Facile, low-cost fabrication of Ag₂Se-MSe (M = Cd, Zn) nano-heterojunctions exhibiting significantly enhanced third-order optical nonlinearity

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ABSTRACT. Semiconductor-semiconductor nano-heterojunctions (Ag_2Se - CdSe and Ag_2Se - ZnSe) with uniform morphologies and high crystallinity have been synthesized by a facile and low-cost method. HRTEM investigations reveal that the growth follows a catalyst-assisted mechanism. A preliminary investigation of nonlinear optical properties shows that the nano-heterojunctions exhibit significantly enhanced third-order nonlinear optical properties, two orders of magnitude higher than the corresponding single component metal selenide nanocrystals.

KEYWORDS. Nano-heterojunction, Synthesis, Semiconductor, Catalyst-assisted growth, Optical nonlinearity

The content and morphology of semiconductor nanostructures correlates strongly with their opto-electronic performance and therefore their potential applications.¹⁻⁴ Semiconductor-semiconductor nano-heterojunctions (SSNHs) 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} SSNHs may also potentially play an important role in the nonlinear optical (NLO) materials sphere, because efficient delocalization of the excited carriers is an important procedure for improving the NLO properties of conjugated organic molecules,^{7,8} metallic clusters,⁹⁻¹¹ and carbon nanotubes¹² or graphene hybrids.¹³

In comparison with their sulfide counterparts, SSNHs constructed by metal-selenide components are attracting increasing attention due to the wide absorption range,¹⁴ strong light emission,^{15,16} and high carrier mobility,¹⁷ and the large two-photon absorption coefficients¹⁸ of metal selenides. Although numerous approaches have been developed for the fabrication of SSNHs thus far,^{15,16,19-26} these strategies are mainly based on the seed-growth mechanism, which requires critical conditions: high reaction temperature, seed particles showing specific facets, a proper 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 SSNHs that is needed for applications. Catalyst-assisted growth, which is usually utilized to synthesize metal-semiconductor nano-heterojunctions,^{27,28} may be an alternative approach for the fabrication of SSNHs. However, the reports on catalyst-assisted growth of SSNHs are rare, and thus far limited to metal-sulfides, with few group 11 metal-sulfides successfully functioning as the catalyst so far.²⁹⁻³² In particular, the synthesis of multicomponent metal-selenide SSNHs with high crystallinity and uniform morphology is still a major challenge, although it is a prerequisite for exploring fundamental nanoscale semiconductor physics and affording technological devices with optimized characteristics.

In this paper, we report a facile and low-cost method for the fabrication of multicomponent metal selenide SSNHs, the uniform morphologies and highly crystalline structures of the SSNHs, mechanism

confirmation by HRTEM of a catalyst-assisted growth process for the SSNHs, and a preliminary investigation of their NLO properties, the first such study for multicomponent metal selenide SSNHs. The method introduced here possesses several advantages: 1) the nano-heterojunctions are fabricated from commercially available low-cost reagents, removing the need to source/synthesize a complicated precursor; 2) the reactions occur at temperatures as low as 180 °C; 3) it avoids the use of the toxic, pyrophoric, and expensive alkylphosphines that are commonly used as capping ligands in the synthesis of metal selenides; 4) the reactions are scalable and suitable for mass production (e.g. gram scale) with high productivity and convenient handling. We demonstrate a convenient strategy for the fabrication of metal-selenide SSNHs, and thereby a new approach to the design and exploitation of materials exhibiting significantly-enhanced NLO capabilities.

The principle of catalyst-assisted growth is that the catalyst should behave as a liquid or in other words be “fluid” at the growth temperature, so that the secondary semiconductor component can be dissolved into and then aggregate in the catalytic component. As implied by their high ionic conductivity, semiconductors such as Ag₂Se should possess a large number of cation vacancies, and therefore might behave like fluids. Accordingly, silver selenide (Ag₂Se) was adopted as catalyst for the one-pot synthesis of SSNH. Oleylamine (boiling point ~ 348 °C) was used as both a solvent and a surface-capping ligand in these experiments. All metal selenides were synthesized from reactions between the relevant metal nitrate and selenium in oleylamine. The nano-heterojunction fabrication is discussed in detail in the Supporting Information. In brief, the preparation consists of two steps. Firstly, Ag₂Se was synthesized by sequentially adding silver nitrate and selenium to hot oleylamine (180 °C) (Step 1, Scheme 1), and then the metal nitrate (e.g. Cd(NO₃)₂ or Zn(NO₃)₂) and selenium were added simultaneously to the 180 °C oleylamine containing the as-synthesized silver selenide nanoparticles. The temperature of the oleylamine was maintained at 180 °C for a specific time, resulting in the formation of Ag₂Se-MSe (M = metal) nano-heterojunctions (Step 2, Scheme 1).

