Electronic Supplementary Information

Nano- and Micro-Hexagons of Bismuth on Polycrystalline Copper: Electrodeposition and Heavy Metal Sensing

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Electrochemical studies of bismuth deposition – CV, LSV in bismuth nitrate bath as functions of scan rate, bismuth ion concentration, nitric acid concentration, CA, nucleation mechanism studies, LSV in nitric acid solution, SEM images under different conditions of deposition, and TEM images of the obtained bismuth hexagons are provided.

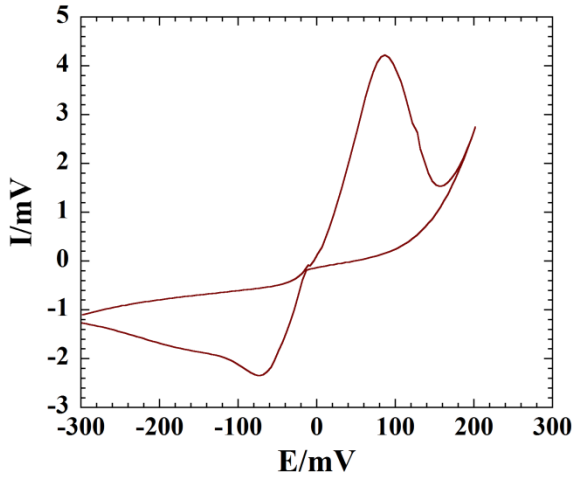


Figure S1. Cyclic voltammetry for bismuth onto copper electrode from 10mM of Bi^{3+} solution in 0.2M HNO_3; Scan rate was 50 mV/s.

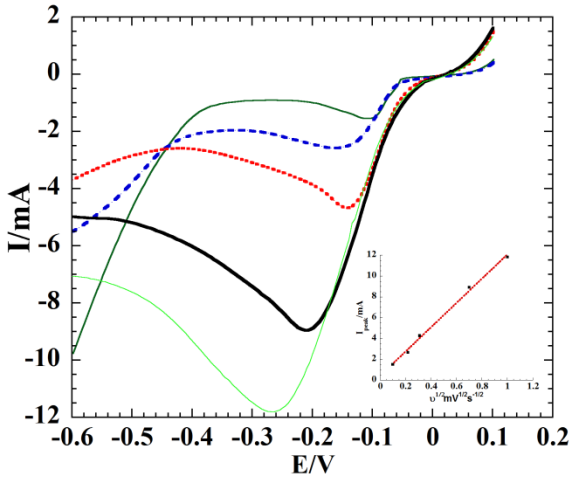


Figure S2a. LSV for bismuth onto copper from 10mM of Bi^{3+} solution in 0.2M HNO_3 at different scan rates (10, 50, 100, 500, 1000 mV/s); Inset: Cathodic peak current (I_{peak}) vs. Square root of scan rates.

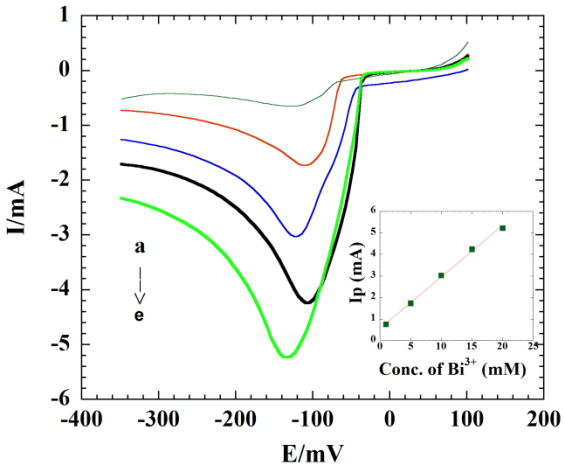


Figure S2b. LSV for bismuth electrodeposition onto copper from various concentrations of Bi^{3+} (a) 1, (b) 5, (c) 10, (d) 15, (e) 20mM in 0.2M HNO_3. Scan rate was 50 mV/s; Inset: Plot of peak current (I_{peak}) vs. Concentration of Bi^{3+}.

