Electrodeposit Copper from alkaline cyanide free baths containing 5, 5'-dimethylhydantoin and citrate

Jie Zhang, Anmin Liu, Xuefeng Ren, Jinqiu Zhang, Peixia Yang and Maozhong An*

State Key Laboratory of Urban Water Resource and Environment,
School of Chemical Engineering and Technology,
Harbin Institute of Technology,
No. 92 Xidazhijie Street, Nangang District, Harbin, 150001, China.
Tel.: +86-451-86418616. Fax: +86-451-86418616.
E-mail address: mzan@hit.edu.cn (Maozhong An)

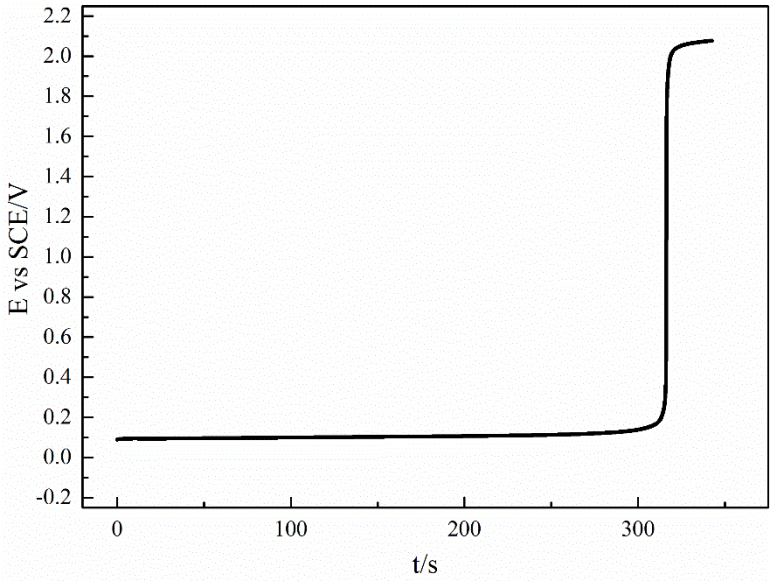

Figure S1. Potential vs. time curves for anodic oxidization of the copper deposits electrodeposited at 15 mA/cm^2 from S2 for 10 min. The oxidization current density was 20 mA/cm^2.

Table S1 The detail data of the voltammetry at various scan rates for the calculation of α

Pt electrode in Sp4			GC electrode in Sp4			GC electrode in Sp1		
V (mV/s)	E_p-$E_{p/2}$ (V)	α	V (mV/s)	E_p-$E_{p/2}$ (V)	α	V (mV/s)	E_p-$E_{p/2}$ (V)	α
10	0.072	0.73	10			10	0.247	0.11
20	0.075	0.70	20	0.254	0.21	30	0.084	0.311
40	0.076	0.69	40	0.253	0.21	60	0.08	0.33
60	0.077	0.68	60	0.265	0.20	80	0.077	0.34
80	0.079	0.66	80	0.284	0.19	100	0.072	0.36
100	0.079	0.66	100	0.261	0.20	150	0.082	0.32
150	0.079	0.66	150	0.269	0.19	200	0.080	0.33
200	0.081	0.64	200	0.279	0.19			

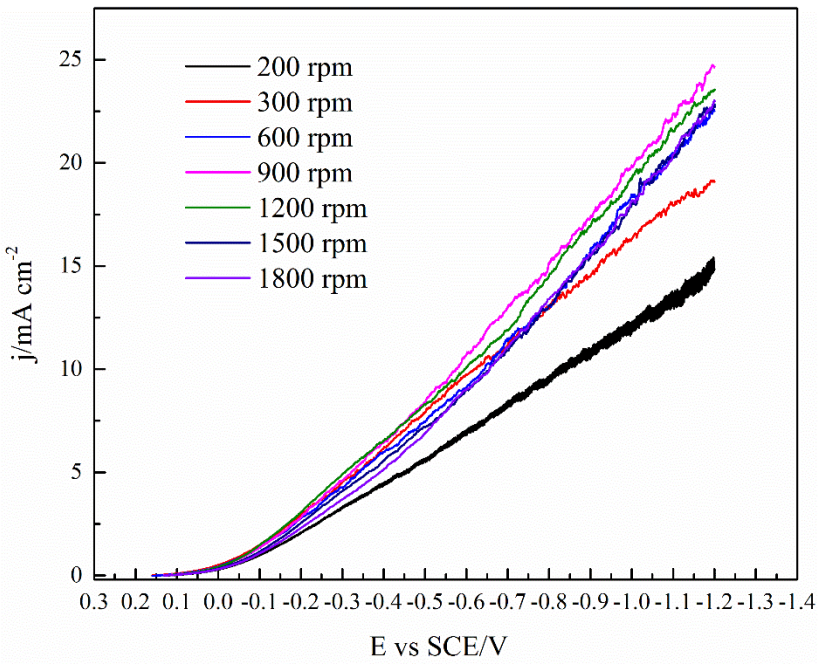

Figure S2. Cathodic polarization curves on GC rotating disk electrode in solution Sp4 with only DMH as the complex agent

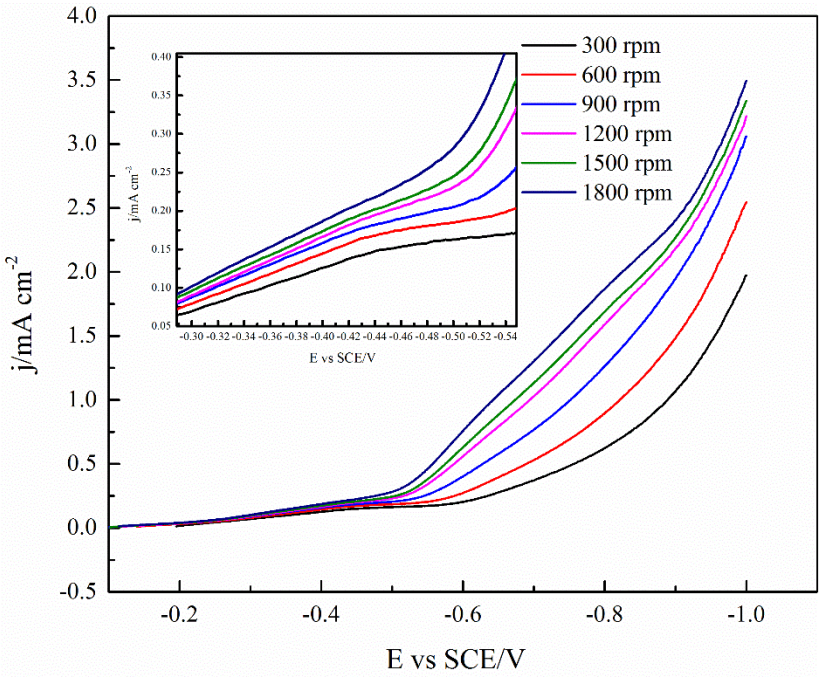

Figure S3. Cathodic polarization curves of GC rotating disk electrode in solution Sp2 with only citrate as the complex agent

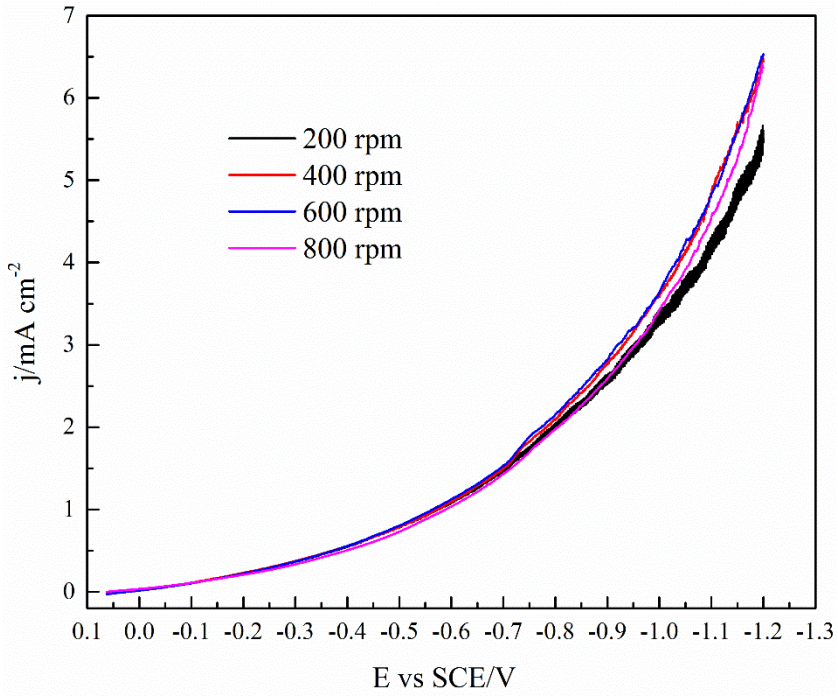

Figure S4. Cathodic polarization curves of GC rotating disk electrode in solution Sp3 with both DMH and Citrate as the complex agents

