Supplementary Information (SI) for Dalton Transactions.

Supplementary Information

Kinetically Controlled Morphology and Composition of Colloidal Nanoparticles: Cation Exchange Reactions from Copper Sulfide to Transition Metal (Mn, Zn, Fe, and Co) Sulfides

Boeun An, Wooseok Jeong, Yun Jae Hwang, Hyeonseok Lee, Yeongbin Lee, Heesoo Jeong, Gyuhyeon Kim and Don-Hyung Ha*

School of Integrative Engineering, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul, 06974, Republic of Korea

* To whom correspondence should be addressed.

Email: dhha@cau.ac.kr (D-H. Ha), Phone: +82-2-820-5565

Cation exchange reactions of Fe^{2+}

The cation exchange reaction was conducted using a modified version of previously reported method. [1] The cation exchange reactions were conducted with a molar ratio of copper to manganese set at 1:3. Initially, 120mg of roxbyite Cu_7S_4 NPs was dispersed in 4ml of toluene and 6ml of TOP in a 20ml vial. The vial was degassed at room temperature, refilled with nitrogen gas, and sonicated for 1 hour. During the sonication, 0.148g of $FeCl_2·4H_2O$and 15ml of OLAM were introduced into a 50ml three-neck round-bottom flask. This mixture was degassed under vacuum with stirring for 30min at room temperature. Subsequently, the mixture was degassed at 70°C for 30min and then at 120°C for 30min under vacuum with vigorous stirring. The temperature was raised to 180°C and maintained for 30min to prepare the metal cation precursor solution. The temperature was then lowered to 90°C and 10ml of toluene was injected into the precursor solution. When the temperature reached 70°C, the solution containing the Cu_7S_4 nanoparticles was rapidly injected into the three-neck flask. The cation exchange reaction was then progressed for 5 hours. The aliquots were collected at various reaction time (from 10min to 5 hours) for analysis of intermediate products. After the reaction, all the exchanged samples were dispersed in toluene and precipitated with ethanol. The suspensions were isolated by centrifugation three times at 10,000rpm for 3 min.

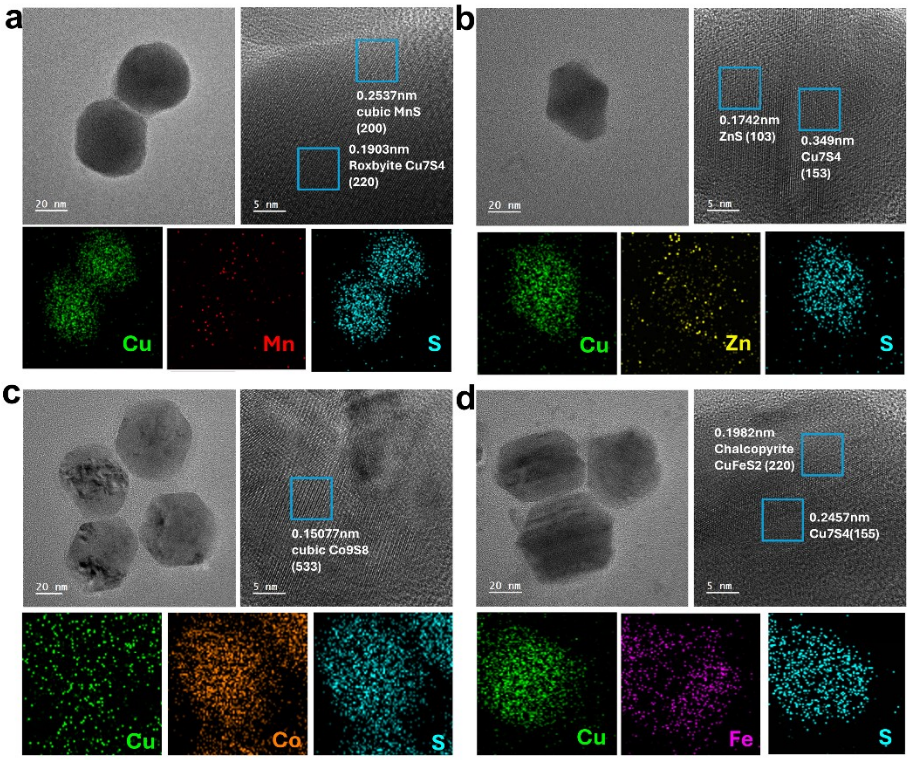

Figure S1. TEM images for analyzing the morphological transformation of the cation-exchanged sample at reaction times of 10 min. (a) Mn (b) Zn (c) Fe (d) Co

