Electronic Supporting Information

Solution Chemistry based Nano-structuring of Copper Dendrites for efficient use in Catalysis and Superhydrophobic Surfaces

Rangarajan Bakthavatsalam[†], Subrata Ghosh[†], Ratul Krmar Biswas[†], Aayushi Saxena[†], Alagar Raja[‡], Musthafa Ottakam Thotiyl[‡], Sandip Wadhai[§], Arun G. Banpurkar[§], Janardan Kundu[†*]

[†] Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra, India, 411008.
[‡] Department of Chemistry, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pune, Maharashtra, India, 411008.
[§] Department of Physics, Savitribai Phule Pune University, Ganeshkhind, Pune, Maharashtra, India, 411007

Electronic Supporting Information Available: Photographs of vials containing Al foil in $CuSO_4$ and $Cu(NO_3)_2$ in absence of Cl^- anion; TEM/SAED characterization of prepared Cu dendrites; SEM images of Cu deposit obtained using $CuSO_4$ (50 mM) and NaCl (500 mM) [Cu^{2+} : Cl^- = 1: 10]; SEM images of the Cu deposit obtained using CuSO4 (50 mM) and HCl (500 mM); HRTEM image of the tip of the central trunk and tip of the primary branch; UV-Vis spectra of various Cu^{2+} solutions; SEM images of Cu deposit obtained from $Cu(NO_3)_2$ (50 mM) and NaCl/HCl (100 mM) after 2 and 12 hrs.; Photographs of reaction vials in presence of externally added sulphate/nitrate salts; Photograph of reaction vial confirming catalytic reduction; Schematic representation liquid drop on smooth surfaces (Young-Dupre equation) and rough intrinsically hydrophobic surfaces (Cassie-Baxter equation); Real time video of water droplet rolling off of the superhydrophobic surface. This material is available free of charge via the Internet at http://pubs.acs.org

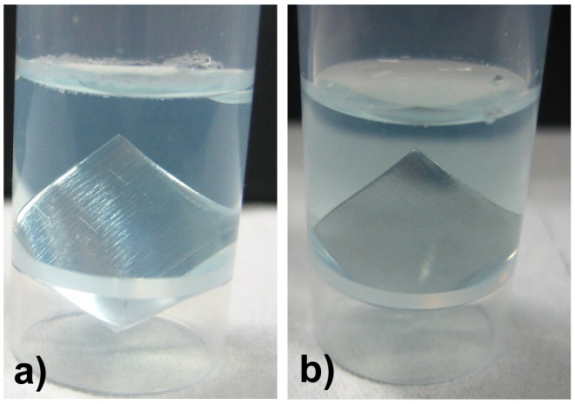

Figure S1: Photographs of vials containing Al foil immersed for an hour in a) $CuSO_4$ b) $Cu(NO_3)_2$ in the absence of Cl^- anion wherein the GRR deposition of Cu is highly retarded/inhibited.

