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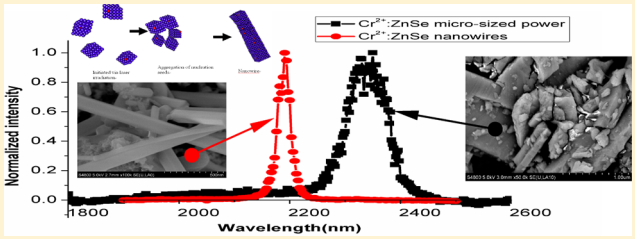
Nanocrystalline Cr^{2+}-doped ZnSe Nanowires Laser

Guoying Feng,* Chao Yang,† and Shouhuan Zhou†

Department of Opto- Electronics, Sichuan University, Chengdu 610064, China

Supporting Information

ABSTRACT: By using femtosecond laser pulses to ablate microsized targets that are dispersed in liquid media, nanocrystalline Cr^{2+}-doped ZnSe nanowires have been successfully fabricated for the first time. The phase and stoichiometries of the original materials are preserved while the sizes are reduced down to 30−120 nm for these nanowires. X-ray diffraction results show that the products are nanocrystalline ZnSe with cubic sphalerite structure. Scanning electron microscope results indicate that the products be ZnSe nanowires. The nanowires are usually 30−120 nm in diameter and several tens of micrometers in length. Photoluminescence of the nanocrystalline Cr^{2+}-doped ZnSe nanowires shows strong emission at around 2000−2500 nm under excitation of 1300−2250 nm wavelength at room temperature. By using the Cr^{2+}-doped ZnSe multiple nanowires as the gain medium, mid-infrared oscillation at 2194 nm has been established. The oscillation wavelength of the multiple nanowires laser is 150 nm shifted to shorter wavelengths in comparison with that of microsized powder random laser.



KEYWORDS: *Nanocrystalline Cr^{2+}-doped ZnSe nanowires, mid-infrared random laser, shift to shorter wavelengths, femtosecond pulsed laser ablation in liquid media (FPLAL)*

In recent years, transition metal (TM) doped II−VI semiconductor materials, such as Cr^{2+}/ZnS, Cr^{2+}/ZnSe, Cr^{2+}/$Cd_{1-x}MnxTe$, Cr^{2+}/CdSe, Fe^{2+}/ZnSe, and so forth, were considered promising as gain media for solid state lasers.[1−6] Zinc selenide (ZnSe) is a wide-band gap semiconductor. The heavy anions in the ZnSe crystals provide a very low energy optical phonon cutoff that makes them transparent in a wide spectral region (0.5−22 μm) and decreases nonradiative decay. ZnSe exhibits great potential, such as light emitting diodes, photoluminescent, and ZnSe-based laser. Great efforts have been made to synthesis ZnSe doped with different transition metal ions, such as Cr^{2+}, Co^{2+}, and Fe^{2+}, which have open d-shell electronic configurations.[2,7,8]

In contrast to their metallic and dielectric counterparts, semiconductor nanocrystals exhibit more pronounced quantum confinement effects. The optical charecteristics may be affected by a variation in the particle size. It is therefore attractive to transfer semiconductor material from bulk to nanoscale compounds or to study the size effects. Many literatures focused on near-continuous tuning of the bandgap of a semiconductor material by changing its size in the nanometric regime, or changes of optical properties with size that are often spectacular.[9] In the late 2000s, pioneering work performed at University of California demonstrated room-temperature ultraviolet lasing in zinc oxide nanowire arrays with well-defined end surfaces. These zinc oxide nanowires form natural laser cavities with diameters varying from 20 to 150 nm and lengths up to 10 μm.[10,11] Another pioneering work performed at Harvard University further demonstrated laser action in single-crystal cadmium sulphide nanowires as Fabry−Perot optical cavities with mode spacing inversely related to the nanowire length.[12] But literatures rarely focus on photoluminescence (PL) spectra of active-ion doped nanocrystals when the size reduced down to the nanometric size regime.

