Supporting Information

Reversible Kirkwood-Alder Transition Observed in Pt_3Cu_2 Nanoctahedron Assemblies under Controlled Solvent Annealing/Drying Conditions

Jun Zhang,[†,#] Zhiping Luo,[‡] Benjamin Martens,[‖] Zewei Quan,[†] Amar Kumbhar,[§] Nathan Porter,[†] Yuxuan Wang,[‖] Detlef-M. Smilgies*,[⊥] and Jiye Fang*,[†,‖]

[†]Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902, USA
[‡] Microscopy and Imaging Center and Materials Science and Engineering Program, Texas A&M University, College Station, Texas 77843, USA
[‖] Materials Science and Engineering Program, State University of New York at Binghamton, Binghamton, New York 13902, USA
[§]Chapel Hill Analytical and Nanofabrication Laboratory, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA
[⊥]Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York 14853, USA
[#]Present address: Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA

jfang@binghamton.edu; dms79@cornell.edu

1. Synthesis of Pt_3Cu_2 Nanoctahedra

Pt_3Cu_2 nanoctahedra were prepared using a co-reduction of platinum (II) acetylacetonate (Gelest, 49.3-49.8%Pt, $Pt(acac)_2$) and a mixture of copper (I)/(II) chloride (Alfa Aesar, 99.999% and 99.995% respectively) with an optimized Pt/Cu input molar ratio in the presence of tungsten hexacarbonyl [$W(CO)_6$] (Sigma-Aldrich, 99.9%). A combination of oleylamine (Sigma-Aldrich, 70%) and oleic acid (Sigma-Aldrich, 90%) was used as both reaction solvent and capping agents. In a typical experiment, 0.001g of Cu(I)Cl, 0.005 g of $Cu(II)Cl_2$, 0.020g of $Pt(acac)_2$, 9.0 mL of oleylamine and 1.0 mL of oleic acid were loaded into a three-neck flask and heated to 140 °C under an argon stream. 0.050 g of $W(CO)_6$ was then added into the solution, and the temperature was subsequently raised to 200°C and kept for 20 min with stirring. The resultant products were precipitated by adding anhydrous ethanol (AAPER, 200 proof) followed by centrifugation. The obtained Pt_3Cu_2 nanoctahedra were re-dispersed in hexane (BDH, 98.5%) and subject to a size-selection post-treatment process prior to a characterization.

2. Details of Characterization

TEM images were recorded on a Hitachi 7000 (75kv) and FEI Tecnai G^2 F20 FEG-TEM (200 kv) electron microscopes. SEM images were taken from a Carl Zeiss field emission scanning electron microscope (Supra 55VP). For the 3D reconstruction study, TEM tomography was carried out and a series of images were taken at different angles, and then reconstructed by the backprojection method using the FEI Xplore3D program. All images, diffraction, and tomography were acquired using zero energy loss electrons by excluding the inelastic electrons with the post column Gatan Image Filter (GIF), and recorded using Gatan Tridiem 2K×2K slow scan CCD camera.

GISAXS measurements were performed at D1 station at the Cornell High Energy Synchrotron Source (CHESS), Cornell University. The beamline delivers 10 keV photons at a 1.5% bandwith obtained with a multilayer monochromator. The x-ray beam is collimated with a set of precision slits (ADC). The sample sits in a closed sample cell (see Figure S1 (a)) with a hexane reservoir and a controlled He flow to vary the hexane vapor pressure. Scattered x-rays are detected with a CCD detector (MedOptics) at 778 mm from the sample, as calibrated with a silver behenate standard. The beamstop consists of a 2mm tantalum rod to protect the CCD from the reflected beam and the intense diffuse scattering in the incident plane. The scattering geometry is depicted in Figure S1 (b). GISAXS images were analyzed using the *fit2D* program distributed by the European Synchrotron Radiation Facility (ESRF) and indexed using the home-made program package *indexGIXS*.