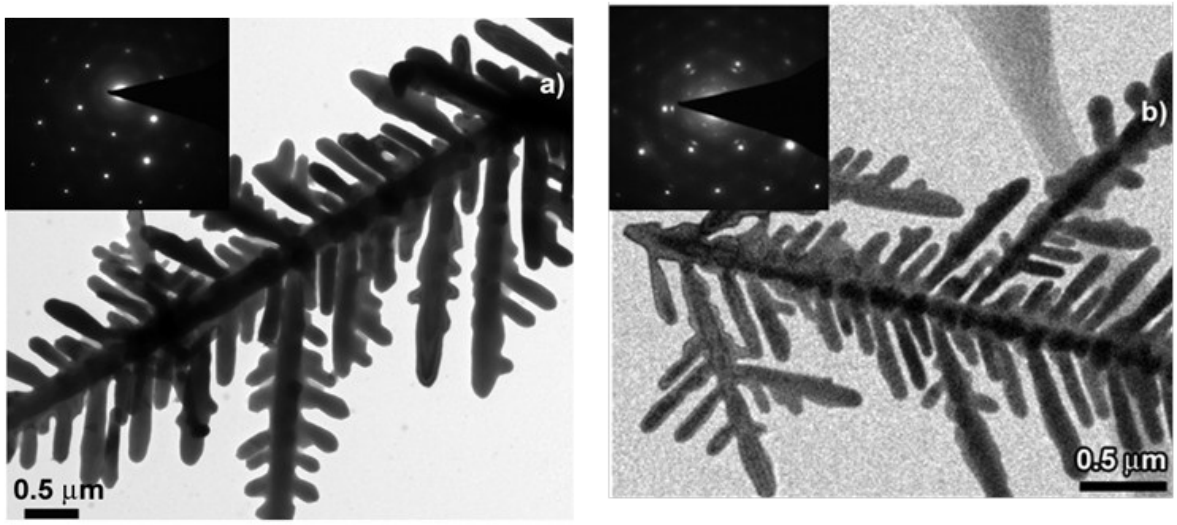

Figure S2: TEM image of Cu dendritic structures prepared using a) $CuSO_4$ (50mM), HCl (100mM), Inset shows the corresponding SAED pattern; b) $CuSO_4$ (50mM), NaCl (100mM), Inset shows the corresponding SAED pattern. Angles between the central trunk and primary branches for a) and b) are 55^o and 60^o respectively (Measured using NIH open source software: ImageJ)

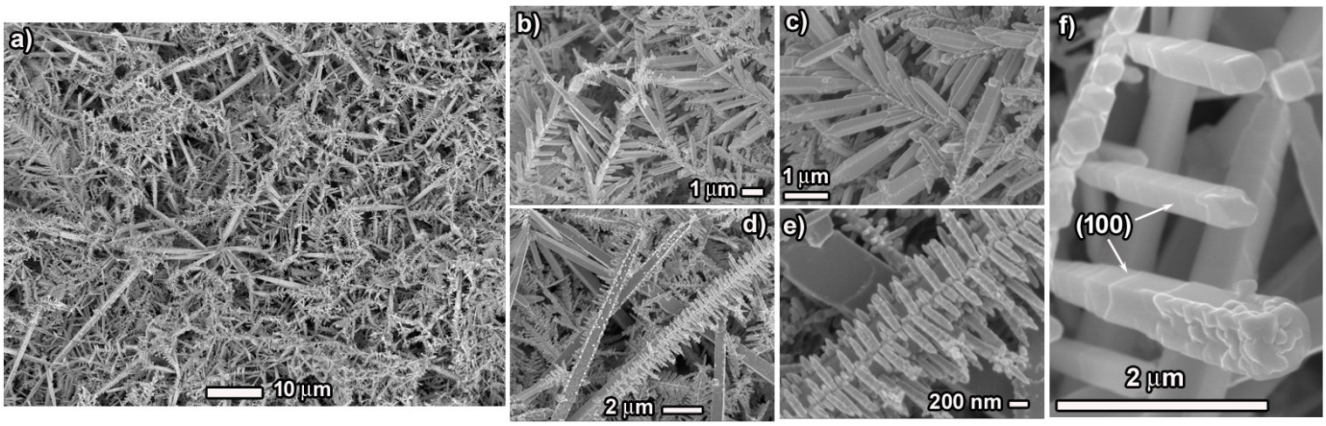

Figure S3: SEM images of the Cu deposit on Al foil obtained using $CuSO_4$ (50 mM) and NaCl (500 mM) [Cu^{2+} : Cl^- = 1: 10] showing the a) low magnification image, b)-c) high magnification image of the "dendritic like" structures, and d)- f) high magnification image of the "micro rod like" structures.