In this work, using the femtosecond pulsed laser ablation in liquid mediums (FPLAL), we proposed a synthesis method to prepare nanocrystalline Cr^{2+}-doped ZnSe nanowires with monodispersed distributions in diameter and preservation in stoichiometries and phase. The Cr^{2+}-doped ZnSe nanowires laser shows a 150 nm shift to shorter wavelengths in comparison with the bands of microsized powder random laser.

The FPLAL has demonstrated the following advantages: (i) a chemically "simple and clean" synthesis, and (ii) at overall ambient conditions, not extreme temperature and pressure are required. A femtosecond pulsed laser can easily achieve very high peak intensities that can fully ionize almost any material.[13] The energy of the ultrashort pulse is deposited mainly in a small layer of particles in the laser-materials interaction process. The ablation depth of the femtosecond pulsed laser is on the order of 0.01−1 μm per pulse.[14] The most important aspect in laser ablation of solids in liquids is that liquids confine the movement of the plasma plume. This confinement can greatly influence the thermodynamic and kinetic properties of the evolution of the plasma plume and further cause distinctly the different environments of the condensing phase formation from that of solids ablation by laser in vacuum or diluted gases. Thus, the FPLAL can produce nonequilibrium process and extreme conditions with high temperature and high pressure, leading to

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the formation of the novel nanostructures and producing special nanomaterials that may not be obtained by other conventional methods.

A schematic of the FPLAL experimental setup is shown in Figure 1a. A small amount (0.36 mg) of microsized Cr^{2+}- doped

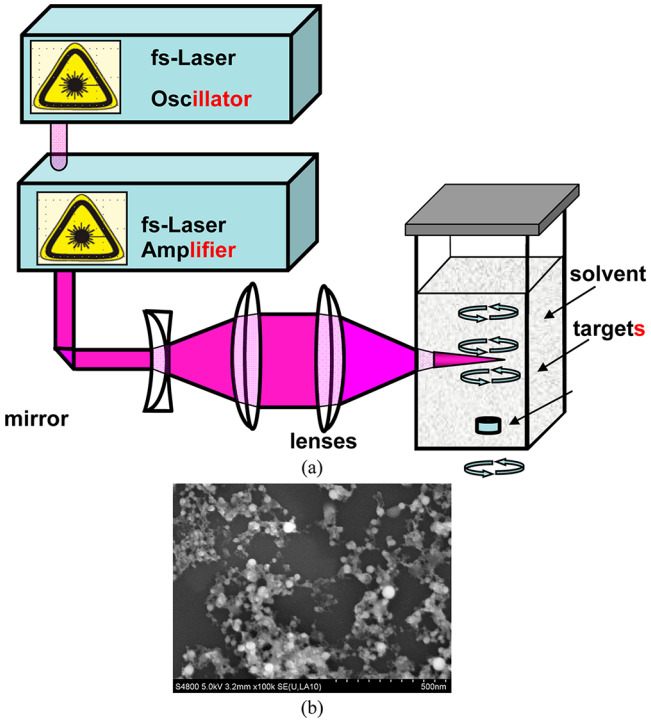

Figure 1. (a) Scheme of the FPLAL experiment. The femtosecond laser pulses are focused on the liquid that is continuously stirred with a magnetic stirrer during laser irradiation. A plasma is generated from which the nanocrystals are formed. (b) SEM image of Cr^{2+}- doped ZnSe nanoparticles prepared by FPLAL.

particles was mixed with water in a rectangular quartz vessel ($1 \times 1 \times 5$ cm^3) with a vessel thickness of 1 mm. The laser radiation of a fundamental mode beam produced by a regenerative amplified mode-locked Ti:sapphire laser (Coherent Inc., 35 fs in duration and 1 kHz repetition rate) operating at a wavelength of 800 nm was focused via a lens onto the water-suspended Cr^{2+}- doped ZnSe microsized particles. The typical beam waist diameter and laser energy fluence were estimated to be ~4 μm and 6.3×10^3 J/cm^2, respectively. The polarization of the laser light was set linear or circular by a half-wave or a quarter-wave plate placed in the incident beam before the focusing optics.