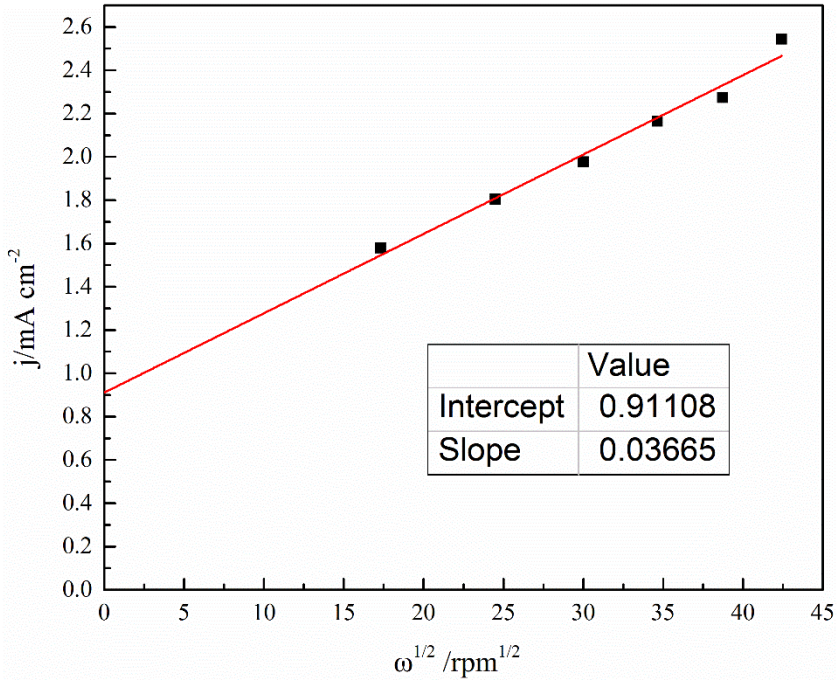

Figure S5. The line of j vs. $\omega^{1/2}$ fitted from the data in figure 6 at -0.48 V according to the Koutecky´ – Levich equation

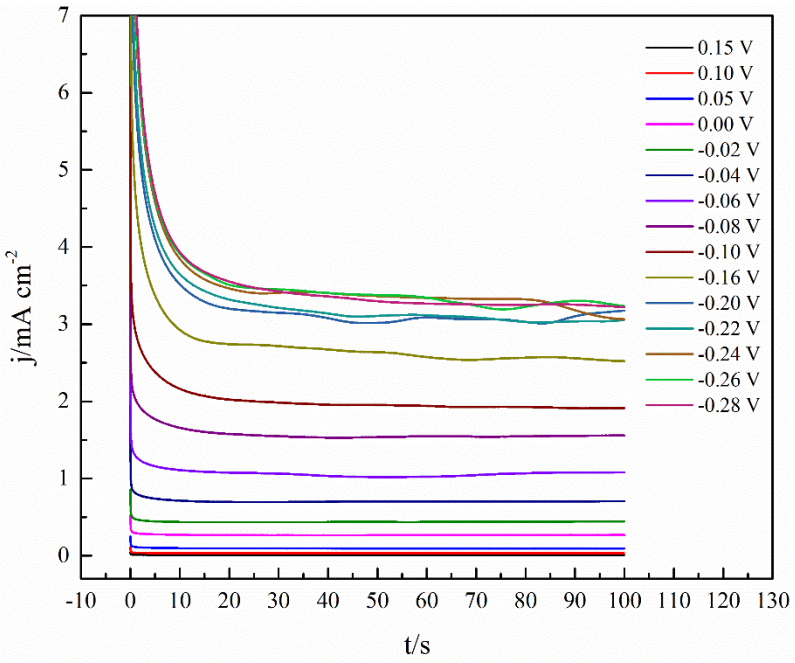

Figure S6. Current vs. time curves on the Pt electrode in solution Sp4 with only DMH as the complex agent

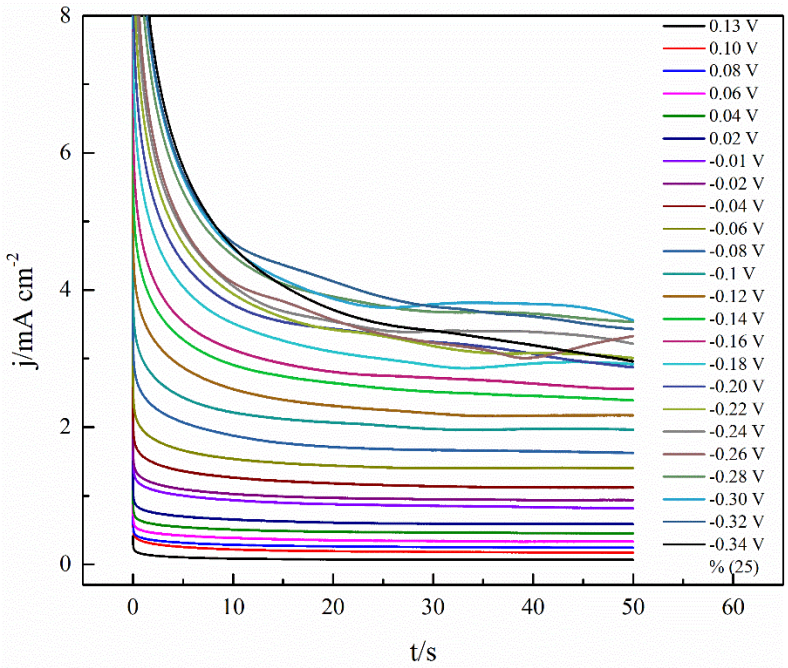

Figure S7. Current vs. time curves on the GC electrode in solution Sp4 with only DMH as the complex agent

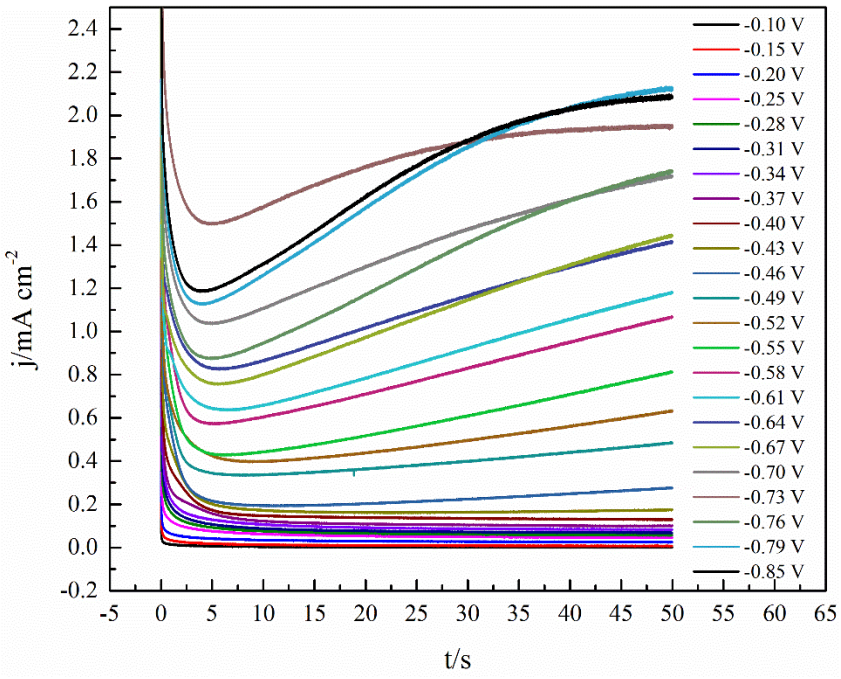

Figure S8. Current vs. time curves on the GC electrode in solution Sp2 with only citrate as the complex agent

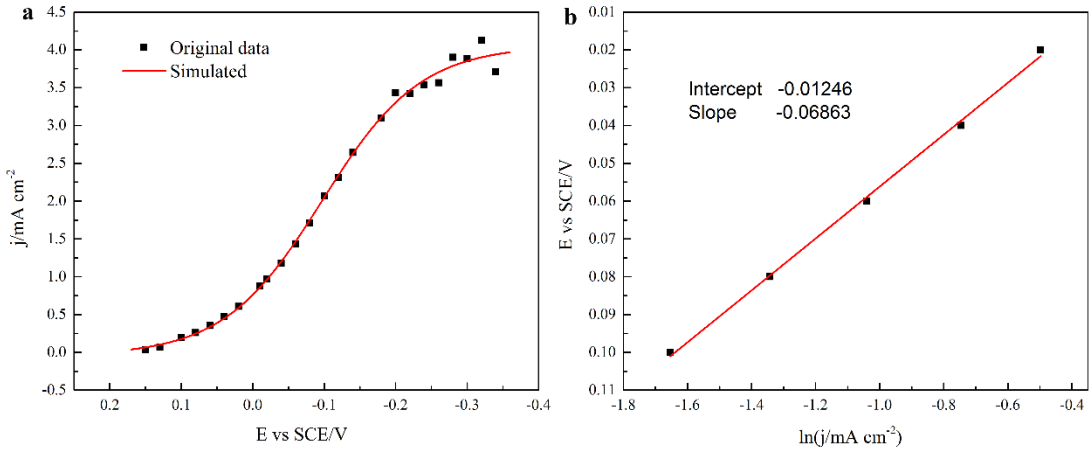

Figure S9 (a) The sample current voltammogram of the GC electrode in the solution Sp4 with only DMH as the complex agent. (b) The E vs. lnj line fitted from the data of the sample current voltammetry. The table in (a) is the kinetic parameters according to.