3. EDS Composition Analysis Results of Pt_3Cu_2 Nanoctahedra

Spectrum	In stats.	Cu	Pt	(in atomic%)
Spectrum 1	Yes	33.15	66.85	
Spectrum 2	Yes	34.68	65.32	
Spectrum 3	Yes	33.83	66.17	
Spectrum 4	Yes	32.16	67.84	
Spectrum 5	Yes	33.41	66.59	
Spectrum 6	Yes	32.80	67.20	
Mean		**33.34**	**66.66**	
Std. deviation		0.87	0.87	
Max.		34.68	67.84	
Min.		32.16	65.32	

Figure S1: Schematic of experimental setup. (a), structure of GISAXS sample chamber; (b), GISAXS measurement profile. In a hexane vapor environment, a Si-wafer substrate with drop-cast NC film was placed onto a metal stage surrounded by a trough as solvent reservoir. The hexane vapor pressure was controlled by flowing helium gas through the chamber at specific flow rates. (refer to ref. 33.)

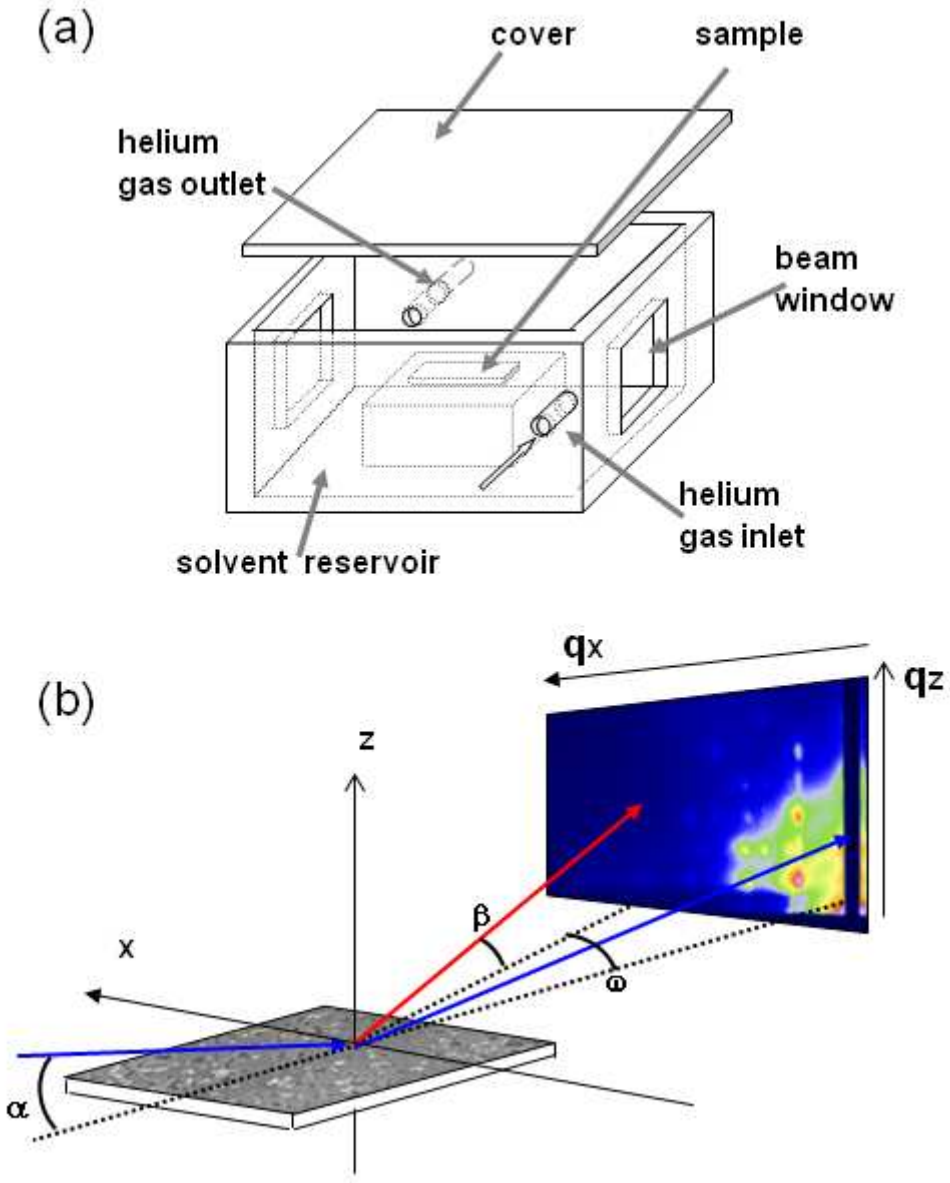
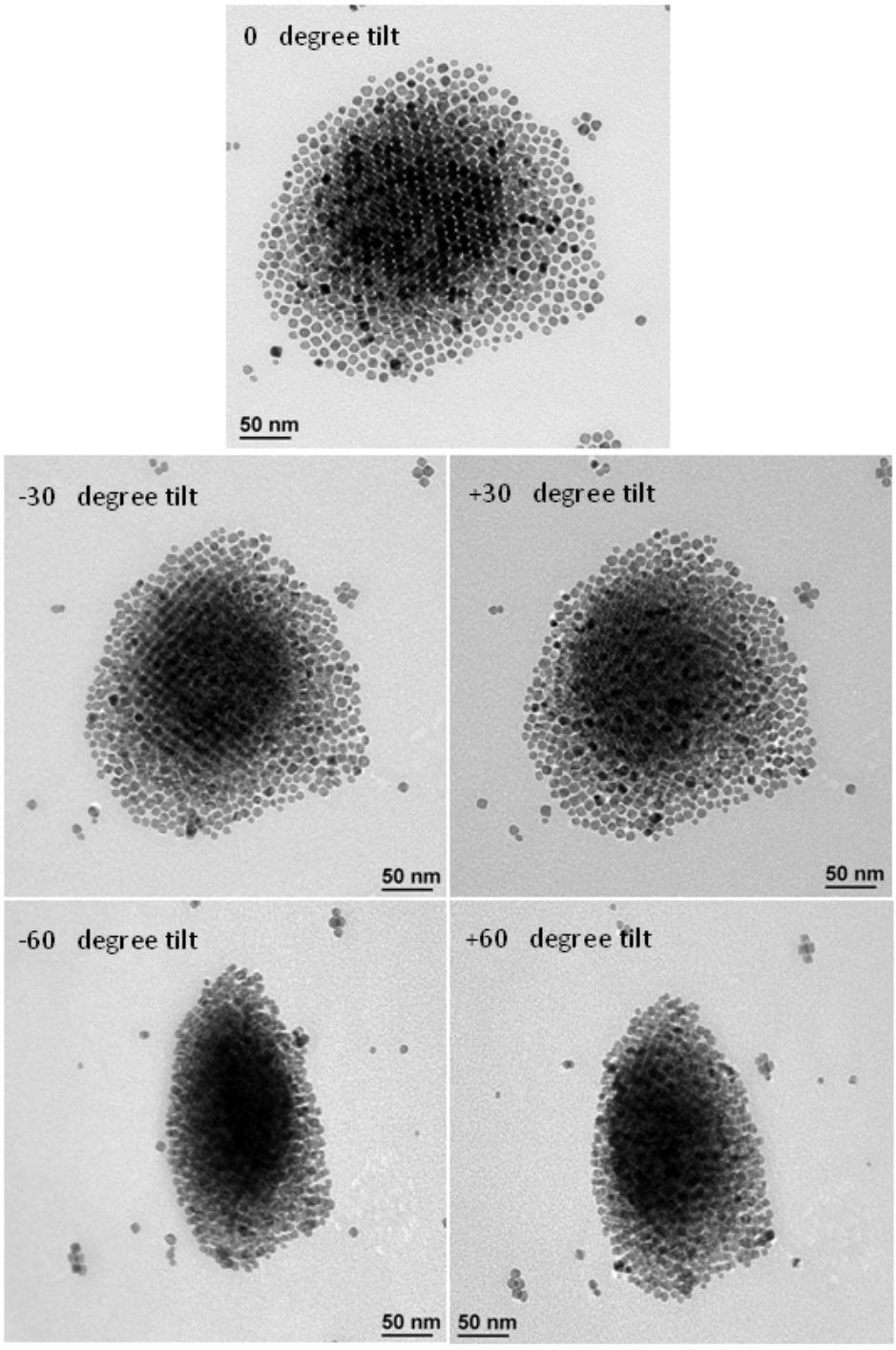


Figure S2: A series of representative TEM images taken at different tilting angles.