The targets, microsized Cr^{2+}- doped ZnSe particles, for laser ablation were prepared by standard mechanical grinding method. To keep Cr^{2+}- doped ZnSe microsized particles as many as possible suspended in the solution, the solution was continuously stirred with a magnetic stirrer during laser irradiation. In order to analyze the products just after femtosecond pulsed laser irradiation, the suspension was immediately dropped onto a silicon substrate and the solvent was evaporated at room temperature. Figure 1b shows SEM image of Cr^{2+}- doped ZnSe nanoparticles prepared by FPLAL. The variation of laser wavelength, pulse duration, ablation environment produced nanoparticles of different sizes.[2] Nanoparticles with an average size of 20 nm have been created in aqueous environment by using 800 nm radiation with 1 mJ femtosecond pulsed laser.

The aqueous suspension of nanoparticles was dried naturally under ambient condition. Then the products were characterized by a field-emission scanning electron microscopy. Spectroscopic characteristics of Cr^{2+}- doped ZnSe nanowire in mid-IR spectral region were studied under optical parametric oscillator (OPO) (GWU-Lasertechnik GmbH) laser excitation with a tuning range from 410 to 2500 nm and pulse duration of 8 ns. All the experiments were carried out at ambient temperature and pressure.

It should be interesting to investigate growth process of nanowires because in the FPLAL process only nanoparticles were prepared, as shown in Figure 1b. After FPLAL, the suspensions were ultrasonic dispersed for 30 min and left at rest in a temperature-controlled bath having a constant temperature of 30 °C. The liquid surface has a large accommodation coefficient and is therefore a preferred deposition site for prepared nanoparticles. Interaction forces between atoms in different nanoparticles can induce translational and rotational movements of the nanoparticles, driving them to find appropriate locations and orientations for aggregation.[15] After the liquid becomes supersaturated with nanoparticles, growth of Cr^{2+}- doped ZnSe nanowires occurs at the solid−liquid interface. The growth mechanism of Cr^{2+}- doped ZnSe nanowires may be illustrated in Figure 2a. Figure 2b demonstrates the typical SEM images

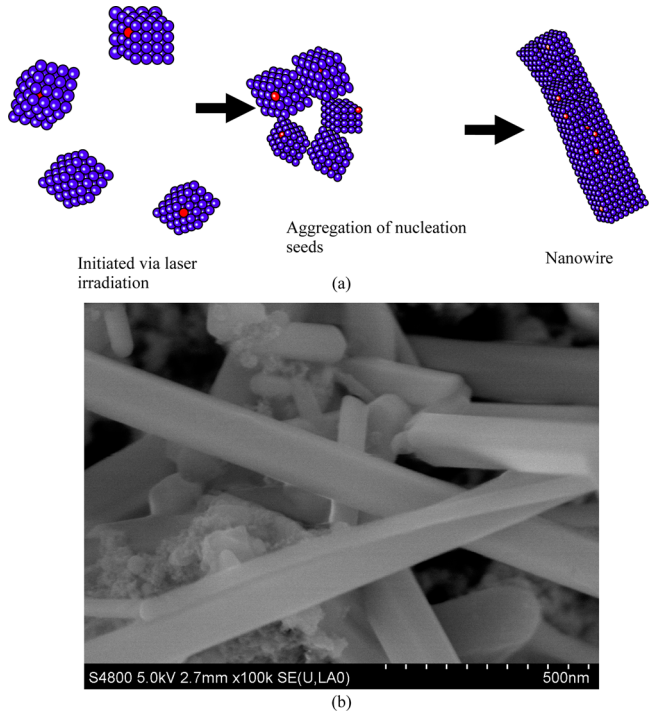

Figure 2. (a) Schematic representation of the formation of nucleation sites and the growth of Cr^{2+}- doped ZnSe nanowires in aqueous solutions. (b) Scanning electron microscope images of Cr^{2+} - doped ZnSe nanowires.

of Cr^{2+}- doped ZnSe nanowires. The diameters of nanowires are in the range of 30−120 nm and the lengths are several micrometers or longer.