In a typical experiment, an Ag₂Se-CdSe nano-heterojunction was fabricated according to the method above, after which a transmission electron microscope (TEM) study was performed for morphological characterization of the product. Figure 1a displays a representative low magnification TEM image of an Ag₂Se-CdSe sample, showing that the products typically exhibit a rod-like structure with a diameter of about 10 nm and a length between 10 to 20 nm. A closer examination of the TEM image reveals that the nanoparticles show matchstick-like morphology, consisting of a hemispherical head in darker contrast and a rod-like stick in brighter contrast. In order to identify the components in the matchstick-like structure, a compositional line profile was performed by energy dispersive X-ray (EDX) spectroscopy working in scanning TEM (STEM) mode. The EDX line profiles show that the hemispherical head is Ag-rich and the rod-like stick is Cd-rich (Figure 1b), consistent with the resultant structure being an Ag₂Se-CdSe SSNH composed of an Ag₂Se head and a CdSe stick.

Detailed structural information of the Ag₂Se-CdSe nano-heterojunction was obtained from X-ray diffraction (XRD). Figure 2 shows the powder XRD pattern of the SSNH, with blue lines marking the peaks from Ag₂Se and red lines from CdSe. The three peaks at 23.87°, 25.36°, and 27.15° correspond to the characteristic peaks of hexagonal phase CdSe (Cadmoselite, JCPDS No. 77-21), and can be indexed to the (100), (002), and (101) planes, respectively. The peak located at 30.52° is helpful in identifying the specific phase of the Ag₂Se component. Because tetragonal phase Ag₂Se shows a peak at $\theta = 30.4^\circ$,³³ while the orthorhombic phase (Naumannite, JCPDS No. 24-1041) has a peak at 31.0°, it is more reasonable to assign Ag₂Se to the tetragonal phase (with lattice constants $a = b = 7.06 \text{ \AA}$, and $c = 4.98 \text{ \AA}$).³⁴ The tetragonal phase has been postulated to be a meta-stable phase of Ag₂Se at low temperature. It should be noted that the Ag₂Se pattern shown in Figure 2 is labeled according to the computational results introduced by Norris et al.,³³ because the XRD pattern from the tetragonal phase Ag₂Se is not available in the database. The crystal size of each component of the nano-heterojunctions can be estimated from the XRD patterns according to the Scherrer equation $\tau = K\lambda/(\beta \cos \theta)$, where τ is the mean crystal size, K is the shape factor, which has a typical value of about 0.9, λ is the X-ray

wavelength (1.5418 Å), β is the line broadening at half the maximum intensity (in radians), and θ is the Bragg angle. The necessary parameters were extracted from the pattern of the CdSe component (strongest peak, $2\theta = 25.66^\circ$, $\beta = 0.01326$), and the crystalline size calculated to be ca. 11 nm. Similarly, the Ag₂Se pattern at $2\theta = 33.6^\circ$ ($\beta = 0.00942$) suggests that the average size of the Ag₂Se component in these nano-heterojunctions is ca. 15 nm. These sizes estimated from XRD are in accord with those revealed by TEM.

To gain insight into the crystallinity of these SSNHs, high resolution TEM (HRTEM) investigations were undertaken. A representative HRTEM image of Ag₂Se-CdSe SSNHs is shown in Figure 3. Well-defined lattice fringes are clearly observed in the two components, suggesting that both Ag₂Se and CdSe are highly crystalline. A fast Fourier transform (FFT) of the atomic lattice image of the brighter component in the nano-heterojunction (particle 1 in Figure 3a) results in a hexagonal diffraction pattern (Figure 3b), which can be indexed to the [001] zone-axis diffraction pattern of hexagonal-phase CdSe ($d_{(100)} = 3.71$ Å). The pattern generated from a FFT of the darker component is shown in Figure 3c; the spots can be assigned as the [010] zone-axis diffraction pattern of tetragonal phase Ag₂Se, with the measured distances and angles between the lattice planes ($d_{(101)} = 4.00$ Å, $d_{(202)} = 2.01$ Å, $d_{(301)} = 2.13$ Å, $d_{(002)} = 2.48$ Å, $\angle AOC = 35.3^\circ$, $\angle AOD = 29.5^\circ$, $\angle COD = 74.8^\circ$) agreeing closely with the corresponding computed values.

