsorption of DEDM on the hollow site, with an energy preference of 0.05 eV/nm² on three-layer slab and 0.04 eV/nm² on two-layer slab. This result suggests that two-layer models are capable of obtaining reliable energy differences between various adsorption structures.

First of all, the structure of the motif composed by one DEDM molecule and two Ag adatoms was optimized. The resulted model of the structural motif (Figure S1a) was applied to build the models of co-assembled layer of Structures B, C, D and E. Following that, the location of Ag adatoms in the co-assembled structures was studied by comparing the adsorption energy of Structure B in which all Ag adatoms locate on hollow sites of the Ag(111) substrate (Figure 2i) and Structure B with all Ag adatoms locating on top sites (Figure S1b). The former was found 0.42 eV per unit cell lower than the latter, which indicates the higher stability of the co-assembled structures with Ag adatoms locating on hollow sites as shown in Figure 2i. Based on this, molecular models in which all the lattice Ag adatoms locate on hollow sites of the Ag(111) substrate were drawn as shown in Figures 2i-I. The calculations of the interaction energy ($^{E_{inter}}$) between the Ag adatom and DEDM molecule, as well as the difference in charge density ($d\rho$) of the DEDM/Ag(111) system with and without Ag adatoms were performed according to these molecular models.



Fig. S1 (a) Optimized molecular model of the structural motif formed by one DEDM molecule and two Ag adatoms. (b) Molecular model of Structure B with all Ag adatoms locating on top site of the Ag(111) substrate.

2. The Evolution Process from Structure A to D

Structures B (Figure S2c), C (Figure S2e) and D (Figure S2g) were obtained by subsequently annealing the sample of Structure A (Figure S2a) at RT for different periods of time (15 min, 40 min and 60 min, respectively). The evolution of these structures could be proved by the co-existence of two or even more structures on the same sample (Figures S2b, S2d and S2f) during the annealing process.



Fig. S2 STM images obtained by annealing the sample at RT for different periods of time showing (a) domains of Structure A (0.80 V, 250 pA, 77 K), (b) the co-existence of Structures A and B (0.60 V, 50 pA, 4.2 K), (c) Structure B (0.50 V, 150 pA, 4.2 K), (d) the co-existence of Structures B and C (0.50 V, 60 pA, 4.2 K), (e) Structure C (0.40 V, 250 pA, 77 K), (f) the co-existence of Structures C and D (0.50 V, 30 pA, 4.2 K), and (g) Structure D (0.08 V, 100 pA, 77 K). The annealing times are marked in the images. The boundaries of different structures are highlighted with black dashed lines in (b), (d) and (f).

3. 3D Isosurface Plots of Charge Density Difference of Structure B



Fig. S3 (a) Top view and (b) side view along the cross sections marked by the dashed lines in (b) and (a), respectively, of 3D isosurface of $10^{-5} e/Bohr^3$ for charge density difference of Structure B. Yellow is for charge density accumulation while cyan is for depletion.

REFERENCES

- 1. G. Kresse and J. Hafner, Phys. Rev. B, 1993, 47, 558.
- 2. G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, 54, 11169.
- 3. J. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 4. J. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1997, 78, 1396.
- 5. A. Tkatchenko and M. Scheffler, Phys. Rev. Lett., 2009, 102, 073005.
- 6. P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953.
- 7. G. Kresse, D. Joubert, Phys. Rev. B, 1999, 59, 1758.