The X-ray diffraction (XRD) patterns of Cr^{2+}-doped ZnSe nanowires, Cr^{2+}- doped ZnSe microsized powders, ZnSe microsized powders, and ZnSe bulk are shown in Figure 3a. The XRD peaks can be indexed as the cubic zinc blende structure,

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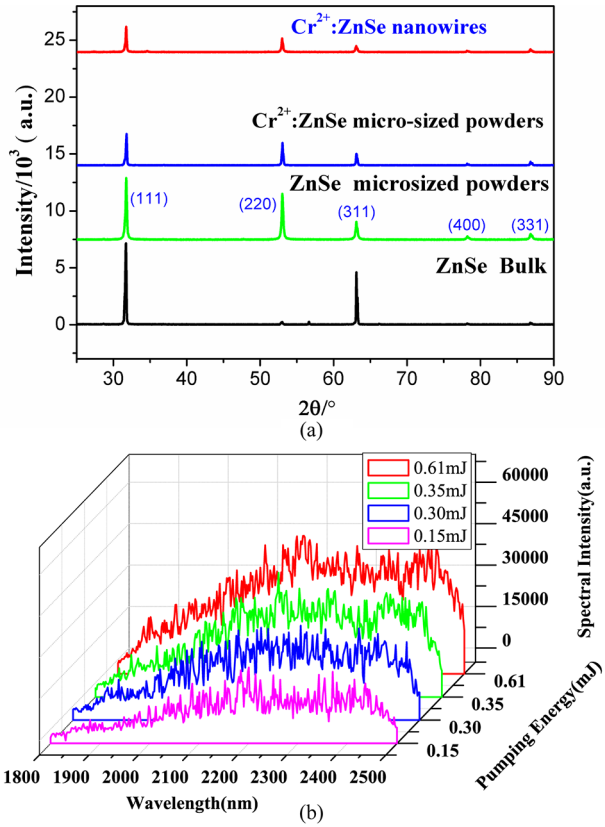

Figure 3. (a) X-ray diffraction patterns of Cr^{2+}- doped ZnSe nanowires, Cr^{2+}- doped ZnSe microsized powders, ZnSe microsized powders, and ZnSe bulk. (b) Measured PL spectra of Cr^{2+}- doped ZnSe nanowires by 1.75 μm excitation at different intensities.

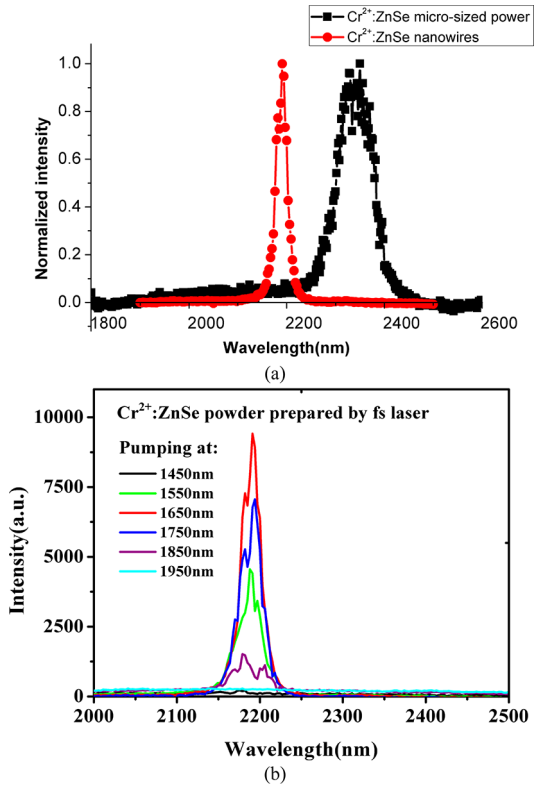

Figure 4. (a) Laser emission spectra of Cr^{2+}- doped ZnSe nanowires (red line) and microsized Cr^{2+}- doped ZnSe powders (black line). (b) Laser emission spectra of Cr^{2+}- doped ZnSe nanowires under pulsed 1.45−1.95 μm excitation.