Interestingly, all CdSe components shown in Figure 3a have grown along the $\langle 100 \rangle$ direction, implying a well-defined epitaxial relationship between CdSe and Ag₂Se. It can be deduced from the measured angles between the Ag₂Se-CdSe interface and the (202), (002) and (301) planes of the Ag₂Se component (70° , 35° , and 80° , respectively) that the Ag₂Se-CdSe interface is parallel to the $(20\bar{2})$ plane of the Ag₂Se component. The epitaxial relationship between the CdSe and Ag₂Se components in particle 1 (Figure 3a) is therefore unequivocally established as $(202)_{\text{Ag}_2\text{Se}} \parallel (100)_{\text{CdSe}}$ with $[010]_{\text{Ag}_2\text{Se}} \parallel [001]_{\text{CdSe}}$. Analysis of the remaining nano-heterojunctions shown in Figure 3a and the other nano-heterojunctions

(Figure S1, Supporting Information) results in the same epitaxial relationship. Although the exact location of the silver atoms in tetragonal Ag₂Se is unknown, the Se atoms are known to be located at the face-centered positions of a tetragonal lattice.^{35,36} Because the two components in the SSNHs are both selenides, it is reasonable to postulate that the interface between CdSe and Ag₂Se is a Se plane. Accordingly, the lattice mismatches can be estimated from the difference of distances between the Se atoms along the epitaxial directions in the CdSe lattice and the Ag₂Se lattice. Figures 3d and 3e show projections towards the interface of the Cd and Se atoms in the CdSe lattice and of the Se atoms in the Ag₂Se lattice, revealing a good superposition of the Se atoms from a (100) plane of the CdSe lattice with those from a (202) plane of the Ag₂Se lattice. The lattice mismatches are $(7.06 - 7.02)/7.06 \times 100\% = 0.57\%$ and $(4.32 - 4.30)/4.32 \times 100\% = 0.46\%$ along the two epitaxial directions ([010] and $[\frac{1}{2}0\frac{1}{2}]$ of the Ag₂Se lattice, respectively). These relatively small lattice mismatches facilitate the epitaxial growth of CdSe on the Ag₂Se particles.

To understand the role of Ag₂Se in the growth of CdSe, a comparative experiment was performed, in which cadmium nitrate and selenium were reacted in oleylamine at 180 °C for a duration identical to that for the growth of Ag₂Se-CdSe shown in Figure 1a. TEM characterization shows that the products from the control experiment are irregular-shaped quantum dots with sizes smaller than 3 nm (Figure 4a). The lattice fringes shown in the HRTEM reveal that the quantum dots are crystalline, with a *d* spacing, 3.7 Å, corresponding to the {100} plane of hexagonal CdSe. The morphological difference between the CdSe grown with (Figure 1a) and without (Figure 4a) Ag₂Se under otherwise-identical conditions is consistent with Ag₂Se acting as a catalyst or seed for the growth of CdSe.

The growth mechanism of CdSe has been further investigated by monitoring the morphological evolution of Ag₂Se-CdSe SSNHs at the early stage of growth. A series of aliquots were extracted from the hot growth solution at 10 minute intervals following the addition of cadmium nitrate and selenium into 180 °C oleylamine containing the Ag₂Se nanocrystals. Representative HRTEM results of aliquots extracted at 30, 40, and 50 minutes are shown in Figures 4b-4d, respectively, revealing the

morphological evolution of the Ag₂Se and CdSe phases in the SSNHs with increasing reaction time. The spacing between the lattice fringes confirms that the dark and bright components are Ag₂Se and CdSe, respectively. Thirty minutes after the addition of cadmium nitrate and selenium, the Ag₂Se particles maintain a spherical shape, while a secondary CdSe phase begins to emerge inside the Ag₂Se matrix (Figure 4b). On prolonged reaction (ca. 40 minutes), the volume of the CdSe phase expands and the CdSe phase extends to the surface of the two-phase particles. The particles extracted at 50 minutes exhibit typical Janus-type nano-heterojunctions, and the Ag₂Se phase evolves from a sphere (Figure 4b) to a hemisphere. The morphological evolution of the Ag₂Se-CdSe nano-heterojunctions shows that a catalyst-assisted growth mechanism is responsible for the growth of the CdSe phase.