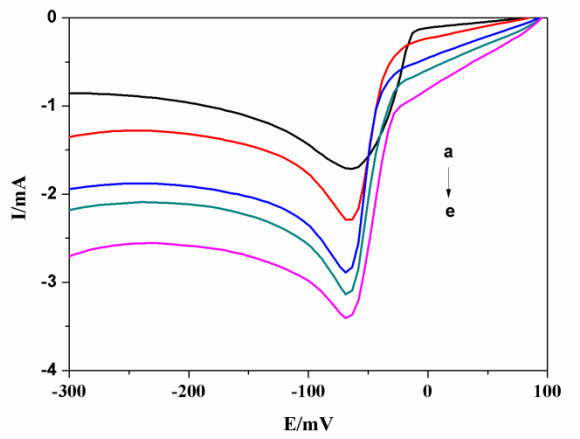


Figure S2c. LSV for bismuth onto copper from 10mM of Bi^{3+} in various concentration of HNO_3 (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8, (e) 1M. Scan rate was 50 mV/s.

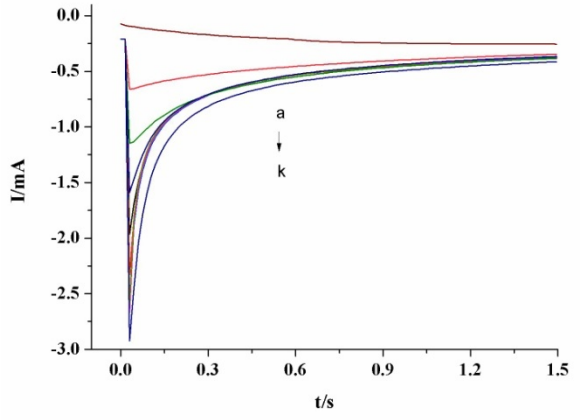


Figure S3a. Chronoamperometry for bismuth electrodeposition on copper in the presence of 10mM of Bi^{3+} solution in 0.2M HNO_3. The electrode potential was stepped from 0 to (a) -25, (b) -50, (c) -75, (d) -100, (e) -125, (f) -150, and (g) -175, (h) -200, (i) -225, (j) -250, (k) -275 mV with a deposition time of 1.5 sec.

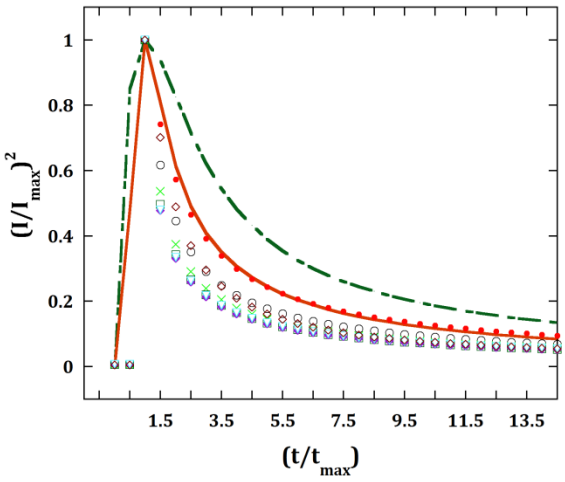


Figure S3b. Chronoamperometry (10mM of Bi^{3+} and 0.2M HNO_3). The electrode potential was stepped from 0 to (•) −125, (o) −150, (×) −175, (□) −200, (♦) −225, (∇) −250, (◊) −275mV. The theoretical transients for instantaneous (double dotted line) and progressive (solid line) nucleation were calculated according to the Scharifker-Hills model.