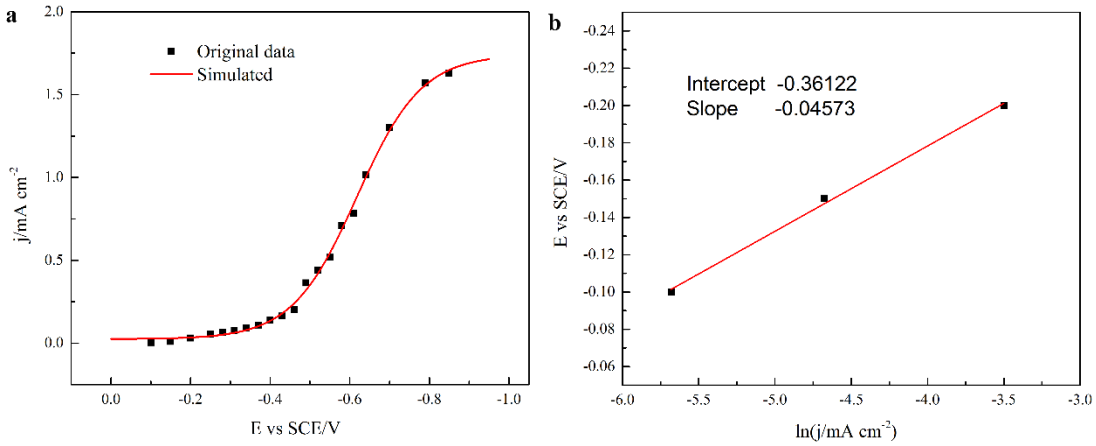

Figure S10. (a) The sample current voltammogram of the GC electrode in the solution Sp1 with only citrate as the complex agent. (b) The E vs. lnj line fitted from the data of the sample current voltammetry. The table in (a) is the kinetic parameters according to.

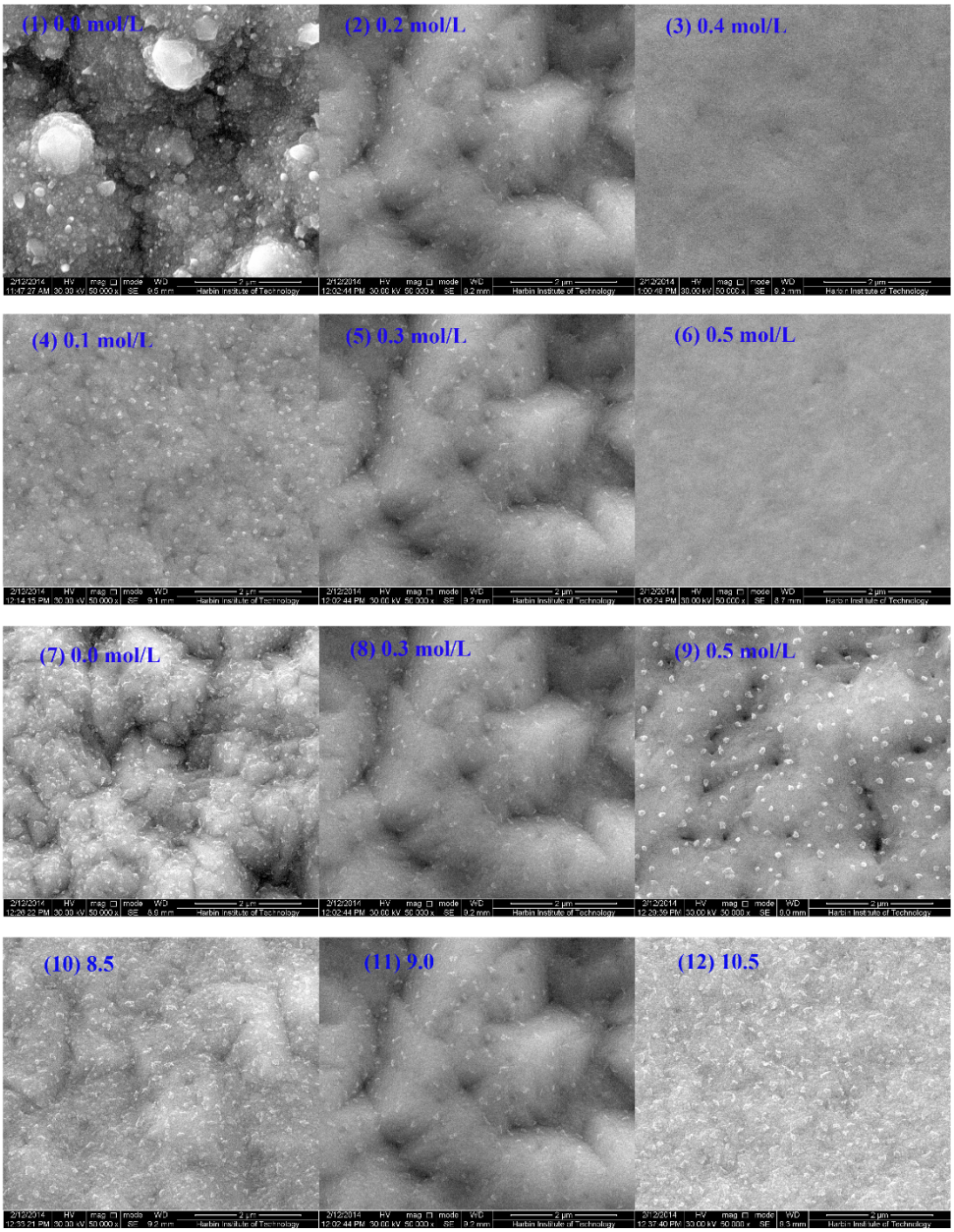

Figure S11. SEM images illustrating the morphology of copper layers electrodeposited from various solutions at pH 9 and 50℃: (1) S1, (2) (5) and (8) S2, (3) S3, (4) S4, (6) S5, (7) S6, and (9) S7, and from S2 with various pH at 50℃: (10) pH 8.5, (11) pH 9, and (12) pH 10.5

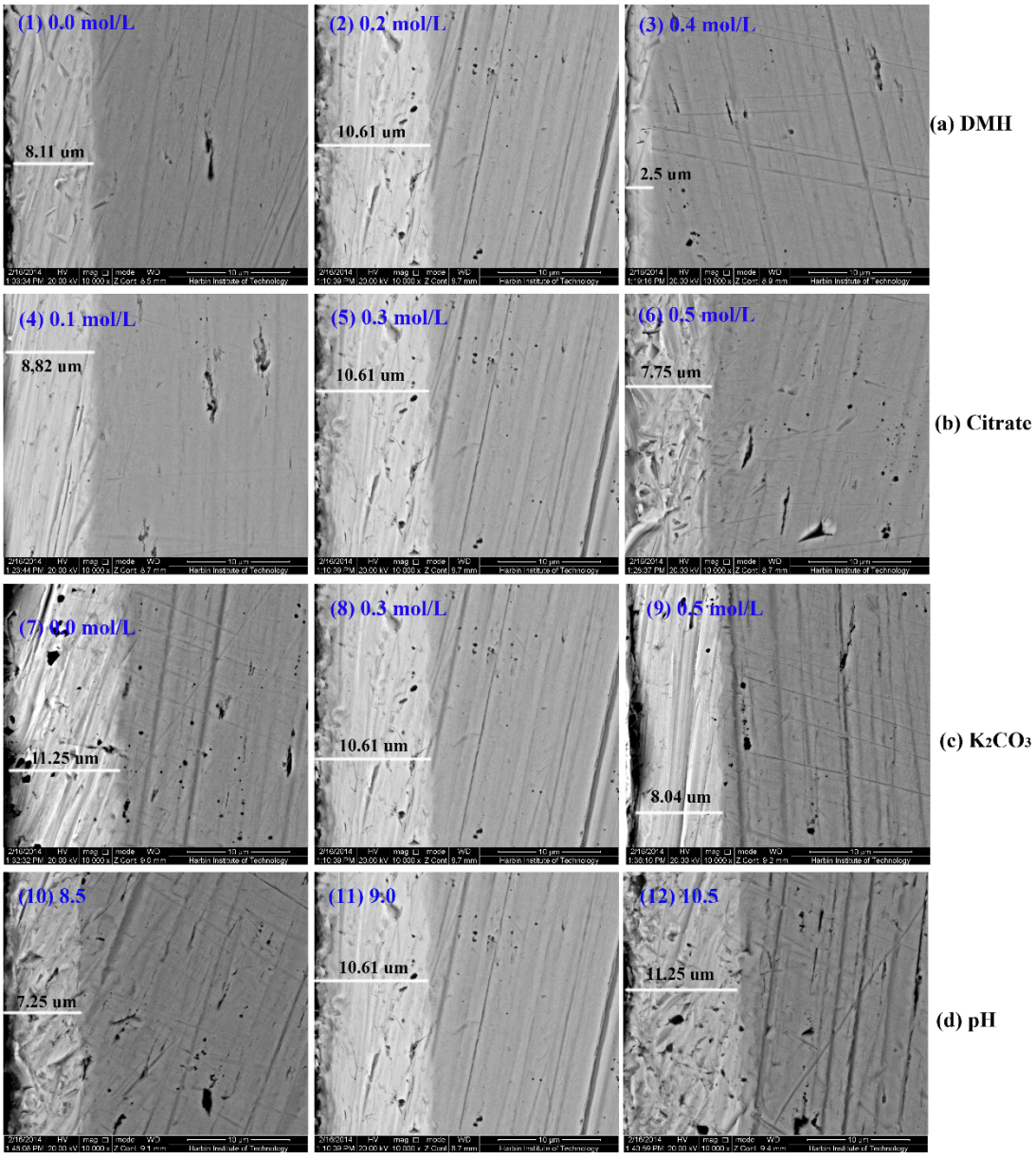

Figure S12. Section-cross images copper layers electrodeposited corresponding to the images in figure S11.