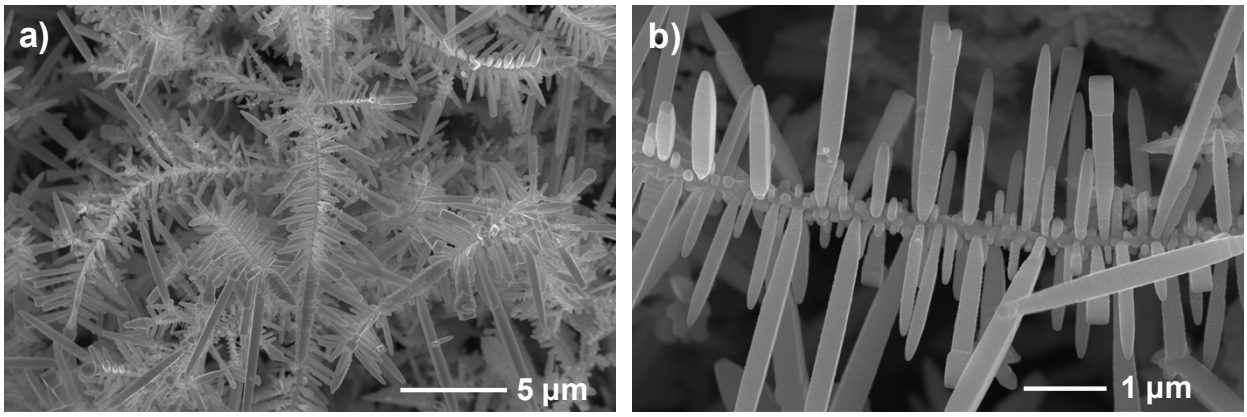

Figure S4: SEM images of the Cu deposit on Al foil obtained using $CuCl_2$ showing the a) low magnification image, b) high magnification image of the "dendritic like" structures with 3 dimensional growth of the smooth faceted rod like structures constituting the primary branches.

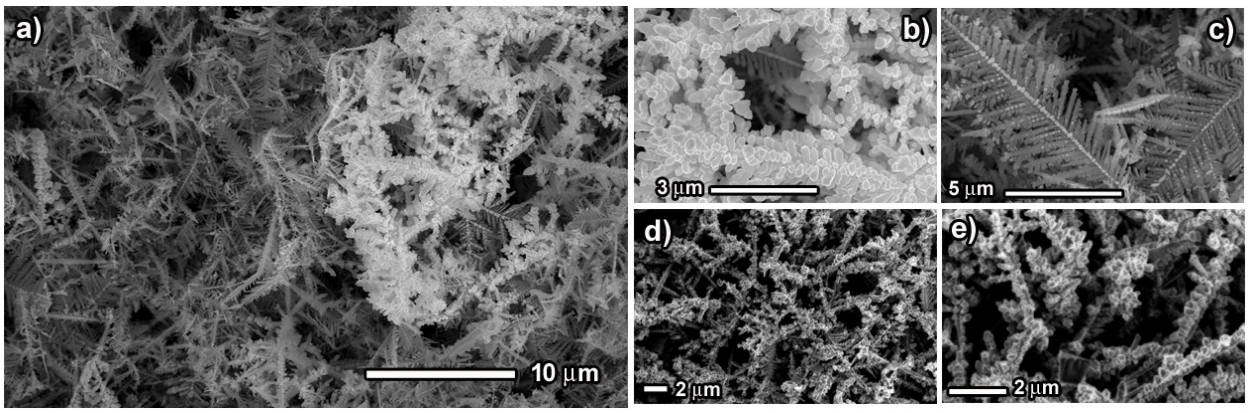

Figure S5: SEM images of the Cu deposit on Al foil obtained using $CuSO_4$ (50 mM) and HCl (500 mM) showing the a) low magnification image, c) high magnification image of the "dendritic like" structures, and b), d), e) high magnification image of the rough "wire like" structures.