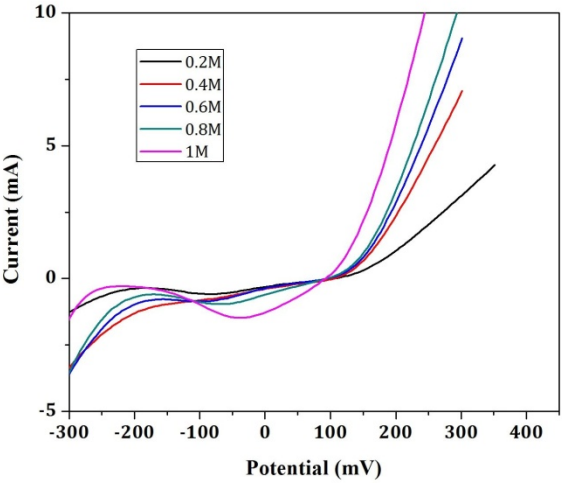
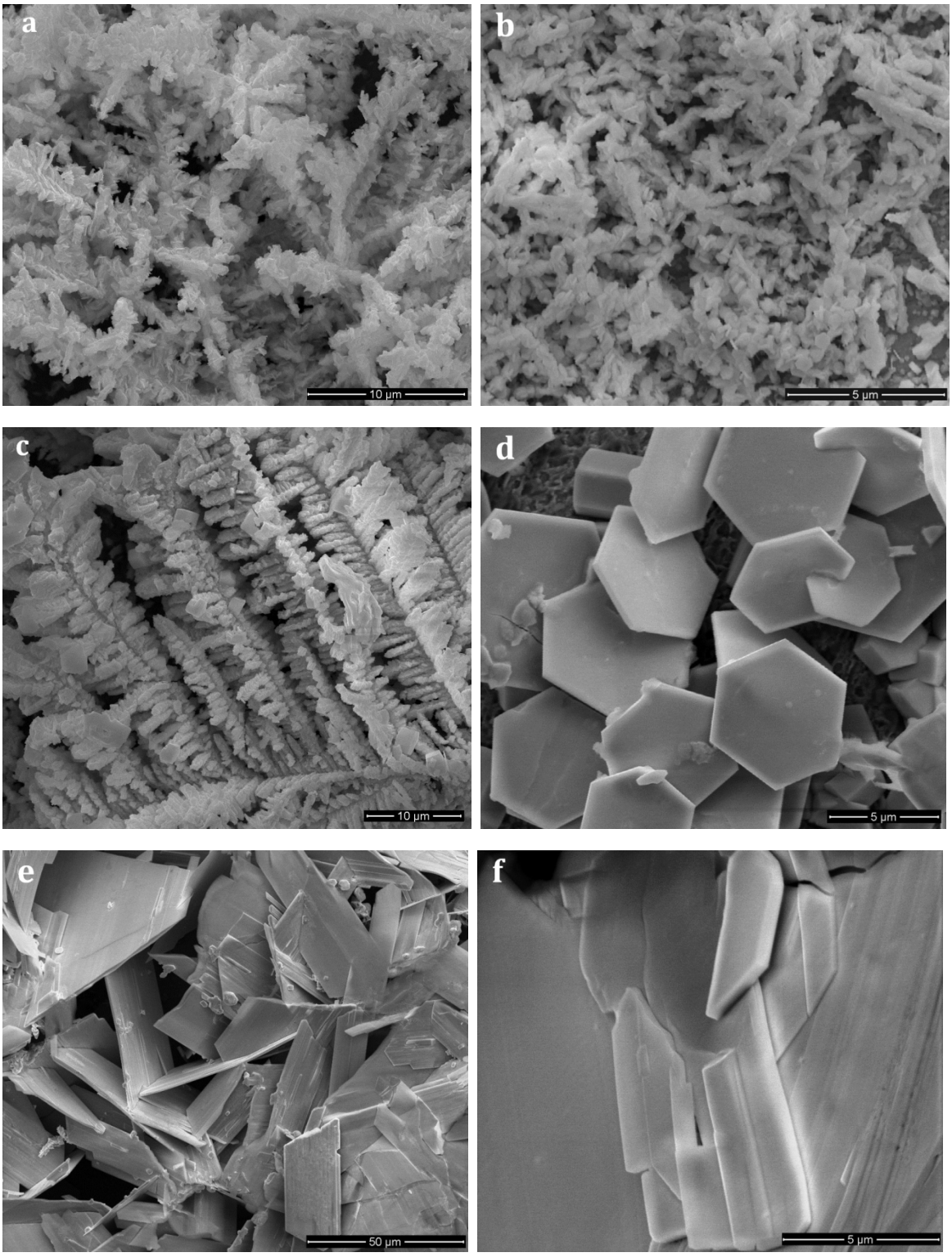


Figure S4. LSV for nitric acid solutions (0.2, 0.4, 0.6, 0.8, 1M) on polycrystalline copper electrode in the absence of Bi^{3+} ions; Scan rate was 50mV/s.