In catalyst-assisted growth, a catalytic particle behaves as a liquid or a virtual “fluid” at the reaction temperature. Two kinds of material can act as the catalyst: those with melting points lower than the reaction temperature, and those possessing large numbers of cation vacancies so that the cation behaves as a fluid. Because the reaction temperature (180 °C) is far below the melting point of Ag₂Se (880 °C) in our experiment, the catalytic activity of Ag₂Se can be exclusively attributed to the large number of Ag vacancies in the Ag₂Se phase, and consistent with the high ionic conductivity of Ag₂Se. The growth process of CdSe catalyzed by Ag₂Se can therefore be described as follows. Due to the significant number of Ag vacancies in Ag₂Se particles, cadmium ions can be dissolved into such particles. The cadmium ions begin to aggregate into a CdSe phase when the concentration of Cd in the Ag₂Se is sufficiently large (Figure 4b). As its volume increases, the CdSe phase is expelled to the surface of the two-phase particles to reduce the interfacial energy between CdSe and Ag₂Se (Figures 4c and 4d), and a Janus nanostructure is formed. With increasing reaction time, the CdSe phase grows further along the <100> direction, and the morphology of the SSNHs accordingly evolves from Janus to matchstick.

The above-mentioned model suggests that it may be possible to use Ag₂Se to catalyze the growth of other metal selenides. To check this possibility, zinc nitrate was used instead of cadmium nitrate in the synthesis of nano-heterojunctions, the result showing that Ag₂Se-ZnSe can be fabricated by the same

approach as Ag_2Se - CdSe . Figure 5 shows the overall structural and morphological characterization of Ag_2Se - ZnSe nano-heterojunctions. Distinct XRD peaks suggest regular crystallization of the nanostructures, with XRD patterns that can be indexed to the tetragonal phase Ag_2Se and hexagonal phase ZnSe (JCPDS No. 89-2940), as indicated by the blue and red lines in Figure 5a, respectively. TEM characterization shows that the nano-heterojunctions have a typical matchstick-like morphology (Figure 5b) composed of Ag_2Se hemi-spherical heads and ZnSe rods. The diameter of the Ag_2Se particles is ca. 15 nm, similar to those in Ag_2Se - CdSe SSNHs, while the diameter of the ZnSe rod is ca. 7 nm, with a ZnSe rod length longer than 100 nm. HRTEM characterization reveals that the Ag_2Se and ZnSe components are both single crystalline (Figure 5c).

The wurtzite polymorph is a high temperature meta-stable phase of ZnSe , the zinc blende phase being predominant in common syntheses of ZnSe .^{37,38} Wurtzite- ZnO nanowires have been utilized as templates for the fabrication of single-phase wurtzite- ZnSe , the resulting wurtzite- ZnSe consisting of nanotubes composed of small particles.³⁹ In our experiment, ZnSe crystallizes in the wurtzite structure, and forms solid nanowires with high crystallinity in SSNHs. More broadly, CdSe and ZnSe in SSNHs are both wurtzite phase in our experiments, suggesting that the Ag_2Se nanoparticles act not only as the catalyst for the growth of secondary components, but also as the structure-directing agent that influences the crystallization process of the secondary components. In the growth of SSNHs, the secondary component firstly precipitates inside the Ag_2Se particles, and is then ejected. When it is ejected from the Ag_2Se particles, the secondary component will prefer to crystallize on a certain plane of the Ag_2Se particles in order to minimize the lattice mismatch between the secondary component and Ag_2Se . The structure-directing effect of Ag_2Se can therefore be attributed to the tendency to minimize the lattice mismatch during the growth of the secondary component.

In order to explore the excited-state interactions of CdSe and Ag_2Se in Ag_2Se - CdSe SSNHs, the steady-state photoluminescence (PL) of the Ag_2Se - CdSe SSNHs as well as that of monocomponent CdSe nanocrystals separately dispersed in hexane was investigated, the resultant fluorescence spectra

being depicted in Figure 6. The concentrations of the CdSe components in the nanocrystal samples were adjusted to the same value prior to the PL measurements by the aid of atomic absorption spectroscopy. With identical excitation at 468 nm, where the strongest excitation peaks can be found for both single component CdSe nanocrystals and Ag₂Se-CdSe SSNHs (Figure S2, Supporting Information), the emission intensity of the Ag₂Se-CdSe SSNHs hexane suspension is less than 25% of that of the single component CdSe nanocrystal suspended in hexane, as shown in Figure 6. Furthermore, we also examined PL decay profiles of single component CdSe nanocrystals and Ag₂Se-CdSe SSNHs by conducting time-resolved experiments. There is a definite decrease in excited-state lifetime of CdSe component in Ag₂Se-CdSe SSNHs compared to single component CdSe nanocrystals (Figure S3, Supporting Information). The much lower quantum efficiency and the faster PL decay rate of the SSNHs, in comparison with those of single component CdSe nanocrystals, suggest an effective charge-transfer process occurring in the SSNHs. A likely pathway for charge transfer is schematically illustrated in the inset of Figure 6, with photo-generated electrons and holes in the CdSe component transferring to the valence band (VB) and conduction band (CB) of the Ag₂Se component due to the band alignment between CdSe and Ag₂Se.^{40,41}

