Hydrothermal Synthesis of Copper Selenides with Controllable Phases and Morphologies from an Ionic Liquid Precursor

(Supporting Information)

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Fig. S1 1-n-butyl-3-methylimidazolium methylselenite ([BMIm][$SeO_2(OCH_3)$]).

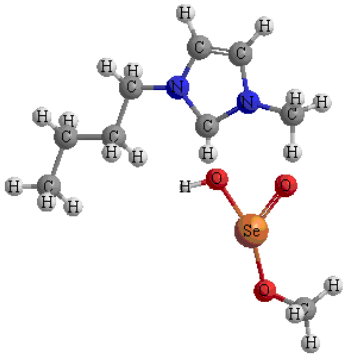
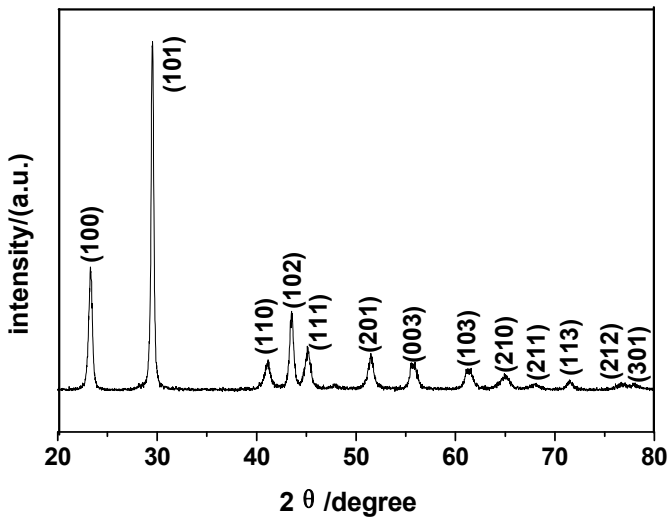


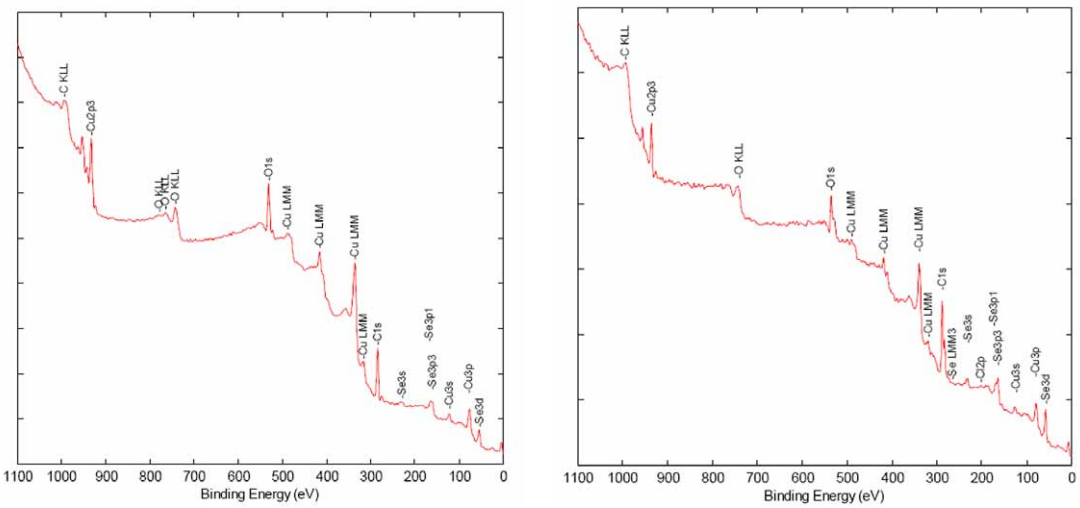
Fig. S2 XRD pattern of Se from [BMIm][$SeO_2(OCH_3)$].



In the experiment, 0.005 mol [BMIm][$SeO_2(OCH_3)$] was dissolved into 5 mL of deionized water under vigorous stirring, following by adding of 0.5 mL of $N_2H_4 \cdot H_2O$ (80%); then the mixture was transferred into a glass beaker; in the end, the solution was heated and aged at 120 °C for 12 h in an oven; finally, the product was wash with deionized water and anhydrous ethanol several times and dried in a vacuum at 60 °C for 6 h.

The XRD pattern of the product is shown in Figure S2. It can be seen that all of the reflection peaks can be indexed as hexagonal Se with the lattice parameters of $a = b = 4.364$ Å, $c = 4.955$ Å, which is in good agreement with the value reported in literature (JCPDS No. 06-0362). No characteristic peaks corresponding to impurities are found in the XRD pattern.

Fig. S3 Survey XPS spectra of (a) $Cu_{2-x}Se$ and (b) CuSe.



(a) (b)

Fig. S4 Schematic illustration of the chemical bonds in [BMIm][$SeO_2(OCH_3)$].