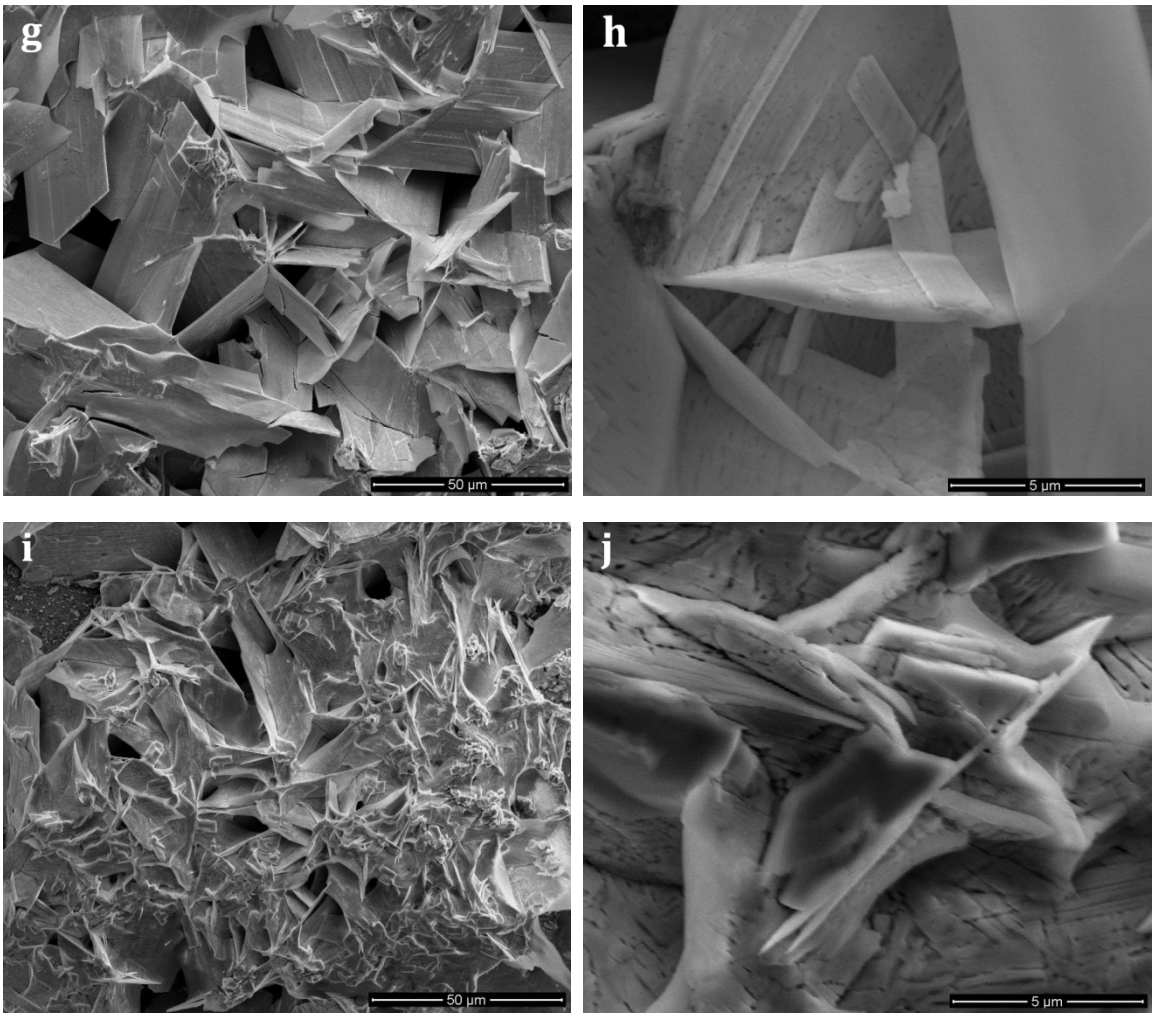