Movie S3: A movie of TEM image during the tilting experiment (separate file).

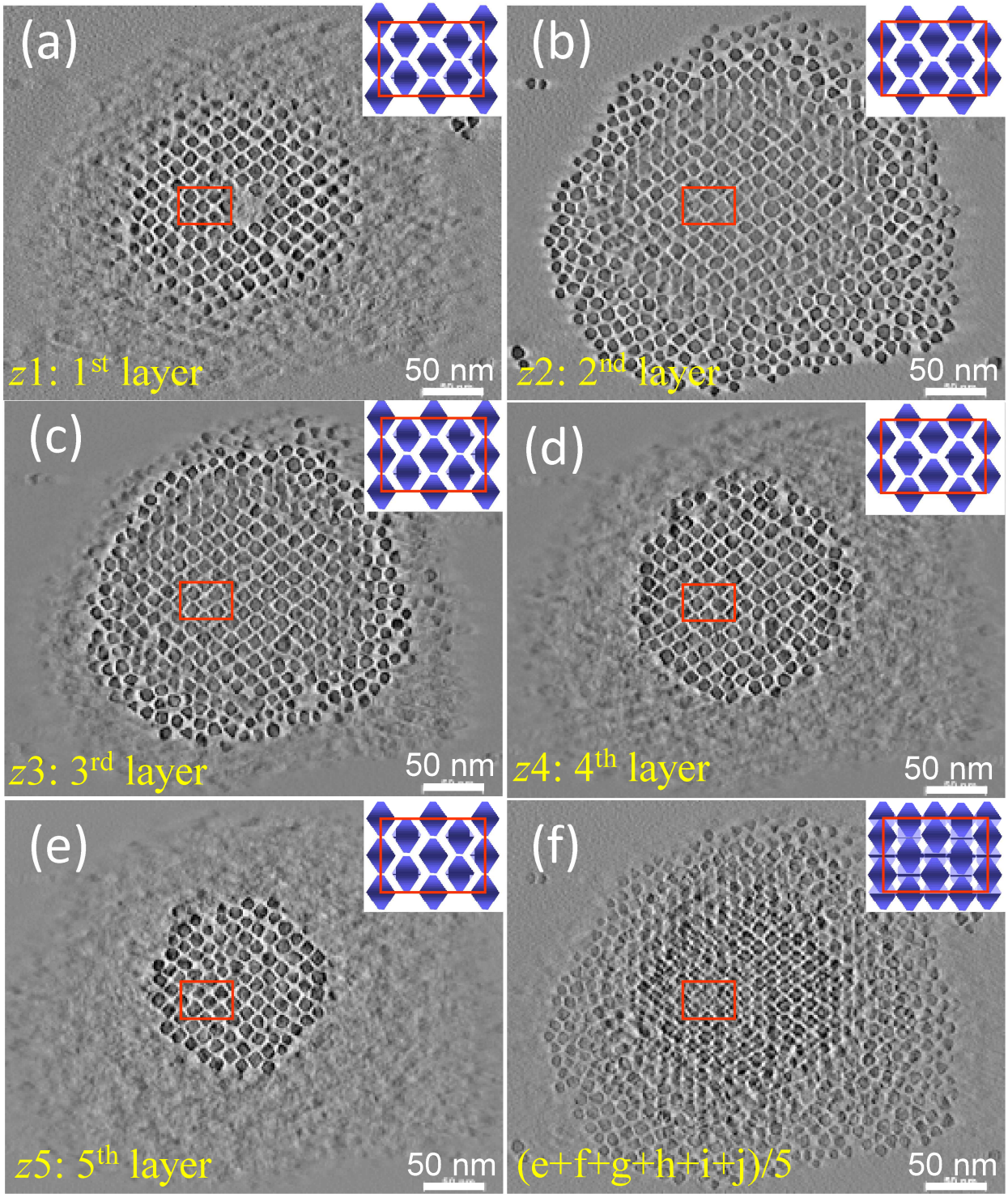
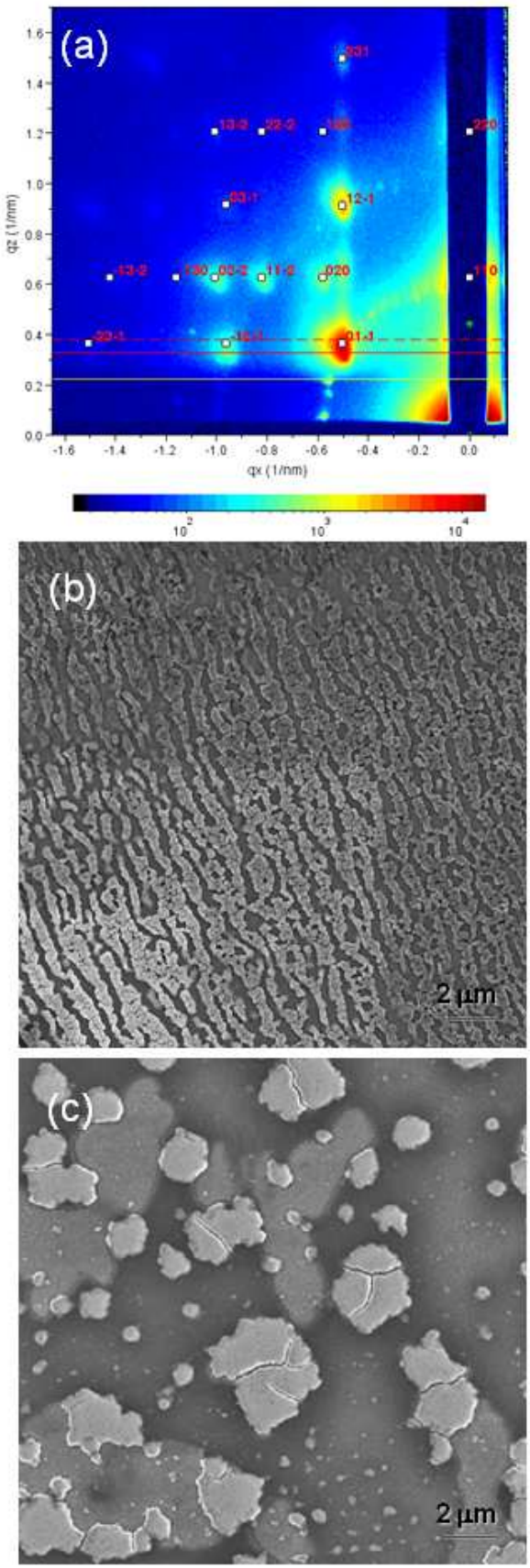


Figure S4. Electron tomographic structure. (a-e) slice plane views at the heights of $z1$ – $z5$ as indicated in Figure 2d; (f) averaged intensities of the images (a) through (e). Planar 2 x 2 unit cells are outlined in (a-f), with schematic structural models showing on the top-right corner of each image.

Figure S5. Images of drop-cast Pt_3Cu_2 nanoctahedron supercrystal. (a), GISAXS pattern of the SC film after the solvent was completely dried, showing a *bcc* superlattice; (b), SEM image of the same SC film used in (a); (c), SEM image of the same sample but after a "solvent annealing" process. The yellow marks in (a) are the theoretical diffraction dots of a uniaxially oriented *bcc* 2D powder, and with the (110) plane oriented parallel to the Si substrate.



Movie S6: A movie of Pt_3Cu_2 nanoctahedron self-assembly GISAXS patterns during a slow drying (separate file).

Figure S7. A large-area SEM image of a supercrystal consisting of Pt_3Cu_2 nanoctahedra, collected after the GISAXS solvent annealing experiment.