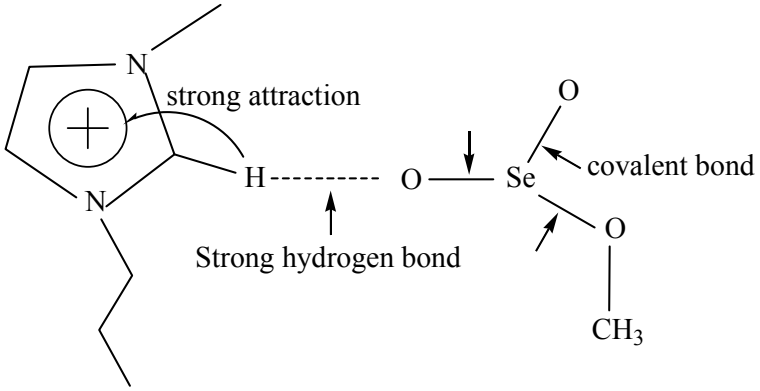
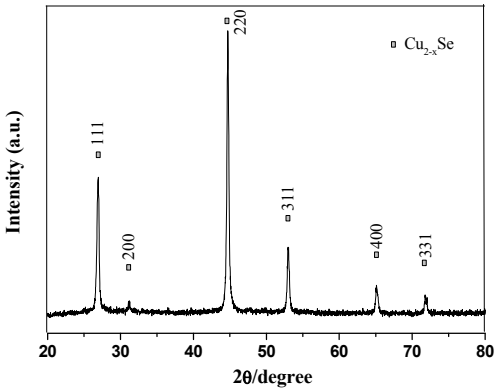
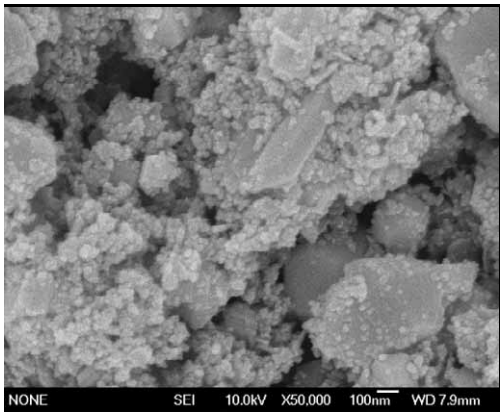


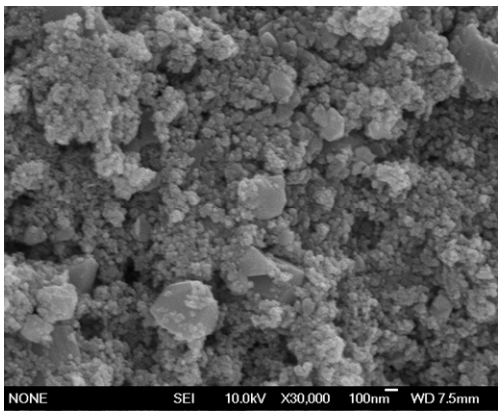
Fig. S5 (a) XRD pattern and (b) SEM image of $Cu_{2-x}Se$ from the Na_2SeO_3 precursor without using [BMIm]Br, (c) SEM image of $Cu_{2-x}Se$ from the Na_2SeO_3 precursor and equal mole amount of [BMIm]Br (XRD pattern is not listed).



(a)



(b)



(c)

Fig. S6a SEM image of sample 2 synthesized under the mole ratio of Cu/Se = 1 and reaction temperature 150 °C.

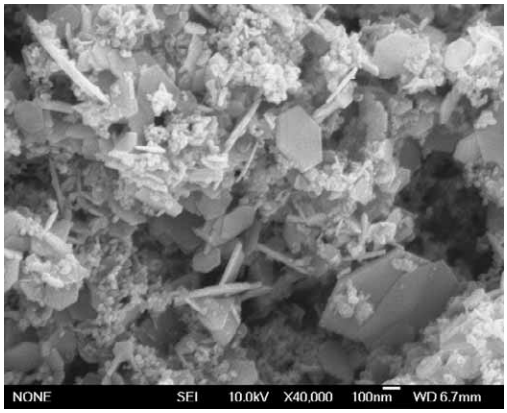
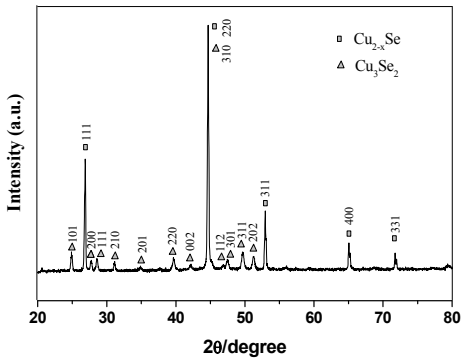


Fig. S6b XRD pattern of sample 1 synthesized under the mole ratio of Cu/Se = 2 and reaction temperature 120 °C.



The reflection peaks marked by triangular symbols can be indexed as Cu_3Se_2 of umangite structure with the cell parameters of $a = b = c = 6.403$ Å, which is in good agreement with JCPDS No. 47-1745.