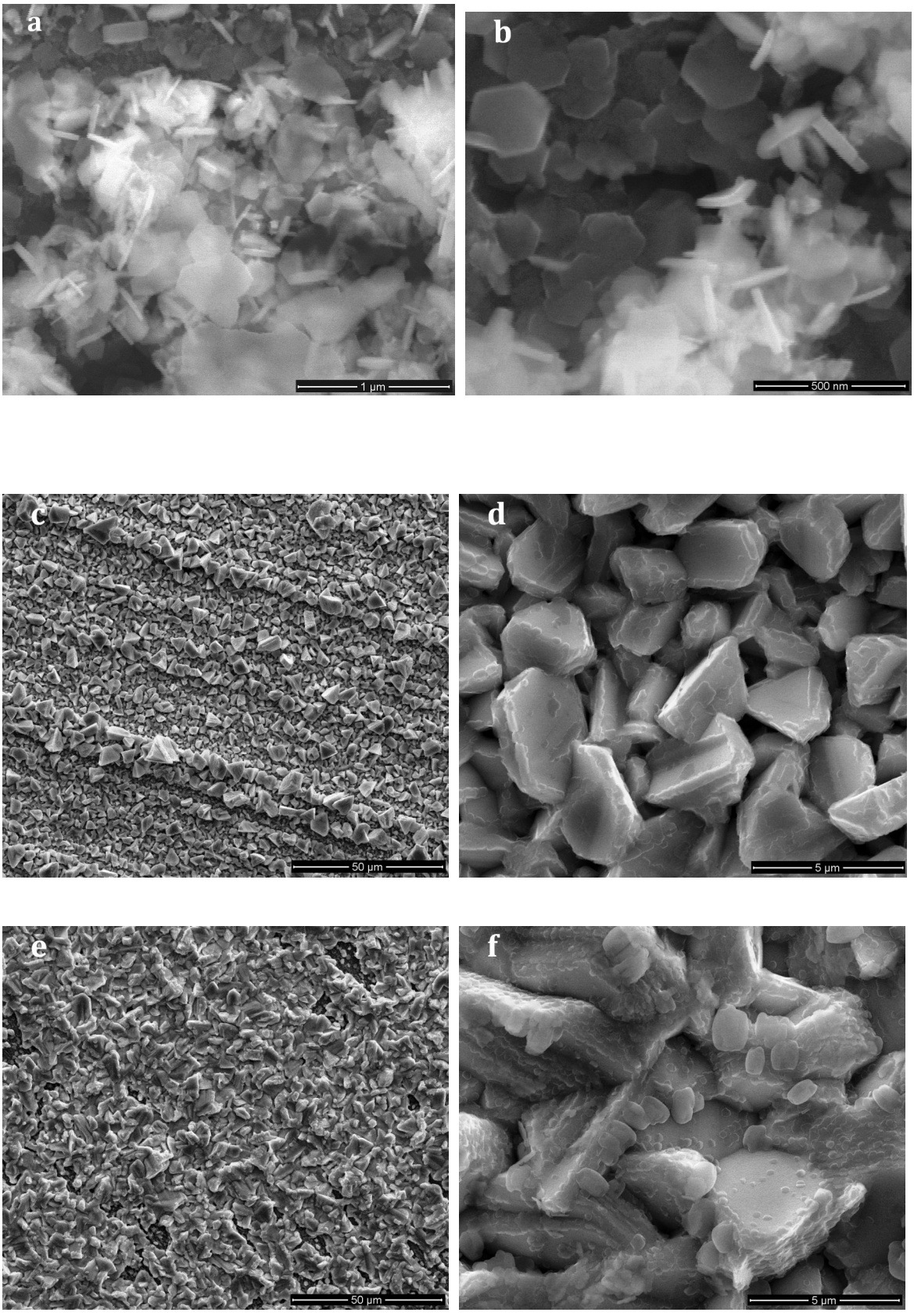