Table S2 the thickness of copper layers corresponding to the images in Figure 12.

DMH (M)	**Thickness (μm)**	**Citrate (M)**	**Thickness (μm)**	**K_2CO_3 (M)**	**Thickness (μm)**	**pH**	**Thickness (μm)**
(1) 0.0	8.11	(4) 0.1	8.82	(7) 0.1	11.25	(10) 8.5	7.25
(2) 0.2	10.61	(5) 0.3	10.61	(8) 0.3	10.61	(11) 9.0	10.61
(3) 0.4	2.50	(6) 0.5	7.75	(9) 0.5	8.04	(12) 10.5	11.21

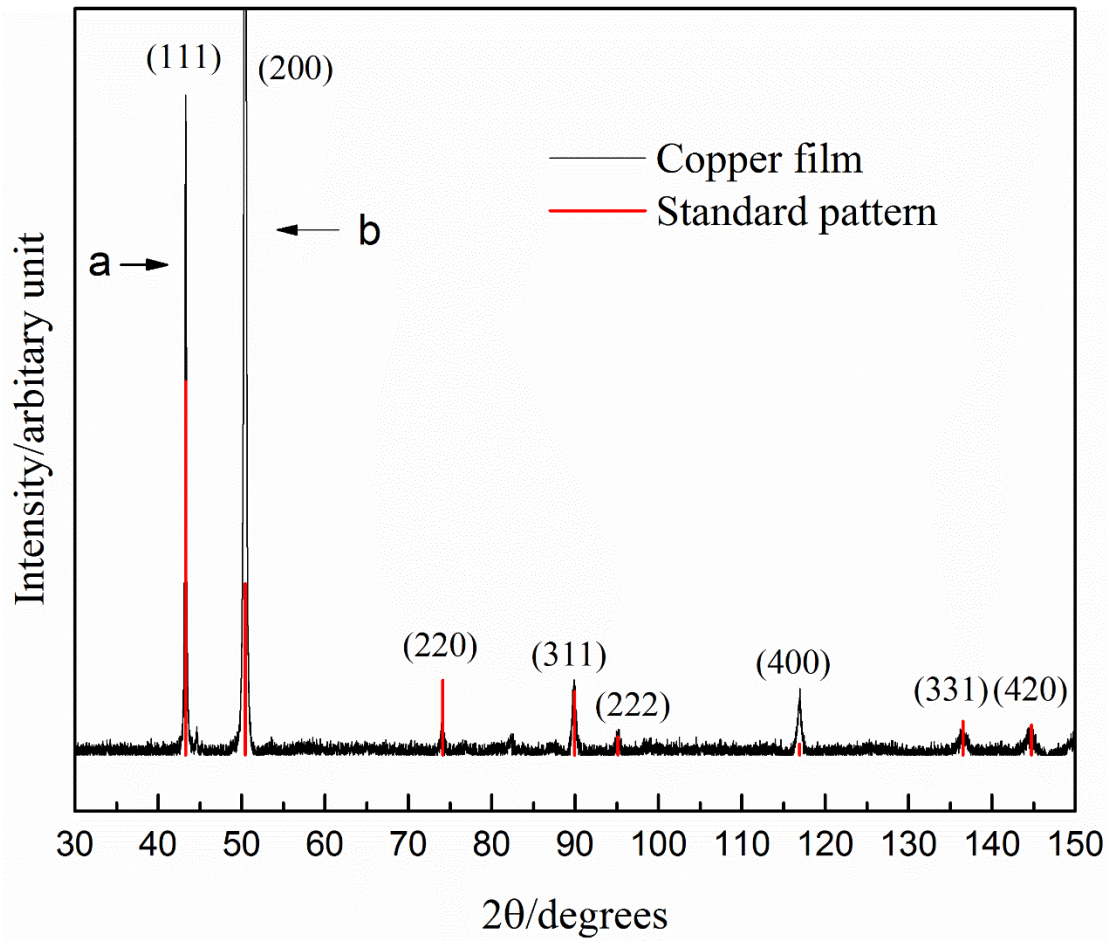

Figure S13. XRD pattern of the copper layer shown in figure 6. Peak (a) and (b)

Table S3. The grain size of copper layers corresponding to the images in Figure S12

DMH (M)	**Grain size (µm)**	**Citrate (M)**	**Grain size (µm)**	**K_2CO_3 (M)**	**Grain size (µm)**	**pH**	**Grain size (µm)**
(1) 0.0	17.2	**(4) 0.1**	20.95	**(7) 0.1**	46.15	**(10) 8.5**	37.15
(2) 0.2	32.7	**(5) 0.3**	32.45	**(8) 0.3**	32.6	**(11) 9.0**	31.7
(3) 0.4	23.05	**(6) 0.5**	24.75	**(9) 0.5**	21.2	**(12) 10.5**	20.75

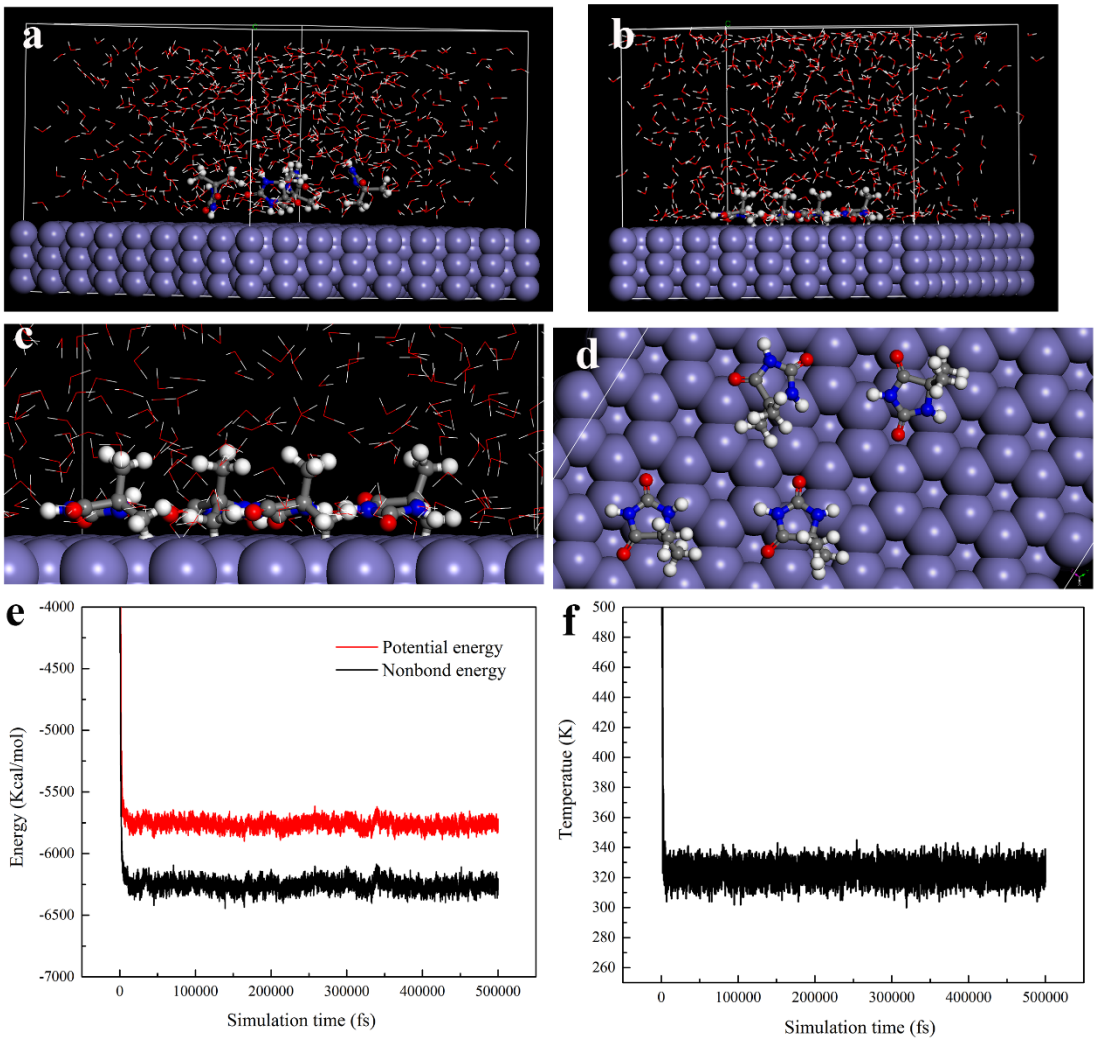

Figure S14. The behaviors simulated of neutral DMH molecules on Fe (111). (a) the initial configuration of the simulated box with four DMH molecules placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