Fig. S6c XRD patterns of samples synthesized under the mole ratio of Cu/Se = 2 and reaction temperature 150 °C (sample 1, a) and 120 °C (sample 4, b).

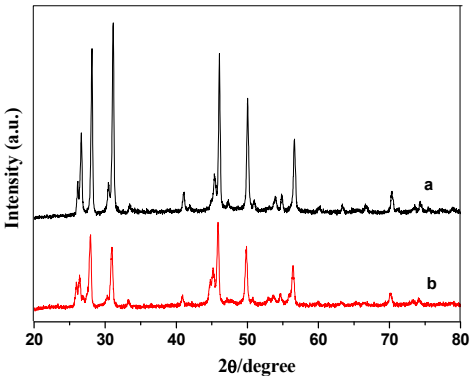


Fig. S6d XRD pattern of sample 6 synthesized under the mole ratio of Cu/Se = 1:2 and reaction temperature 180 °C

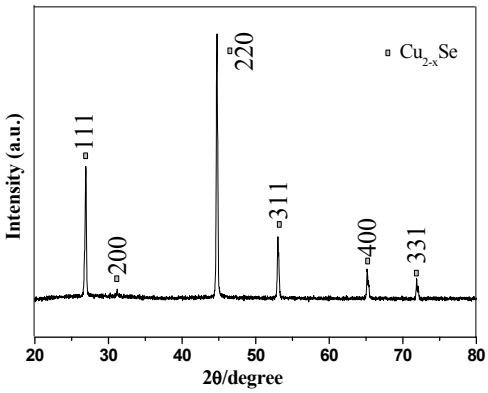


Fig. S6e SEM pattern of sample 6, inset (a) is the magnified SEM image of a $Cu_{2-x}Se$ microcrystal, inset (b) is the corresponding cogeometrical structure of $Cu_{2-x}Se$ microcrystal.

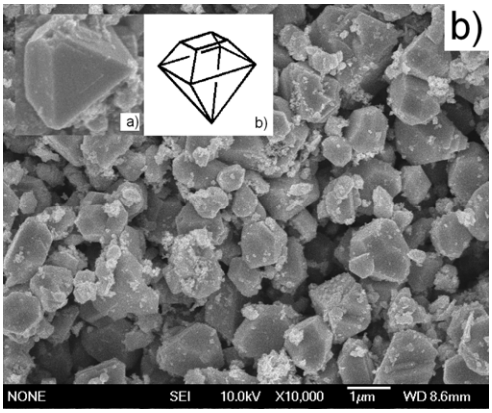


Fig. S6f SEM image of sample 7 synthesized under the mole ratio of Cu/Se = 2:1 and reaction temperature 180 °C.

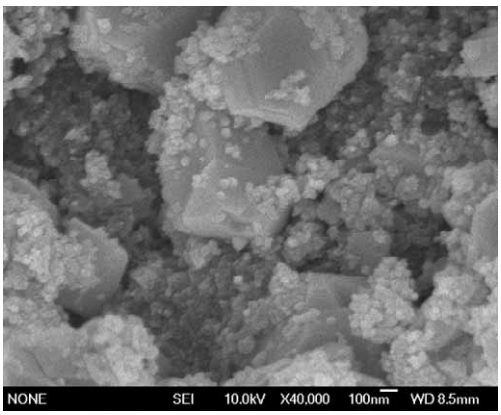
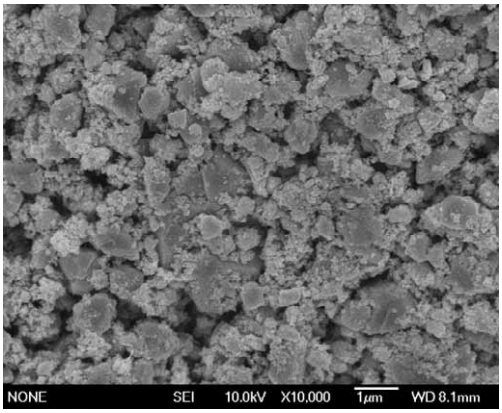
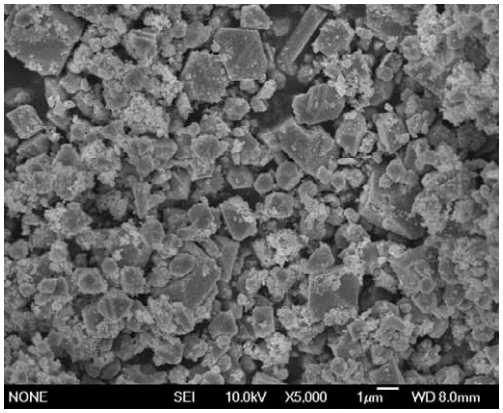


Fig. S7 SEM images of sample 6 synthesized at 180 °C for different reaction times of (a) 4 h, (b) 8 h.



(a)



(b)