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Electronic Supplementary Information

Self-Assembled Monolayer Structures of Hexadecylamine on Cu Surfaces: Density-Functional Theory

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1 Details of the DFT Calculations

The bulk Cu lattice constant we used is 3.615 Å from experiment[1]. The corresponding bulk Cu cohesive energy is E_{bulk} = -4.146 eV by using a face-centered cubic (fcc) primitive cell and agrees with PAW-PBEsol DFT calculations[2]. We considered two Cu surfaces that could occur during colloidal syntheses: Cu(111) and Cu(100), and we proposed five HDA binding patterns in this study (*cf.*, Table 1 in the main text). For $(\sqrt{3} \times \sqrt{3})$R30°-Cu(111) and p(2 × 2)-Cu(111), we used $(\sqrt{3} \times 3 \times 23)$ and $(2 \times 2\sqrt{3} \times 23)$ supercells, respectively. For (5 × 3)-Cu(100), c(2 × 6)-Cu(100), and p(2 × 2)-Cu(100), we used (5 × 3 × 26), (2 × 6 × 26), and (2 × 2 × 26) supercells, respectively. For calculating average isolated HDA-Cu binding energy, we used $(3\sqrt{3} \times 6 \times 23)$ and $(6 \times 4\sqrt{3} \times 23)$ supercells for $(\sqrt{3} \times \sqrt{3})$R30°-Cu(111) and p(2 × 2)-Cu(111), respectively, and we used (5 × 6 × 26), (6 × 6 × 26), and (6 × 6 × 26) supercells for (5 × 3)-Cu(100), c(2 × 6)-Cu(100), and p(2 × 2)-Cu(100), respectively. The unit to describe supercell geometries in x and y axes is nearest neighbor distance, and that in z axis is the interlayer spacing.

These supercells have six layers of Cu with HDA molecules adsorbing on one side of the slabs, and we left a vacuum spacing of ~12 Å between the top of the molecular layer and the top of the supercell, as we did in recent DFT studies[3,4]. The cutoff radius for van der Waals interactions is 40 Å. The bottom 3 layers were fixed at the bulk termination and all the other atomic coordinates were relaxed using a force-convergence criterion of 0.01 eV/Å.

For an HDA molecule in the gas phase, we used a cubic supercell with side length of 25 Å. For a hexagonal HDA monolayer in vacuum, we used an ($M \times \sqrt{3}M \times 40$ Å) supercell, where M varied between 4.0 and 4.4 Å. Wave functions were expanded using a kinetic energy cut-off of 400 eV, and the Brillouin zone was sampled with a Monkhorst-Pack **k**-point grid and with a Methfessel-Paxton smearing of 0.1 eV. For the bulk Cu primitive cell, a (12 × 12 × 12) **k**-point grid was used. For ($\sqrt{3} \times \sqrt{3}$)R30°-Cu(111) and p(2 × 2)-Cu(111), we used (10 × 6 × 1) and (8 × 5 × 1) **k**-point grids, respectively. For (5 × 3)-Cu(100), c(2 × 6)-Cu(100), and p(2 × 2)-Cu(100), we used (4 × 6 × 1), (8 × 3 × 1), and (8 × 8 × 1) **k**-point grids, respectively. For calculating average isolated HDA-Cu binding energy, we used (3 × 3 × 1) and (3 × 3 × 1) **k**-point grids for ($\sqrt{3} \times \sqrt{3}$)R30°-Cu(111) and p(2 × 2)-Cu(111), respectively, and we used (4 × 3 × 1), (3 × 3 × 1), and (3 × 3 × 1) **k**-point grids for (5 × 3)-Cu(100), c(2 × 6)-Cu(100), and p(2 × 2)-Cu(100), respectively. For a hexagonal HDA monolayer in vacuum, a (10 × 6 × 1) **k**-point grid was used.

2 Surface Energies of Bare Cu(111) and Cu(100) with DFT

For calculating the surface energies of the two Cu surfaces (γ_{Cu}), we first built a supercell with the smallest repeat unit for each surface in the $x-$ and $y-$directions parallel to the surface. In the $z-$direction perpendicular to the surface, we had 23 total layers: 8 vacuum and 15 Cu. We relaxed the 3 surface layers at each of the Cu-vacuum interfaces in this periodic cell and the 9 central layers were fixed at the bulk termination, and we used (16 × 9 × 1) and (16 × 16 × 1) **k**-point grids for Cu(111) and Cu(100), respectively. After geometry optimization, we calculated γ_{Cu} using[5]