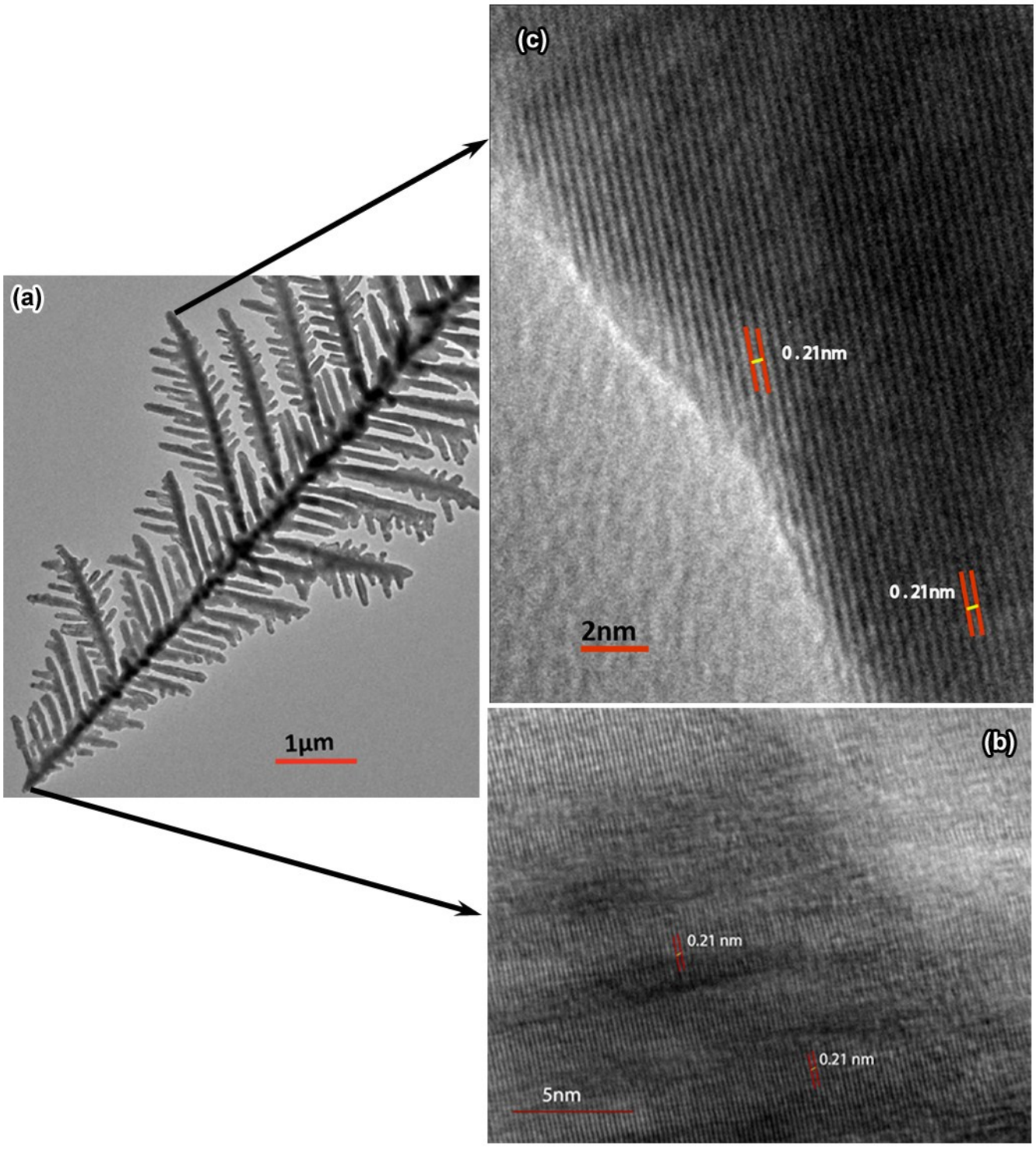

Figure S6: HRTEM image of a) Cu dendrite, b) the tip of the central trunk, c) tip of the primary branch showing fringes with inter-planar spacing of ~ 0.21 nm corresponding to {111} planes.

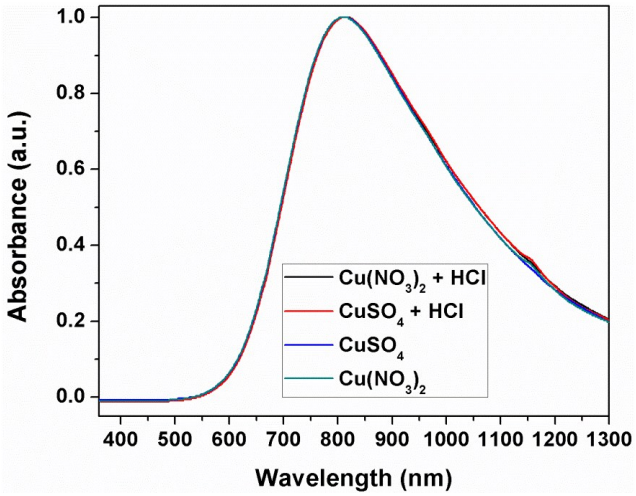

Figure S7: UV-Vis spectra of solution of $CuSO_4$ (25 mM), $Cu(NO_3)_2$ (25 mM), $CuSO_4$ (25 mM) + HCl(50 mM), and $Cu(NO_3)_2$ (25 mM)+ HCl (50 mM) showing almost identical features in the spectra indicating the similarity of the nature of the hydrated Cu^{2+} cation present in these solutions.