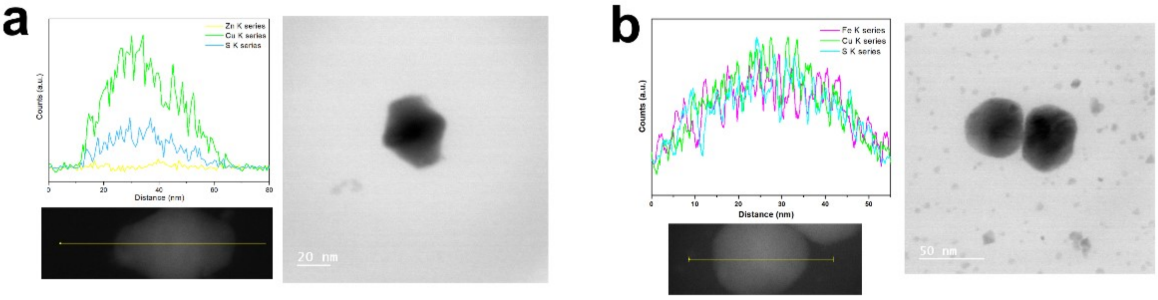

Figure S2. TEM EDS line scanning analysis of cation exchanged samples with distinct structures (a) 10-min Zn-exchanged sample (b) 5-h Fe-exchanged sample

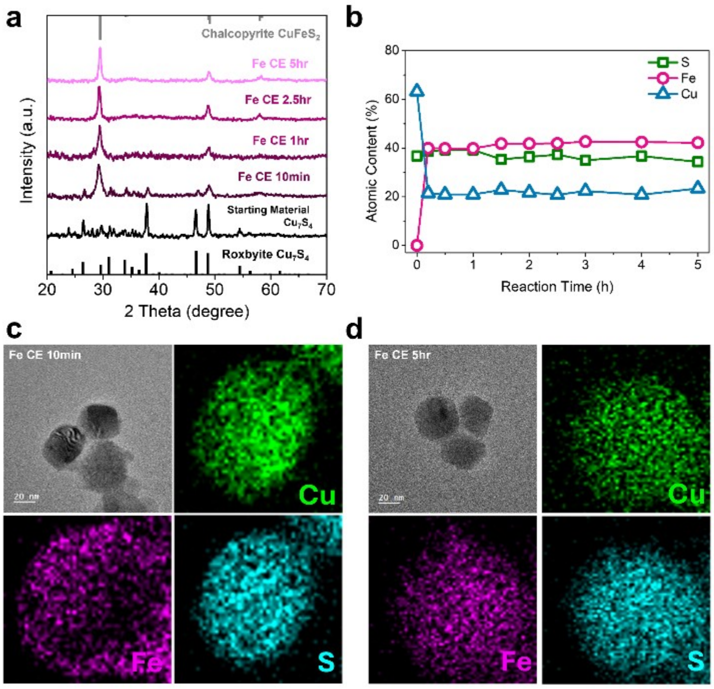

Figure S3. Characterizing the cation exchange reaction of Fe^{2+} for comparing to the case of Fe^{3+} (a) XRD patterns of cation-exchanged samples collected at different reaction times (10 min, 1 h, 2.5 h, and 5 h) (b) SEM-EDS analyses for compositional changes for Fe-exchanged sample at various reaction times from 10 min to 5 h (c-d) TEM images and EDS mappings for analyzing the morphological transformation of the cation-exchanged sample with Fe^{3+} at the reaction times of (c) 10 min and (d) 5 h

References

(1) Powell, A. E.; Hodges, J. M.; Schaak, R. E. Preserving both anion and cation sublattice features during a nanocrystal cation-exchange reaction: Synthesis of metastable wurtzite-type CoS and MnS. *Journal of the American Chemical Society* **2016**, *138* (2), 471-474.