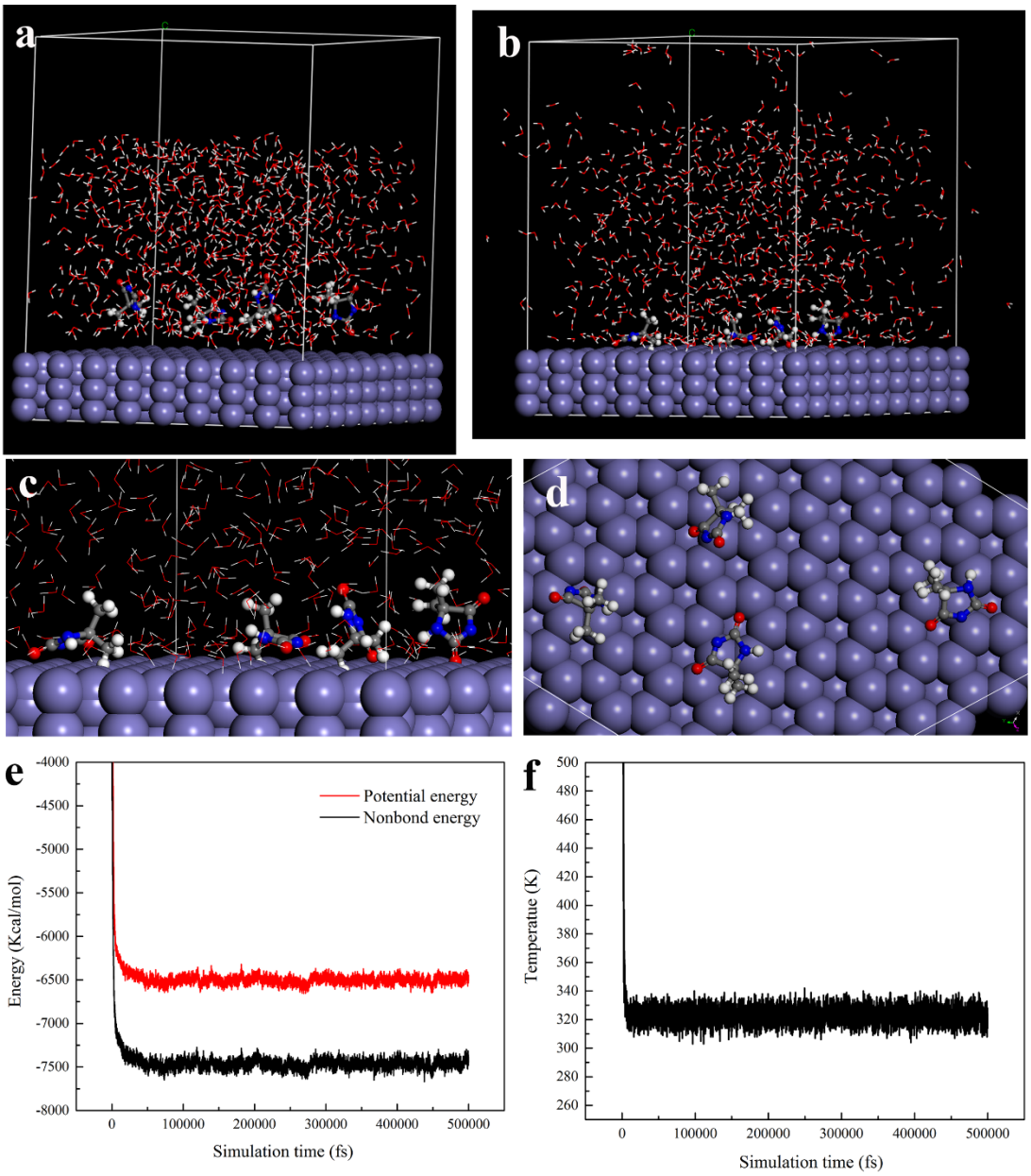

Figure S15. The behaviors simulated of DMH molecules lacking one proton on Fe (111). (a) the initial configuration of the simulated box with four DMH^- ions placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

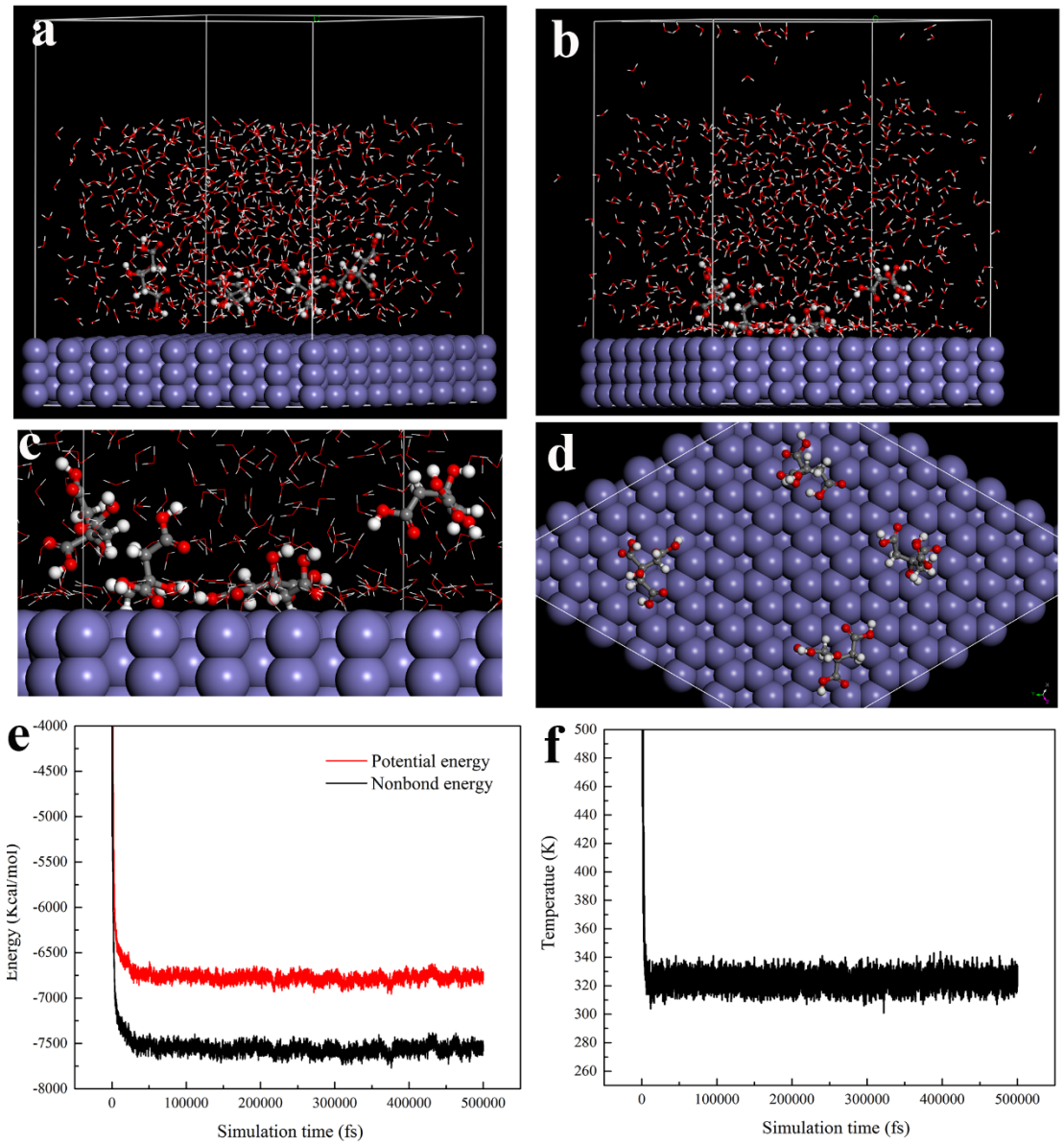

Figure S16. The behaviors simulated of citrate acid molecules on Fe (111). (a) the initial configuration of the simulated box with four citrate acid molecules placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