Figure S5. SEM images of bismuth electrodeposition onto copper substrate are obtained at different electrodeposition bath conditions for 360 s; (a), (b): 10mM Bi^{3+} in 0.2M HNO_3, (c), (d): 10mM Bi^{3+} in 0.4M HNO_3, (e), (f): 10mM Bi^{3+} in 0.6M HNO_3, (g), (h): 10mM Bi^{3+} in 0.8M HNO_3, (i), (j): 10mM Bi^{3+} in 1.0M HNO_3 at a constant current density of 10mA/cm^2.



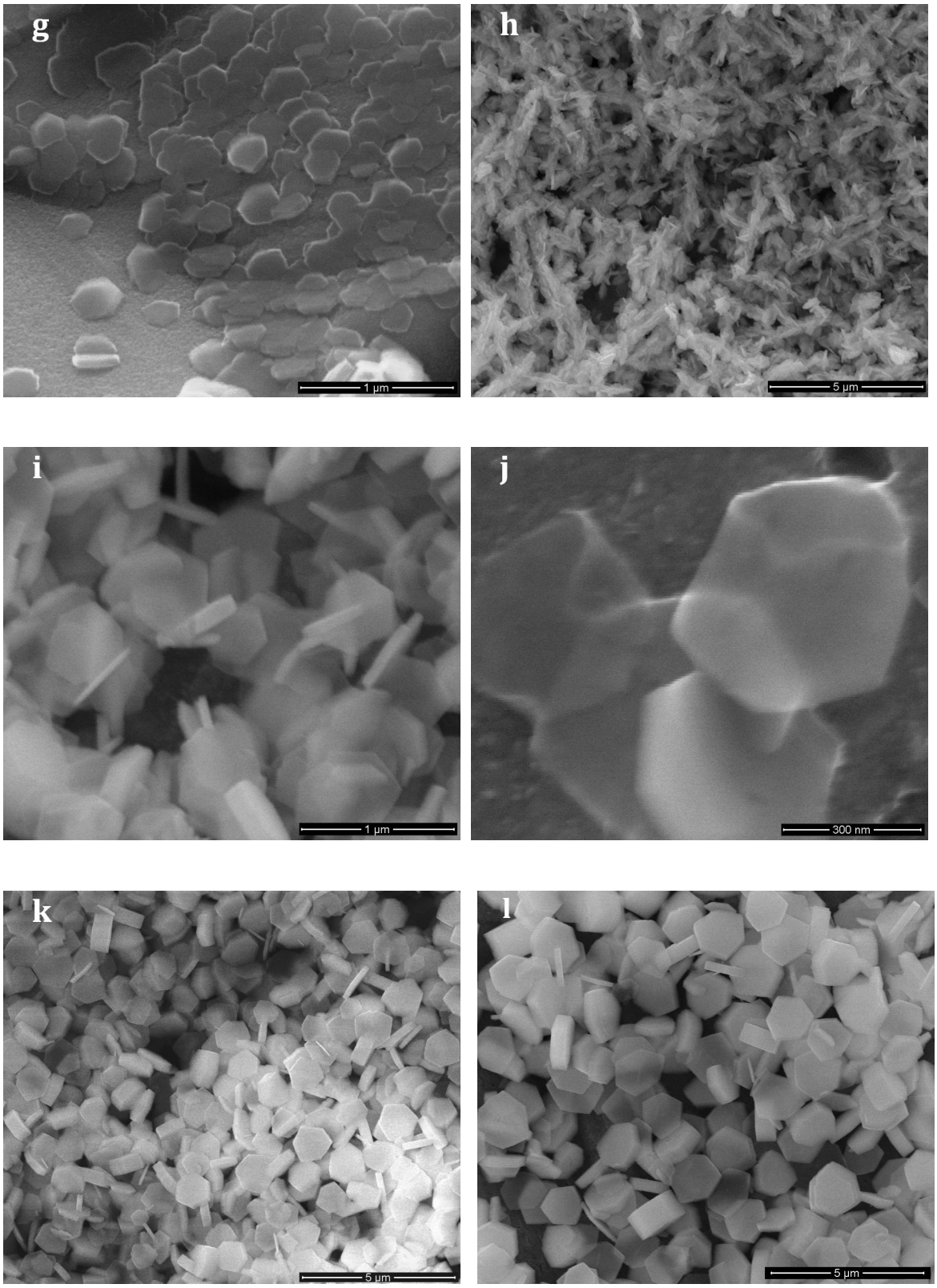


Figure S6. SEM images of bismuth electrodeposition onto copper substrate are obtained at different electrodeposition bath conditions for 360 s; a), b): 1 mM Bi^{3+} in 0.2M HNO_3 at current density of 10

mA/cm^2; c, & d) 20 mM Bi^{3+} in 0.2 M HNO_3 at 10 mA/cm^2; e, f, & g) 10 mM Bi^{3+} in 0.2 M HNO_3 at current density of 1 mA/cm^2; h, i, & j) 10 mM Bi^{3+} in 0.2 M HNO_3 at current density of 25 mA/cm^2, k) 10 mM Bi^{3+} in 0.2M HNO_3 at constant potential −150 mV, l) 10 mM Bi^{3+} in 0.2M HNO_3 at constant potential −150 mV with a nucleation pulse of + 50 mV for 1 s.