$$\gamma_{\mathrm{Cu}} = \frac{E_{\mathrm{Cu}} - nE_{\mathrm{bulk}}}{2A_{\mathrm{surf}}} \quad , \tag{S1}$$

where E_{Cu} is the energy of the optimized supercell, n is the number of metal atoms in the slab, E_{bulk} is the energy per metal atom in the bulk crystal, and $2A_{\mathrm{surf}}$ is the sum of the areas at the top and the bottom of the metal slab. The surface energies of Cu(111) and Cu(100) were found to be 0.106 and 0.117 eV/Å^2 respectively and in agreement with PAW-PBEsol DFT calculations[2]. The surface energy of Cu(111) is consistent with experiment[6], and the average surface energy of the two surfaces is also consistent with experiment[7].

3 Convergence Test on the Total Binding Energy per HDA Molecule

Tables S1 and S2 show the convergence test on the total binding energy per HDA molecule for $(\sqrt{3} \times \sqrt{3})$R30°-Cu(111) with uniform θ and (5×3)-Cu(100) with uniform θ, respectively. The results here indicate that the parameters described in Section 1 are appropriate, and further adjustment to these parameters may only affect the total binding energy per HDA molecule within the energy tolerance of these calculations (*i.e.*, 0.01 eV).

Table S1 Convergence test on the total binding energy per HDA molecule for ($\sqrt{3} \times \sqrt{3}$)R30°-Cu(111) with uniform θ shown in Table 2 of the main text. The parameters in bold indicate those described in Section 1.

Side length of a cubic supercell for an HDA molecule in gas phase (Å)	E_{bind} (eV)
25	1.83
30	1.83
35	1.84
Kinetic energy cut-off (eV)	E_{bind} (eV)
300	1.87
350	1.87
400	1.83
450	1.84
500	1.84
k-point grid	E_{bind} (eV)
(8 × 4 × 1)	1.82
(9 × 5 × 1)	1.83
(10 × 6 × 1)	1.83
(11 × 6 × 1)	1.83
(12 × 7 × 1)	1.82
Relaxed layers of the Cu slabs	E_{bind} (eV)
3	1.83
4	1.83
5	1.83
Interlayer spacing in z direction of the supercell	E_{bind} (eV)
23	1.83
24	1.83
25	1.83
26	1.83
27	1.83
28	1.83

Table S2 Convergence test on the total binding energy per HDA molecule for (5 × 3)-Cu(100) with uniform θ shown in Table 3 of the main text. The parameters in bold indicate those described in Section 1.

Side length of a cubic supercell for an HDA molecule in gas phase (Å)	E_{bind} (eV)
25	1.93
30	1.93
35	1.94
Kinetic energy cut-off (eV)	E_{bind} (eV)
300	2.00
350	1.94
400	1.93
450	1.93
500	1.93
k-point grid	E_{bind} (eV)
(2 × 3 × 1)	1.94
(3 × 5 × 1)	1.93
(4 × 6 × 1)	1.93
(5 × 8 × 1)	1.93
(6 × 10 × 1)	1.93
Relaxed layers of the Cu slabs	E_{bind} (eV)
3	1.93
4	1.93
5	1.93
Interlayer spacing in z direction of the supercell	E_{bind} (eV)
26	1.93
27	1.93
28	1.93
29	1.93
30	1.93
31	1.93

4 Test on Tilt Angle for p(2 × 2)-Cu(111)

Table S3 The initial (with subscript 0) and optimized properties defined in the main text for p(2 × 2)-Cu(111) with initial different α.

α_0	β_0	θ_0	N_0	E_{bind} (eV)	$E_{\text{HDA-HDA}}$ (eV)	$E_{\text{HDA-Cu}}$ (eV)	$\langle d_{\text{N-Cu}} \rangle$ (Å)	$\langle \alpha \rangle$
0°	0°	60°	atop	1.51	0.90	0.61	2.20	1.6°
10°	0°	60°	atop	1.55	0.92	0.63	2.20	11.3°
20°	0°	60°	atop	1.67	1.04	0.63	2.23	25.2°
30°	0°	60°	atop	1.72	1.08	0.64	2.24	30.6°
40°	0°	60°	atop	1.89	1.28	0.62	2.25	38.8°
50°	0°	60°	atop	1.57	0.95	0.62	2.26	32.8°

5 Test on Tilt Angle for $(\sqrt{3} \times \sqrt{3})$R30°-Cu(111) with Uniform θ

Table S4 The initial (with subscript 0) and optimized properties defined in the main text for $(\sqrt{3} \times \sqrt{3})$R30°-Cu(111) with initial different α and β but uniform θ. The references here (ref.) have experimental values from which α_0 and β_0 were built.