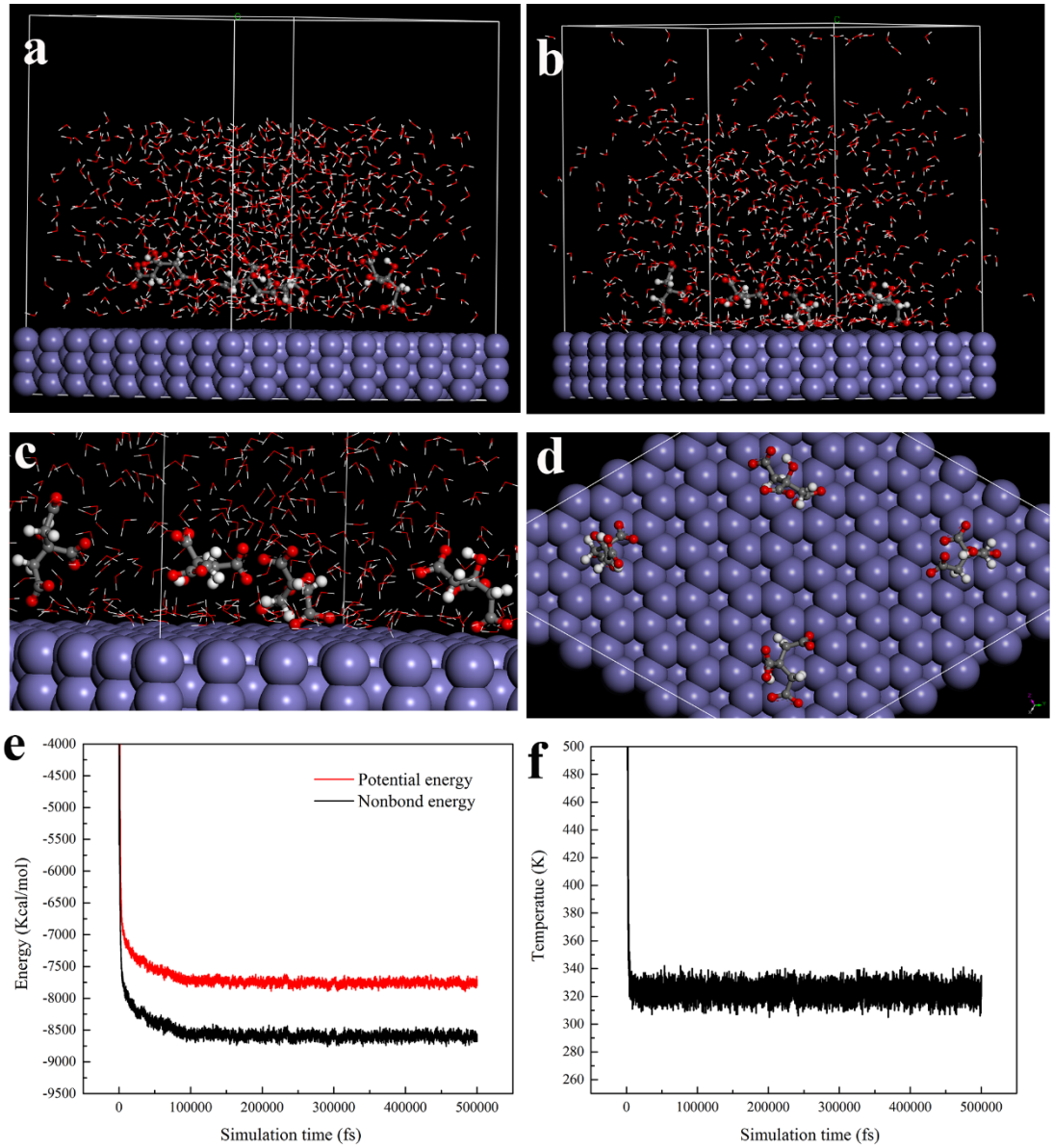

Figure S17 The behaviors simulated of citrate acid molecules lacking three protons on Fe (111). (a) the initial configuration of the simulated box with four citrate ions placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

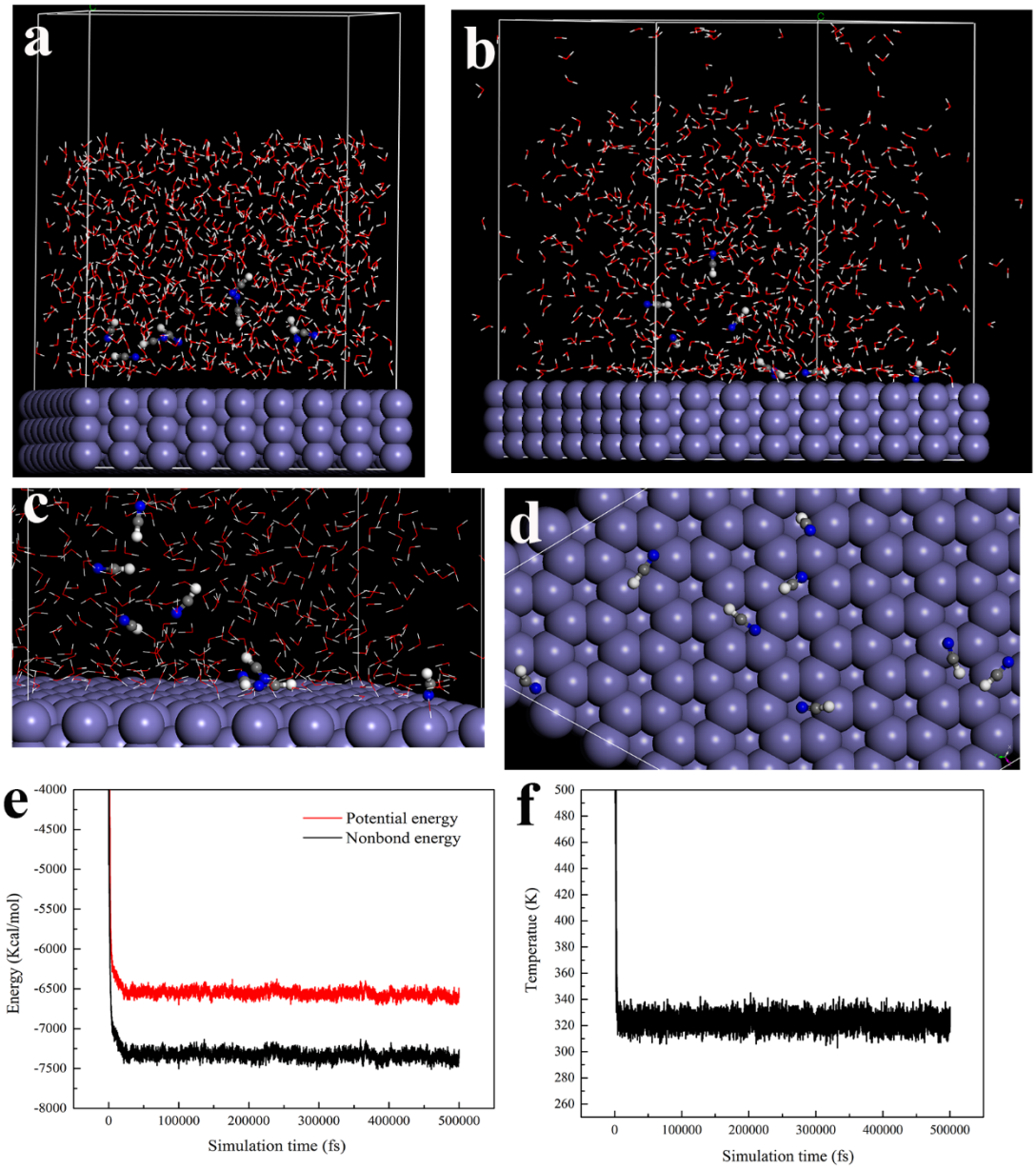

Figure S18. The behaviors simulated of HCN molecules on Fe (111). (a) the initial configuration of the simulated box with eight HCN molecules placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

