Selective formation of ternary Cu–Ge–S nanostructures in solution

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Supporting Information



Fig. S1 (a) XRD pattern and (b) TEM image of the product obtained when the synthesis was carried out using 10 mL DDT as solvent. Note: Red pattern in (a) is from standard JCPDS file [01-081-8819] for Cu_{1.81}S (roxbyite).



Fig. S2 Particle size distribution for the as-prepared (a) Cu_8GeS_6 and (b) Cu_2GeS_3 nanostructures.



Fig. S3 (a) XRD pattern and (b) TEM image of the product obtained when the synthesis was carried out using 10 mL HDA as solvent. Note: Red pattern in (a) is from standard JCPDS file [03-065-5562] for cubic Cu₂GeS₃.



Fig. S4 EDX spectra of the nanostructures produced using the OM–DDT solvent system. The nanostructures were isolated at different stages of reaction: (a) after degassing at 100 °C for 10 min, (b) when the temperature reached 240 °C, (c) when the temperature reached 280 °C, and (d) after heating at 280 °C for 1 h.



Fig. S5 XRD patterns and TEM images of the copper sulfide nanostructures produced when $Cu(dedtc)_2$ was heated in the OM–DDT solvent system. The nanostructures were isolated at two reaction stages: (a,c) after degassing at 100 °C for 10 min, and (b,d) when the temperature reached 280 °C. Note: Red pattern is from standard JCPDS file [01-081-8819] for Cu_{1.81}S (roxbyite).



Fig. S6 High-resolution XPS analysis of the Cu₈GeS₆ nanostructures showing the Cu 2p (blue), Ge 3d (green) and S 2p (red) spectra. The two peaks at 932.3 and 952.3 eV, with a peak splitting of 20.0 eV, is characteristic of monovalent Cu.^{1–3} The peak centered at around 30.7 eV was similarly observed in XPS scans for tetravalent Ge in copper germanium sulfide compounds.^{4,5} The peaks at 161.8 and 163.1 eV are typical for sulfides in multinary sulfide compounds.^{1–5}



Fig. S7 EDX spectra of the nanostructures produced using OM as the only solvent. The nanostructures were isolated at different stages of reaction: (a) after degassing at 100 °C for 10 min, (b) when the temperature reached 200 °C, (c) when the temperature reached 280 °C, and (d) after heating at 280 °C for 1 h



Fig. S8 (a) XRD pattern and (b) TEM image of the product obtained after a solution of Cu(dedtc)₂ in OM was heated to 100 °C and degassed for 10 min. Note: Red pattern in (a) is from standard JCPDS file [42-0561] for CuS (covellite).

Fig. S9 High-resolution XPS analysis of the Cu₂GeS₃ nanostructures showing the Cu 2p (blue), Ge 3d (green) and S 2p (red) spectra. The peak positions are consistent with those previously reported for Cu₂GeS₃ nanocrystals,^{4,5} denoting that the oxidation states are Cu⁺, Ge⁴⁺ and S²⁻.

Fig. S10 XRD pattern of the nanostructures obtained when the amount of Ge precursor was increased such that the Cu:Ge precursor ratio is 1:1. In particular, 0.2 mmol each of Cu(dedtc)₂ and GeCl₂.dioxane were used. The solvent system is a mixture of 5 mL OM and 5 mL DDT. Red pattern is from standard JCPDS file [39-1202] for orthorhombic Cu₈GeS₆.

References

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