The UV-Vis spectra of both MSe nanocrystals and Ag₂Se-MSe SSNHs (M = Cd, Zn) show relatively low linear absorption in the visible and near IR region (Figure S4, Supporting Information); these nanostructures are therefore candidates for optical limiting applications. To assess this possibility, Z-scan experiments employing linearly polarized 4 ns laser pulses at 532 nm have been performed on these nanostructures dispersed in toluene,⁴² with the details of the NLO measurements being described in the Supporting Information. The NLO absorption components of these nanocrystals were evaluated under the open-aperture configuration. Figures 7a and S5a (Supporting Information) display their NLO absorptive behavior and clearly illustrate that the absorption increases with increasing intensity of the incident laser, the light transmittance (*T*) dropping to 85%, 59% and 60% at the focal point for CdSe, Ag₂Se-CdSe and Ag₂Se-ZnSe, respectively, with negligible NLO absorption for ZnSe. A good fit between the experimental data and the theoretical curves was achieved, which suggests that the

experimentally observed NLO effects have an effective third-order characteristic. The nonlinear absorptive coefficients α_2 were calculated to be 8.38×10^{-11} (CdSe), 1.29×10^{-9} (Ag₂Se-CdSe), and 8.75×10^{-10} m W⁻¹ (Ag₂Se-ZnSe). The nonlinear refractive components were assessed by dividing the normalized Z-scan data obtained from the closed-aperture configuration by the normalized Z-scan data obtained from the open-aperture configuration, as depicted in Figures 7b and S5b separately for Ag₂Se-MSe SSNHs, while no detectable refraction signal was found for the MSe nanocrystals under the NLO measurement conditions. The valley/peak patterns of the corrected transmittance curves show a self-focusing behavior of the propagating light in the SSNHs. The theoretical curves, which reproduce the general pattern of the experimentally detected data, afforded the effective third-order nonlinear refractive indexes n_2 of the SSNHs as 6.97×10^{-17} (Ag₂Se-CdSe) and 4.07×10^{-17} (Ag₂Se-ZnSe) m² W⁻¹, respectively. Based on the above NLO absorptive and refractive values of these nanostructures, the concentration-independent hyperpolarizabilities γ , which reflect the integrated third-order NLO properties, were deduced to be 4.73×10^{-31} (CdSe), 3.94×10^{-29} (Ag₂Se-CdSe), and 6.10×10^{-29} (Ag₂Se-ZnSe) esu, respectively. It is noteworthy that, despite these nanostructure semiconductors being constructed of transition-metal elements with the same number of d-orbital electrons and possessing similar nanometer scale morphologies, the NLO measurement data demonstrate a significant enhancement of the third-order optical nonlinearity for Ag₂Se-CdSe and Ag₂Se-ZnSe SSNHs, in contrast with the single component MSe nanocrystals (M = Cd, Zn). Specifically, the hyperpolarizability γ increases by two orders of magnitude upon constructing the Ag₂Se-MSe SSNHs from the Ag₂Se catalyst-assisted growth, compared with MSe nanocrystals. Because of the band alignment between CdSe and Ag₂Se, and the remarkable reduction of PL intensity in Ag₂Se-CdSe, this enhancement in NLO properties can tentatively be attributed to the effective charge-transfer process in SSNHs.¹³

In summary, a facile and low-cost method has been developed to synthesize metal selenide SSNHs. The growth of Ag₂Se-CdSe and Ag₂Se-ZnSe has been successfully demonstrated. The morphologies

and structures of SSNHs have been shown to be uniform with high crystallinity. The growth process of the SSNHs was monitored by TEM on samples at the early stages of growth, the results showing unambiguously that a catalyst-assisted growth mechanism governs the growth of SSNHs. The Ag₂Se particles also direct the crystallization of the secondary component in the wurtzite phase. Z-scan measurements demonstrate that the Ag₂Se-CdSe nano-heterojunctions exhibit significantly enhanced third-order nonlinear optical properties compared to the monocomponent CdSe nanocrystals. The method introduced here offers a convenient approach for the synthesis of multicomponent metal selenide SSNHs with significantly enhanced third-order optical nonlinearities.

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Supporting Information. Experimental details and TEM images revealing the epitaxial relationship; excitation and emission spectra, time-resolved fluorescence, and UV-Vis absorption spectra of single component nanocrystals and nano-heterojunctions; Z-scan spectra of single component nanocrystals and nano-heterojunctions. This material is available free of charge via the Internet at <http://pubs.acs.org>.