Ref.	α_0	β_0	θ_0	N_0	E_{bind} (eV)	$E_{\text{HDA-HDA}}$ (eV)	$E_{\text{HDA-Cu}}$ (eV)	$\langle d_{\text{N-Cu}} \rangle$ (Å)	$\langle \alpha \rangle$
[8,9]	0°	0°	60°	atop	1.83	1.39	0.44	2.30	2.6°
	12°	0°	60°	atop	1.82	1.36	0.46	2.26	4.6°
	20°	0°	60°	atop	1.78	1.32	0.47	2.26	7.1°
[10]	30°	0°	60°	atop	1.79	1.32	0.46	2.26	7.6°
[11]	12°	45°	60°	atop	1.78	1.33	0.45	2.26	9.7°

6 Analysis on HDA-Cu Interaction for the Two HDA Binding Patterns on Cu(111)

Table S5 The initial (with subscript 0) and optimized properties defined in the main text for the two HDA binding patterns on Cu(111).

α_0	β_0	θ_0	$E_{\text{HDA-Cu}}$ (eV)	$\langle E_{\text{HDA-Cu,iso}} \rangle$ (eV)	$E_{\text{HDA-HDA,sub}}$ (eV)	$\langle \alpha \rangle$
			$(\sqrt{3} \times \sqrt{3})$R30°-Cu(111)			
0°	0°	60°	0.44	0.32	0.12	2.6°
0°	0°	60°, 150°	0.42	0.26	0.17	0.2°
			p(2 × 2)-Cu(111)			
40°	0°	60°	0.62	0.44	0.18	38.8°

7 Analysis on HDA-Cu Interaction for the Three HDA Binding Patterns on Cu(100)

Table S6 The initial (with subscript 0) and optimized properties defined in the main text for the three HDA binding patterns on Cu(100).

α_0	β_0	θ_0	$E_{\text{HDA-Cu}}$ (eV)	$\langle E_{\text{HDA-Cu,iso}} \rangle$ (eV)	$E_{\text{HDA-HDA,sub}}$ (eV)	$\langle \alpha \rangle$
			(5 × 3)-Cu(100)			
0°	0°	60°	0.48	0.31	0.17	1.7°
0°	0°	60°, 150°	0.49	0.33	0.16	1.8°
			c(2 × 6)-Cu(100)			
40°	0°	60°	0.55	0.42	0.13	35.9°
			p(2 × 2)-Cu(100)			
60°	0°	45°	0.72	0.67	0.05	50.8°

8 Test on Tilt Angle for c(2 × 6)-Cu(100)

Table S7 The initial (with subscript 0) and optimized properties defined in the main text for c(2 × 6)-Cu(100) with initial different α.

α_0	β_0	θ_0	N_0	E_{bind} (eV)	$E_{\text{HDA-HDA}}$ (eV)	$E_{\text{HDA-Cu}}$ (eV)	$\langle d_{\text{N-Cu}} \rangle$ (Å)	$\langle \alpha \rangle$
0°	0°	60°	atop	1.71	1.16	0.55	2.16	1.7°
10°	0°	60°	atop	1.74	1.16	0.57	2.17	8.5°
20°	0°	60°	atop	1.84	1.26	0.58	2.18	20.5°
30°	0°	60°	atop	1.97	1.40	0.56	2.21	30.8°
40°	0°	60°	atop	1.96	1.41	0.55	2.23	35.9°

9 Test on Tilt Angle for p(2 × 2)-Cu(100)

Table S8 The initial (with subscript 0) and optimized properties defined in the main text for p(2 × 2)-Cu(100) with initial different α.

α_0	β_0	θ_0	N_0	E_{bind} (eV)	$E_{\text{HDA-HDA}}$ (eV)	$E_{\text{HDA-Cu}}$ (eV)	$\langle d_{\text{N-Cu}} \rangle$ (Å)	$\langle \alpha \rangle$
0°	0°	45°	atop	1.33	0.61	0.71	2.14	4.1°
10°	0°	45°	atop	1.36	0.62	0.73	2.15	9.7°
20°	0°	45°	atop	1.44	0.70	0.74	2.21	22.7°
30°	0°	45°	atop	1.72	0.98	0.74	2.20	40.3°
40°	0°	45°	atop	1.89	1.15	0.74	2.23	46.8°
50°	0°	45°	atop	1.94	1.23	0.71	2.26	50.8°
60°	0°	45°	atop	1.96	1.24	0.72	2.25	50.8°

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