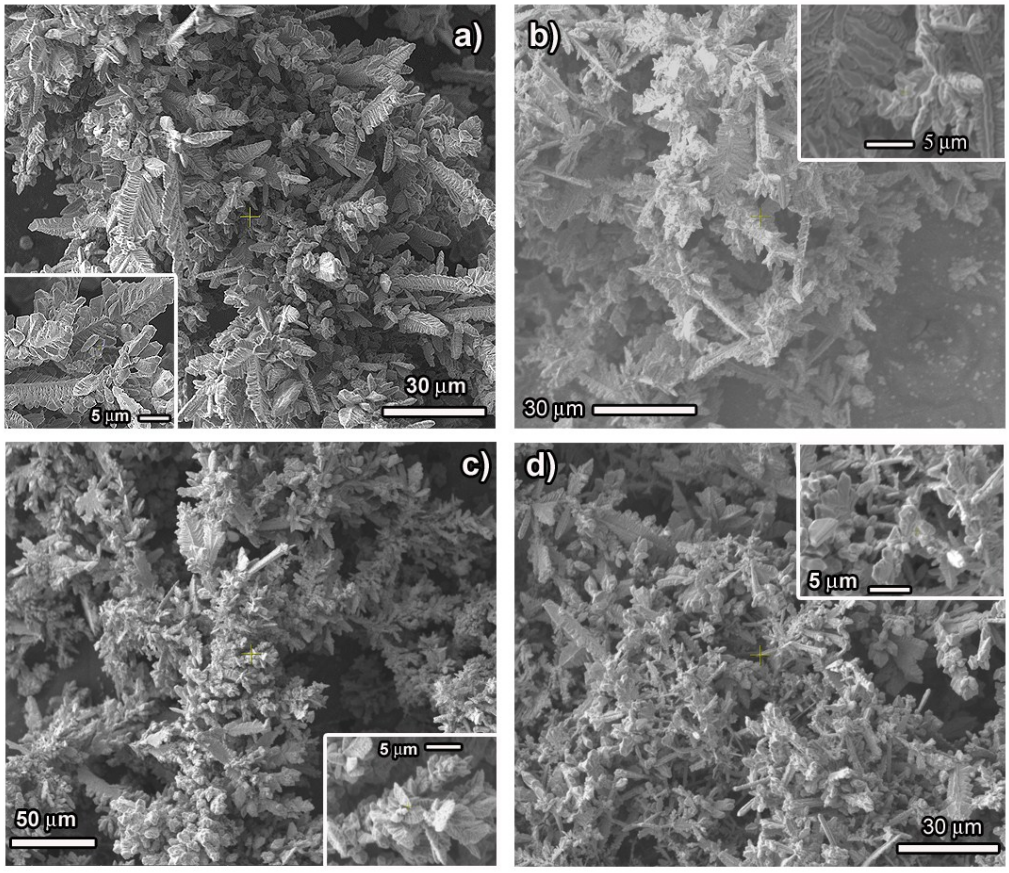

Figure S8: SEM images of the Cu deposit obtained from a solution of $Cu(NO_3)_2$ (50 mM) and a) NaCl (100 mM), 2 hrs., b) HCl (100 mM), 2 hrs., c) NaCl (100 mM), 12 hrs., d) HCl (100 mM), 12 hrs. respectively showing the "poisoning" effect of the Nitrate counter anions.

