Predominated Thermodynamically Controlled Reactions for Suppressing Cross Nucleations in Formation of Multinary Substituted Tetrahedrite Nanocrystals

Suman Bera, Anirban Dutta, Sankararao Mutyala, Dibyendu Ghosh, and Narayan Pradhan*

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata, India

First Author: suman.bera46@gmail.com, Corresponding Author: npiacs@gmail.com

ABSTRACT

Group I-II-V-VI semiconducting $Cu_{12-x}M_xSb_4S_{13}$ (M = Zn^{II}, Cd^{II}, Mn^{II} and Cu^{II}) substituted tetrahedrites nanostructures remains a new class of multinary materials which have not been widely explored yet.[1-2] Having different ions, the formation process of these nanostructures has always the possibility of formation of cross nucleations. Minimizing the reaction time, herein, a predominantly thermodynamically control approach is reported which decoupled the quaternary nucleations with their possible cross nucleations. As a consequence, possible cross nucleations were prevented and series of nearly monodisperse intriguing substituted tetrahedrite nanostructures are formed. The possible LaMer plot for this single- and also multi-materials nucleations is also proposed.

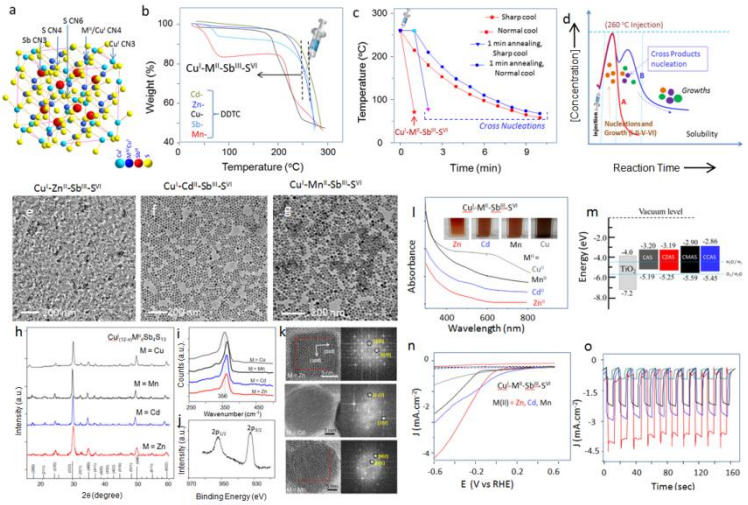


Figure 1. (a) Crystal structure of tetrahedrite crystal. (b) Thermogravimetric (TG) plots of DDTC complexes of Cu^{II}, Zn^{II}, Cd^{II} and Mn^{II}. (c) Reaction temperature vs. time plot. (d) Schematic presentation of LaMer plot for the nucleation and growth of multinary tetrahedrite nanocrystals. (e-g) Tem images of substituted tetrahedrites $Cu^{I}_{10}M^{II}_{2}Sb_4S_{13}$ nanocrystals where M=Zn, Cd and Mn respectively. (h) Powder XRD patterns. (i) Raman spectra of all these nanocrystals. (j) X-ray photoelectron spectra of Cu in $Cu^{I}_{10}M^{II}_{2}Sb_4S_{13}$ (M =Zn) showing absence of Cu^{II} in the nanocrystals. (k) HRTEM of single nanocrystal of these substituted nanocrystals and their selected area FFT patterns. (l) Absorption spectra of different tetrahedrites. (m) Band positions for all nanocrystals calculated from cyclic voltammetry. (n) Linear cyclic voltamogram of different substituted tetrahedrite photoelectrocatalysts. Dotted lines represent for dark and solid lines under illumination. (o) The time-dependent photocurrent density with illumination switched ON and OFF of modes of different photocathodes at −0.5 V vs. SCE.

Furthermore, bandgaps of all these new materials are calculated and preliminarily the applicability of these materials is tested for photoelectrochemical water splitting.

Reference:

(1) Van Embden, J.; Latham, K.; Duffy, N. W.; Tachibana, Y. Near-Infrared Absorbing $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4 Nanocrystals: Synthesis, Characterization, and Photoelectrochemistry. *J. Am. Chem. Soc.* **2013**, *135*, 11562-11571.

(2) Sarswat, P. K.; Free, M. L. Enhanced Photoelectrochemical Response From Copper Antimony Zinc Sulfide Thin Films on Transparent Conducting Electrode. *Int. J. Photoenergy* **2013**, 154694/1-154694/8.