#### **Electronic Supplementary Information (ESI)**

#### Formation of uniform carrot-like Cu<sub>31</sub>S<sub>16</sub>-CuInS<sub>2</sub> heteronanostructures assisted

#### by citric acid at the oil/aqueous interface †

Yongjie Li,<sup>a</sup> Aiwei Tang,<sup>\*ab</sup> Zhenyang Liu,<sup>ab</sup> Lan Peng,<sup>a</sup> Yi Yuan,<sup>a</sup> Xifeng Shi, <sup>c</sup> Chunhe Yang,<sup>\*a</sup> and Feng Teng<sup>b</sup>

<sup>a</sup>Department of Chemistry, School of Science, Beijing JiaoTong University, Beijing 100044, P. R. China.

<sup>b</sup>Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing JiaoTong University, Beijing 100044, P. R. China.

<sup>c</sup>College of Chemistry, Chemical Engineering and Materials Science, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Normal University, Jinan 250014, PR China

E-mail: awtang@bjtu.edu.cn (A. T), chy@bjtu.edu.cn (C. Y); Tel: +86 10 51683627



**Fig.S1** TEM images of  $Cu_{31}S_{16}$ -CuInS<sub>2</sub> HNS synthesized by using different DDT dosage when the Cu/In precursor ratio is kept at 1:1: (A) 3 mL, (B) 5 mL and (C) 8 mL.



**Fig.S2** TEM images of  $Cu_{31}S_{16}$ -CuInS<sub>2</sub> HNS synthesized by using different Cu/In precursor ratios in the presence of 5 mL of DDT: (A) 1:1; (B) 1:1.3; (C) 1:1.7 and (D)1:2.



**Fig.S3** XRD patterns of the  $Cu_{31}S_{16}$ - $CuInS_2$  HNS synthesized by using different Cu/In precursor ratios of 1:1 and 1:1.7 in the presence of 5 mL of DDT, and the bottom vertical lines represent the standard diffraction lines of cubic In(OH)<sub>3</sub> (JCPDS No.16-0161), monoclinic  $Cu_{31}S_{16}$  (JCPDS No.23-0959) and stimulated wurtzite CuInS<sub>2</sub>.



**Fig.S4** (A)TEM image and (B) XRD patterns of the  $Cu_{31}S_{16}$ -CuInS<sub>2</sub> HNS synthesized using 3 mL of DDT and the Cu/In precursor ratio of 1:1.7 at 190 °C, in which the pH value of aqueous solution by adding diluted HNO<sub>3</sub>.



**Fig.S5** TEM images of  $Cu_{31}S_{16}$ -CuInS<sub>2</sub> HNS synthesized in the presence of 3 mL of DDT and the Cu/In precursor ratio of 1:1.7 at 190 °C by incorporation of different types of acids: (A) 50 µL nitric acid, (B) 50 µL acetic acid, (C) the corresponding XRD patterns and the bottom vertical lines represent the standard diffraction lines of cubic In(OH)<sub>3</sub> (JCPDS No.16-0161), monoclinic  $Cu_{31}S_{16}$  (JCPDS No.23-0959) and stimulated wurtzite CuInS<sub>2</sub>.



**Fig.S6** TEM images of  $Cu_{31}S_{16}$ -CuInS<sub>2</sub> HNS synthesized with Cu/In precursor ratio of 1:1 at 190 °C for different DDT dosage in the presence of 0.5 g of citric acid: (A) 1.5 mL; (B) 2 mL.



**Fig.S7** TEM images of  $Cu_{31}S_{16}$ -CuInS<sub>2</sub> HNS under different temperatures: (A)175°C, (B)190°C and (C)205°C, which were synthesized with Cu/In precursor ratio of 1:1 in the presence of 0.5 g of citric acid 0.5g and 3 mL of DDT.