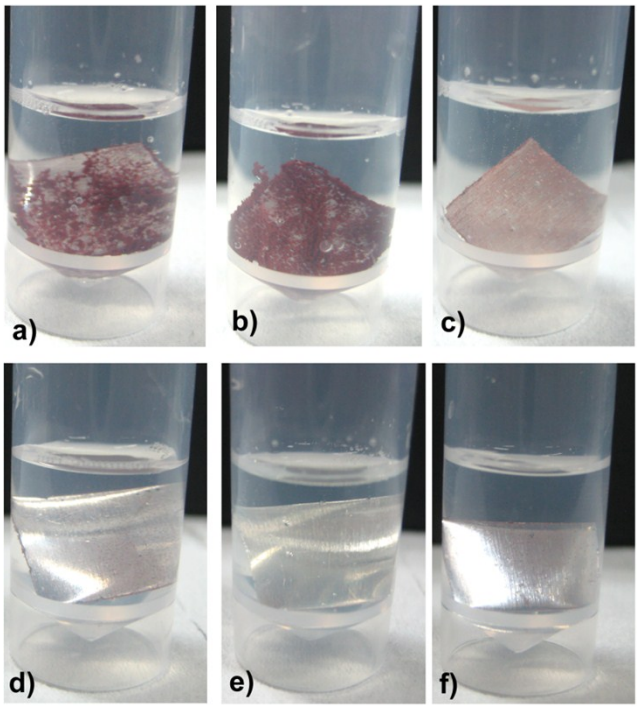

Figure S9: Effect of addition of external salts as depicted by the photographs of Al foil in vials containing a) $CuSO_4$ (25mM), HCl (50mM) and Na_2SO4 (50mM); b) $CuSO_4$ (25mM), NaCl (50mM) and Na_2SO4 (50mM); c) $Cu(NO_3)_2$ (25mM), HCl (50mM) and Na_2SO4 (50mM); d) $Cu(NO_3)_2$ (25mM), NaCl (50mM) and Na_2SO4 (50mM); e) $CuSO_4$ (25mM), HCl (50mM) and $NaNO_3$ (50mM); f) $CuSO_4$ (25mM), NaCl (50mM) and $NaNO_3$ (50mM).

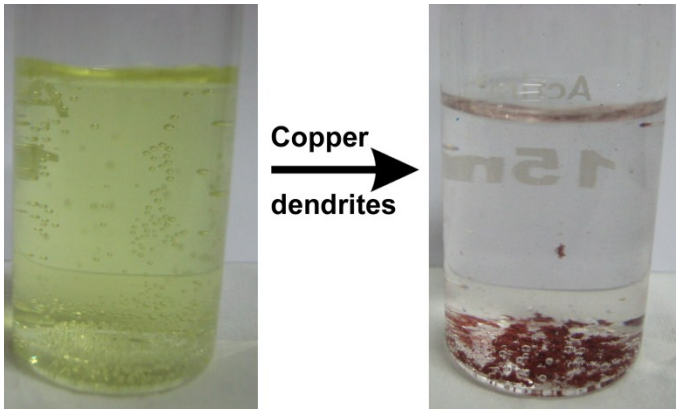

Figure S10: Photograph of a reaction vial containing 4-NP in presence of excess $NaBH_4$ (left) showing the yellow color of the solution. After the addition of the Cu dendrites, the yellow color disappears due to the catalytic reduction of 4-NP to 4-AP as shown by the photograph of the reaction vial in the right.

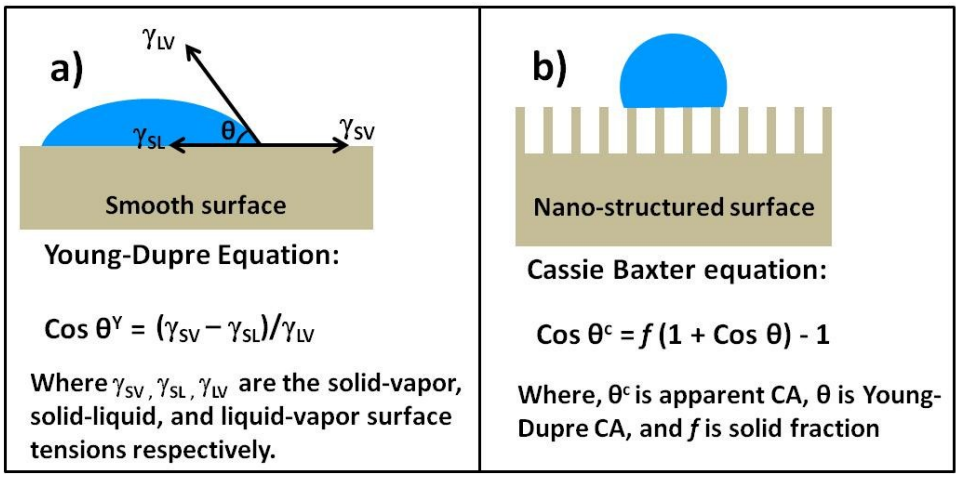

Figure S11: Schematic representation of the behavior of a liquid on a) smooth surfaces and the corresponding Young-Dupre equation, b) rough intrinsically hydrophobic surfaces and the corresponding Cassie-Baxter equation.