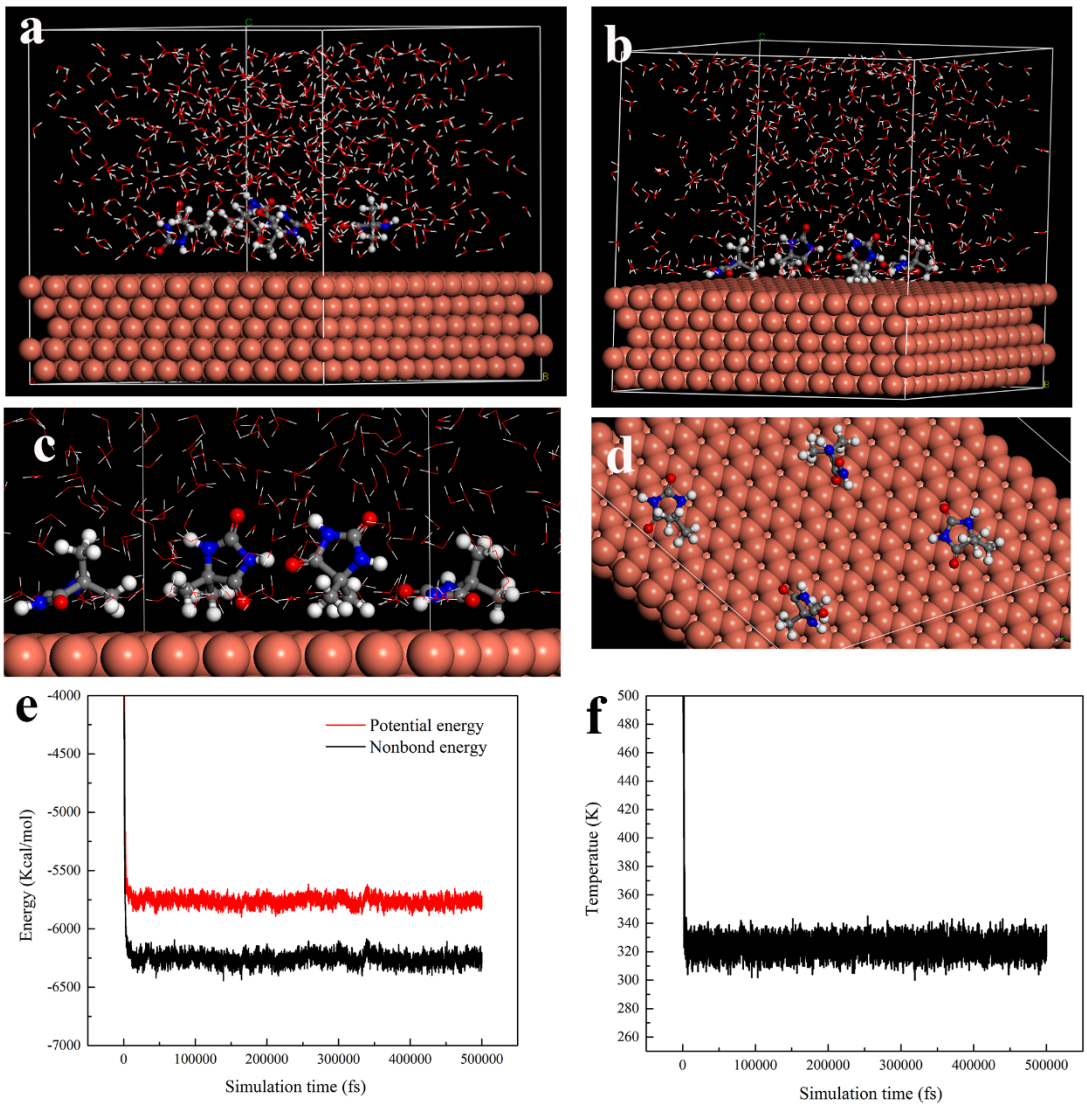

Figure S19. The behaviors simulated of DMH molecules on Cu (111). (a) the initial configuration of the simulated box with four DMH molecules placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

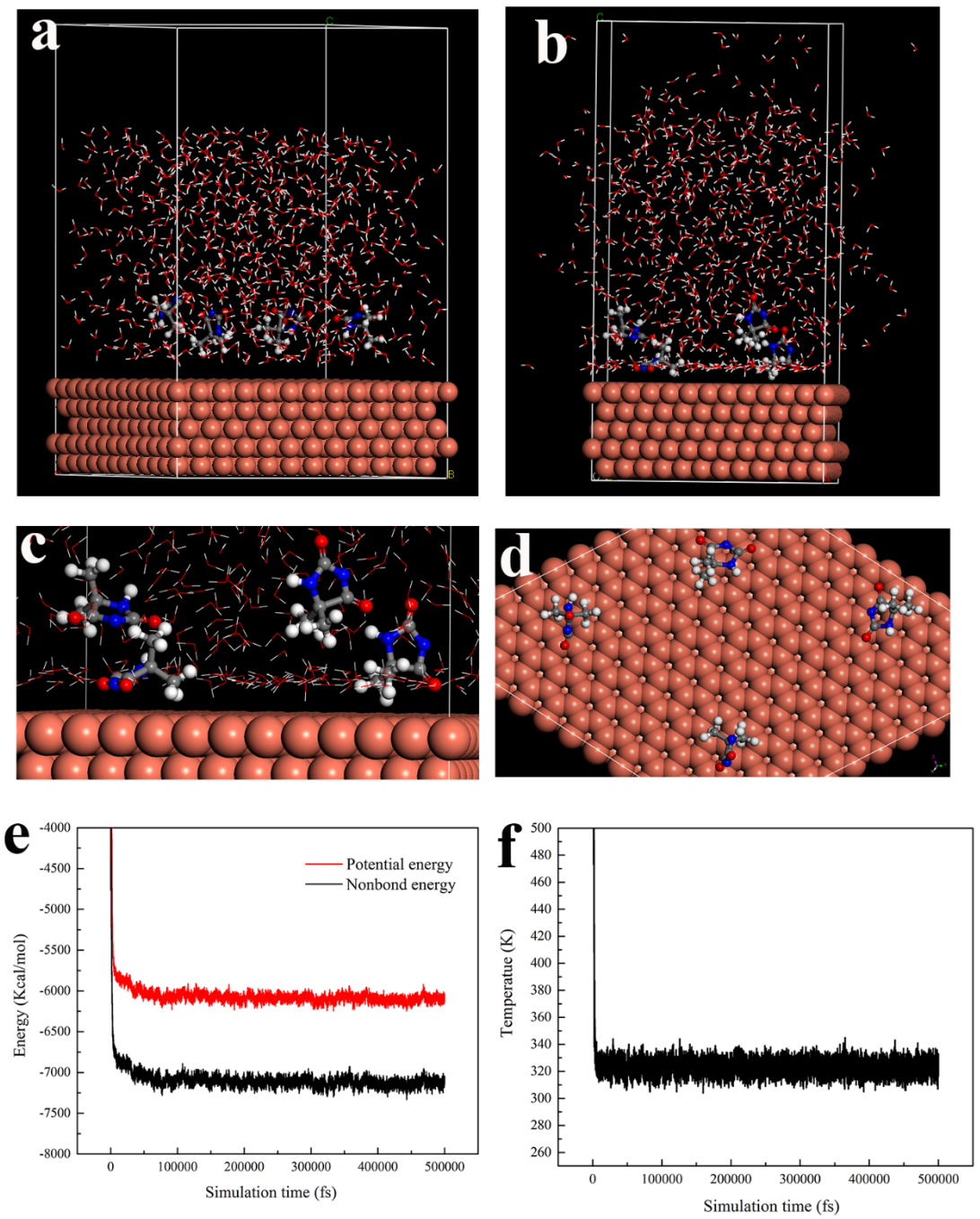

Figure S20. The behaviors simulated of DMH molecules lacking one proton on Cu (111). (a) the initial configuration of the simulated box with four DMH^- ions placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

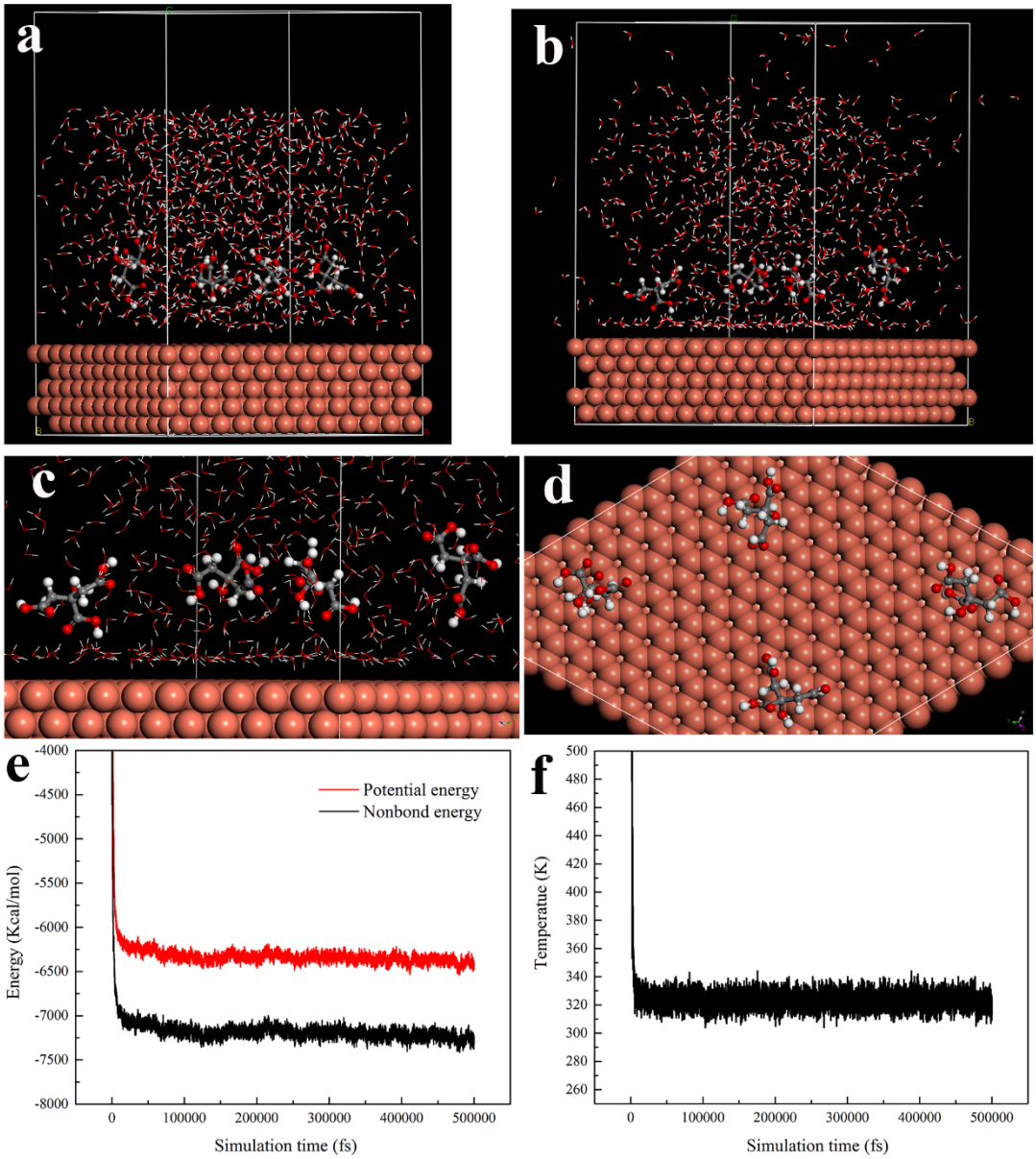

Figure S21. The behaviors simulated of citrate acid molecules l on Cu (111). (a) the initial configuration of the simulated box with four citrate acid molecules placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

