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A facile approach to hetero-nanorods of Ag_2Se–MSe (M = Cd, Zn) with enhanced third-order optical nonlinearity†

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Semiconductor–semiconductor hetero-nanorods (Ag_2Se–CdSe and Ag_2Se–ZnSe) with high crystallinity have been synthesized by a facile and low-cost method. High resolution transmission electron microscopy investigations reveal that the growth follows a catalyst-assisted mechanism. A preliminary investigation of nonlinear optical properties shows that the hetero-nanorods exhibit significantly enhanced third-order nonlinear optical properties. The free carrier absorption cross-section of Ag_2Se–CdSe hetero-nanorods is one order of magnitude higher than that of the corresponding single component CdSe nanocrystals. The results obtained in this study represent a new approach to the design and construction of metal selenide hetero-nanorods with high crystallinity and enhanced nonlinear optical capabilities.

Introduction

The composition and morphology of semiconductor nanostructures correlate strongly with their opto-electronic performance and therefore their potential applications.[1–4] Semiconductor–semiconductor nano-heterostructures can facilitate the delocalization or confinement of excitons; engineering of the band alignment may have broad implications for developments in the fields of solar cells and photocatalysis, as well as biological and biomedical imaging.[5,6] Although it is yet to be demonstrated, semiconductor–semiconductor nano-heterostructures may also potentially play an important role in the nonlinear optical (NLO) materials sphere, because efficient delocalization of the excited carriers is an important prerequisite for improving the NLO properties of conjugated organic molecules,[7,8] metallic clusters,[9–11] and carbon nanotubes[12] or graphene hybrids.[13] Such efficient NLO materials or devices may protect optical sensors and human eyes from undesired intense radiation hazards, thus with wide applications in both military and civilian fields.[14–16]

In comparison with their sulfide counterparts, semiconductor–semiconductor nano-heterostructures constructed by metal-selenide components are attracting increasing attention due to the wide absorption range,[17] strong light emission,[18,19] high carrier mobility,[20] and the large two-photon absorption coefficients[21] of metal selenides. Although numerous approaches have been developed for the fabrication of semiconductor–semiconductor nano-heterostructures thus far,[18,19,22–29] these strategies are mainly based on the seed-growth mechanism, which requires critical conditions: high reaction temperature, seed particles showing specific facets, sufficiently low lattice mismatch between the seed and the secondary component, and the use of toxic and expensive alkylphosphine surfactants, to name a few. These rigorous synthesis requirements have hindered the large scale production of semiconductor–semiconductor nano-heterostructures that is needed for applications. Catalyst-assisted growth, which is usually utilized to synthesize metal–semiconductor nano-heterostructures,[30,31] may be an alternative approach to the fabrication of semiconductor–semiconductor nano-heterostructures. However, the reports on catalyst-assisted growth of semiconductor–semiconductor nano-heterostructures are rare, and thus far limited to metal-sulfides, with few group 11 metal-sulfides successfully functioning as the catalysts so far.[32–35] In particular, the synthesis of multicomponent metal-selenide semiconductor–semiconductor nano-heterostructures with high crystallinity and uniform morphology is

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† Electronic supplementary information (ESI) available: Size distribution of the CdSe portion in Ag_2Se–CdSe SSHNs, EDX spectra recorded from the Ag_2Se portion and the CdSe portion in Ag_2Se–CdSe SSHNs, TEM images of samples extracted at different stages of synthesis, the STEM image of Ag_2Se–ZnSe, EDX line profiles of Zn, Ag, and Se acquired from Ag_2Se–ZnSe, and EDX spectra recorded from the Ag_2Se portion and the ZnSe portion in Ag_2Se–ZnSe, excitation and emission spectra of CdSe and Ag_2Se–CdSe, time-resolved fluorescence for single component CdSe nanocrystals and Ag_2Se–CdSe SSHNs, *Z*-scan results of Ag_2Se–ZnSe hetero-nanorods, and UV-Vis spectra of SSHNs (Ag_2Se–CdSe and Ag_2Se–ZnSe) and single component nanocrystals (CdSe and ZnSe) dispersed in toluene. See DOI: 10.1039/c3tc31919a