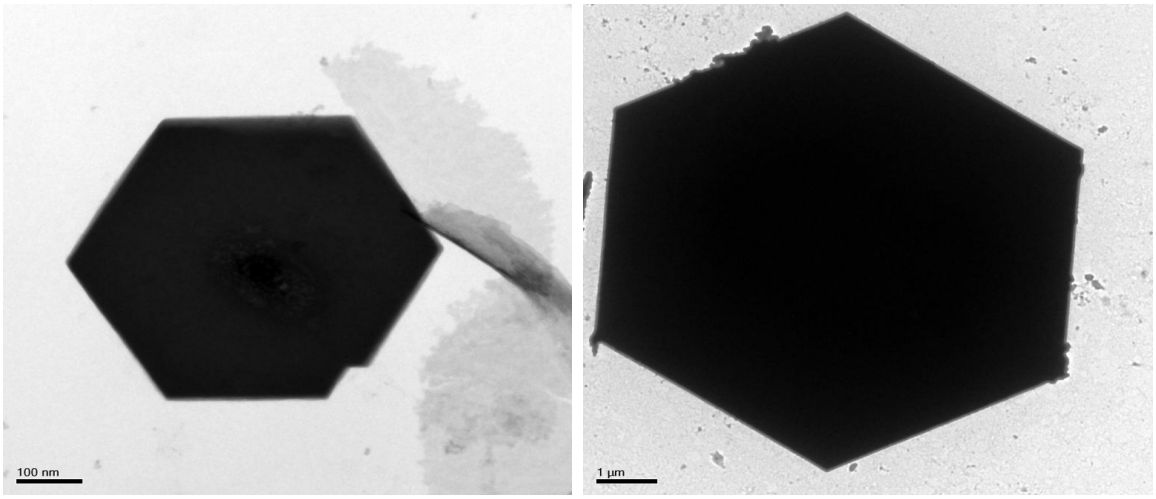


Figure S7. HRTEM images of electrodeposited bismuth hexagons onto copper substrate at obtained at different electrodeposition bath conditions for 360 s; a): 10 mM Bi^{3+} and 0.2 M HNO_3, b): 10 mM Bi^{3+} and 0.4 M HNO_3, at 10 mA/cm^2 current density.

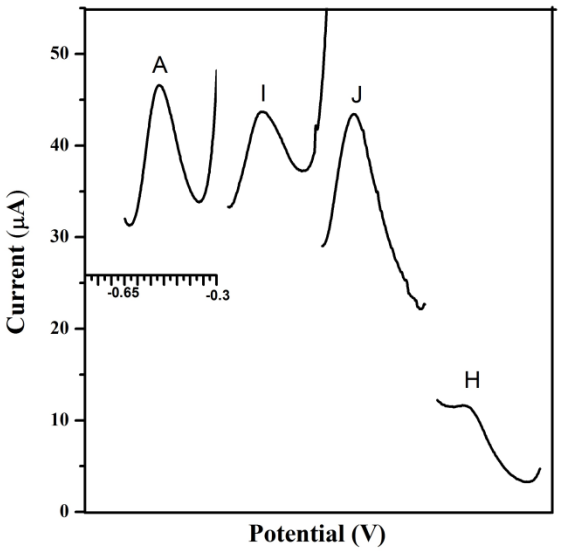


Figure S8a. Square wave anodic stripping voltammograms of Pb at 1 ppb on different bismuth modified electrodes (samples A, H, I & J).

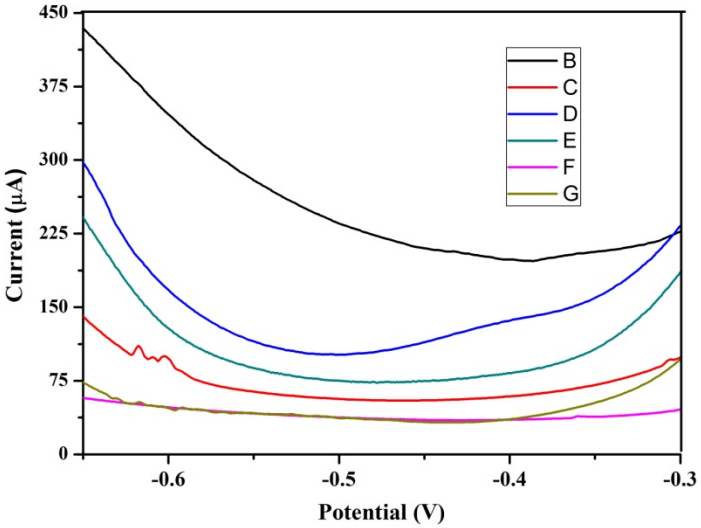


Figure S8b. Square wave anodic stripping voltammograms of Pb at 1 ppb on different bismuth modified electrodes (samples B, C, D, E, F, & G).