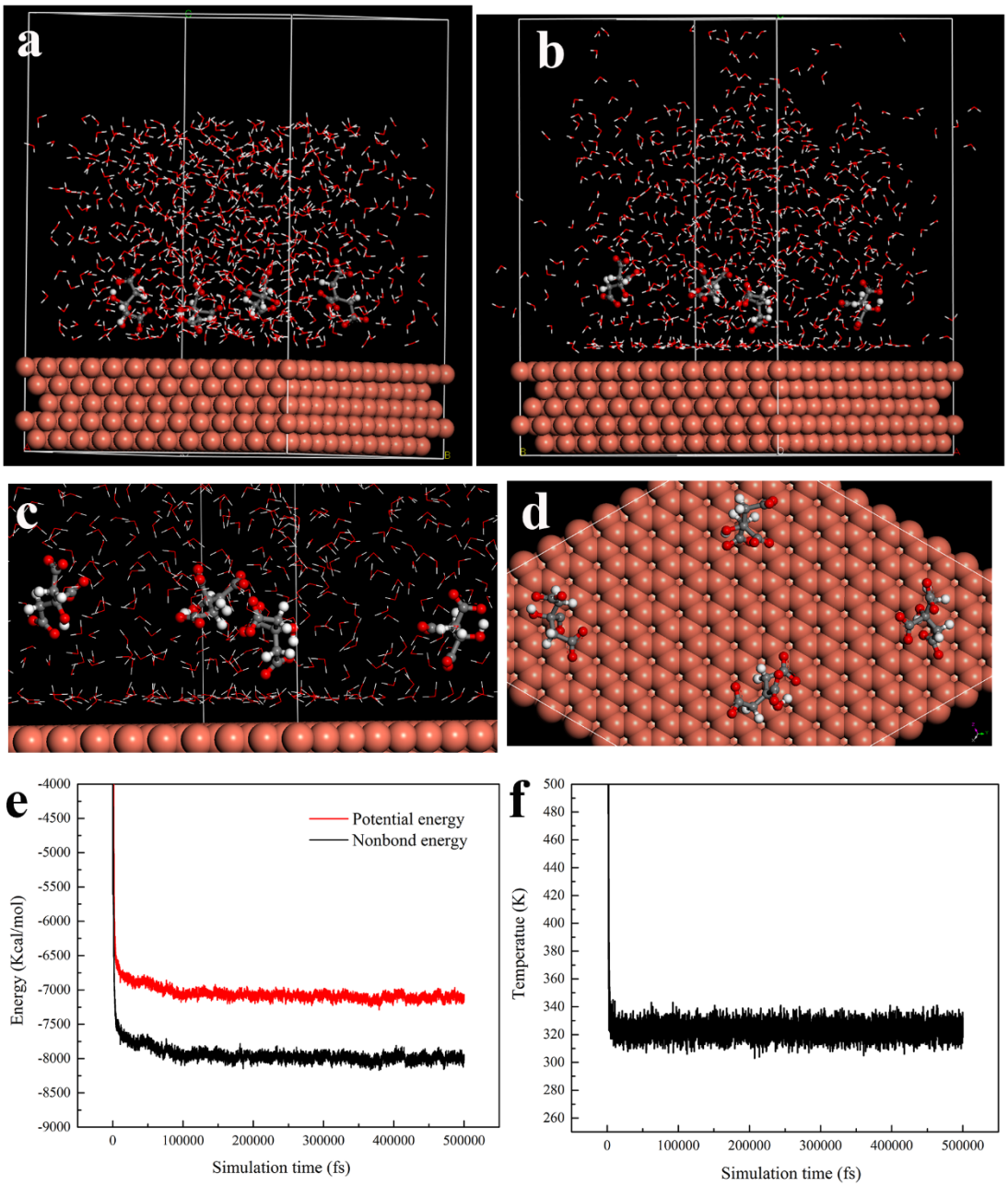

Figure S22. The behaviors simulated of citrate molecules lacking three proton on Ce (111). (a) the initial configuration of the simulated box with four citrate ions placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.

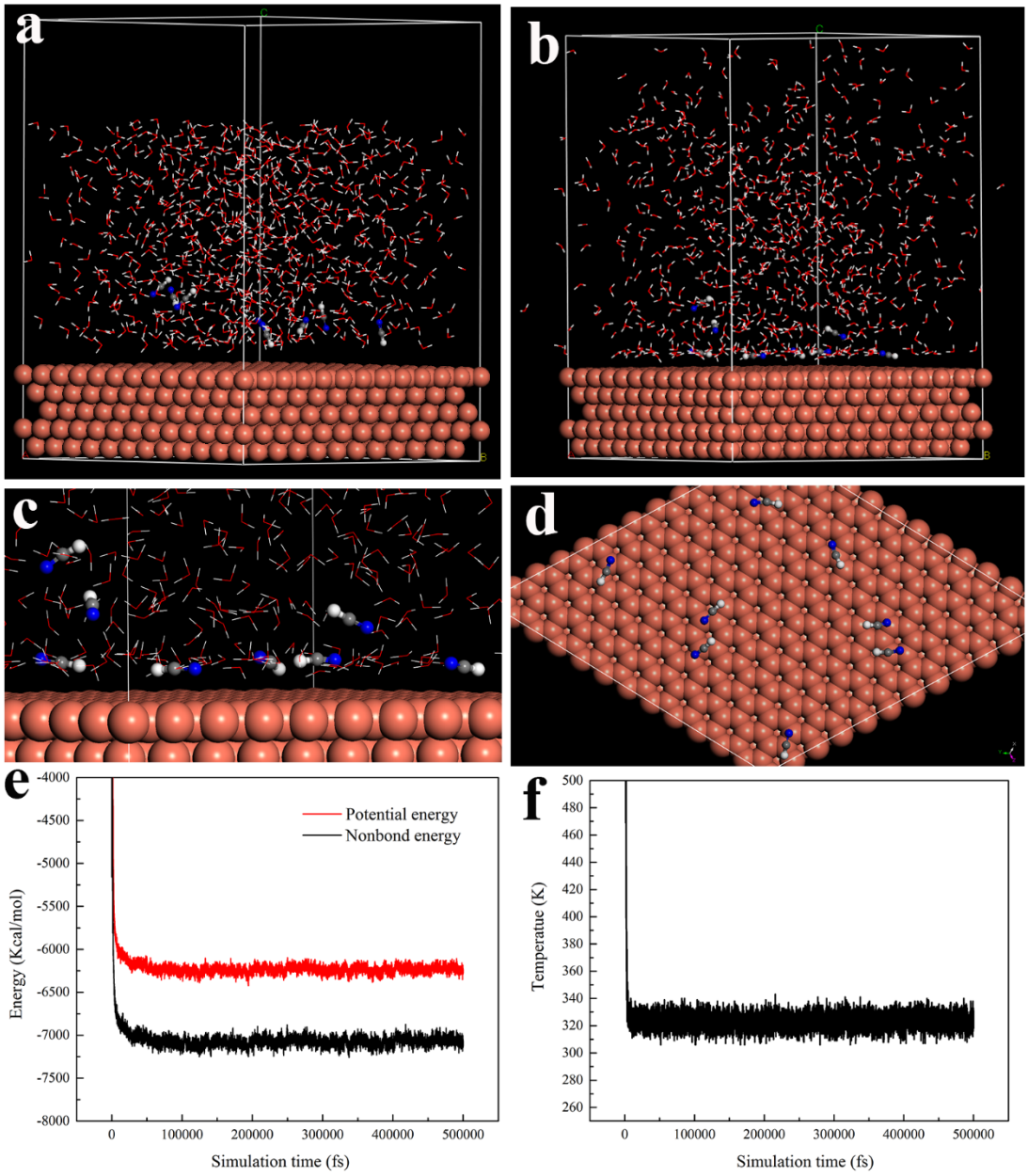

Figure S23. Cu The behaviors simulated of HCN molecules lacking one proton on Cu (111). (a) the initial configuration of the simulated box with eight HCN molecules placed randomly, (b) the final state of the simulated box, (c) the front view of the simulated box, (d) the top view of the simulated box with the water molecules deleted, and (e) energy vs. time curves and (f) temperature vs. time curves of the simulated box.