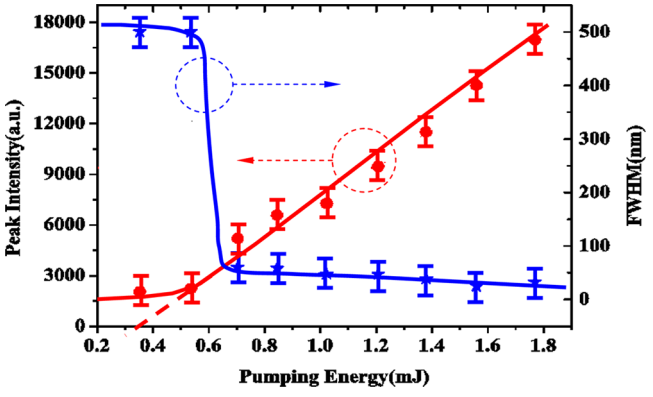

Figure 5. Evolution of PL spectral peak intensity and spectral width (FWHM) as a function of pumping pulse energy.

which is consistent with the values in the Joint Committee on Powder Diffraction Standards (JCPDS) Card (File No. 80-0021). PL spectra of the nanocrystalline Cr^{2+}-doped ZnSe nanowires show strong emission at around 2000− 2500 nm under excitation of 1300−2250 nm wavelength at room temperature. Measured PL spectra of Cr^{2+}- doped ZnSe nanowires by 1.75 μm excitation at different intensities are shown in Figure 3b. The mechanism of the PL process in Cr^{2+}- doped ZnSe nanocrystals or nanowires is more or less well understood. Cr^{2+} ions occupy Zn^{2+} lattice sites in the ZnSe host lattice. In particular, introducing Cr^{2+} ions into ZnSe hosts leads to the formation of strong absorption and PL emission bands in the mid infrared region of the electromagnetic spectrum. The PL bands of Cr^{2+}- doped ZnSe nanowires were blue shifted comparing to the bulk crystals or microsized crystals.[2]

The laser emission bands from Cr^{2+}- doped ZnSe nanowires laser and microsized powder random laser are depicted in Figure 4a. The mid-infrared emission band of Cr^{2+}- doped ZnSe nanowires laser are blue shifted by about 150 nm compared to that of microsized powder random laser[16] and Cr $^{2+}$- doped ZnSe bulk lasers.[17] The transition from spontaneous PL to a stimulated gain is achieved only upon excitation of a high density of carriers in the nanowires, provided by pulsed 1.45−1.95 μm excitation (Figure 4b). The full width at half-maximum (FWHM) of the excited spectra for lasing are considerably broader than 250 nm.

Figure 5 shows an example of the sharp transition from spontaneous to stimulated emission for a Cr^{2+}-doped ZnSe nanowires laser. The power dependences plotted in Figure 5 reveal the threshold nature of the emission from the nanowires. Figure 5 shows the dependence of the averaged intensity of emission at 2194 nm versus pump energy. The output−input characteristics clearly demonstrate a threshold-like behavior of the output signal with a threshold pump energy of 0.34 mJ. Below the critical pump energy (E_{th}), the photoluminescence increases slowly with excitation. Once the threshold is reached, a kink in the power dependence is observed, and after which the output shoots up. The functional relationship of the power dependence above threshold is in linear behavior. Spectra taken at 0.6 mJ pumping energy shows the sharp transition from broad spontaneous emission to lasing. The transition from spontaneous to stimulated emission is clearly demonstrated. We have checked all the SEM images of the nanowires; many nanowires do not have well-defined end surfaces although these

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wires have different diameters. In addition, the laser behavior can be observed no matter the containing vessel of the nanowires is bottle or a transparent plastic bag. These indicate that in our experiment the F−P resonance in individual nanowire may not be achieved. The multiple Cr^{2+}- doped ZnSe nanowires help to form mid-infrared random round trip with lower losses. The 150 nm blue shift in wavelengths in comparison with that of microsized powder random laser, and lower-threshold lasing may be attributed to the contribution of multiple Cr^{2+}-doped ZnSe nanowires. To the best of our knowledge, it is the first observation of the laser action from a nanocrystalling Cr^{2+}- doped ZnSe nanowires.

In summary, we have synthesized nanocrystalline Cr^{2+}-doped ZnSe nanowires with an aspect ratio above 100 by using FPLAL. The Cr^{2+}-doped ZnSe nanowires are highly monodisperse in diameter and show an almost pure Cr^{2+} emission spectral range at 1.8−2.55 μm. PL spectroscopy indicates that the chromium dopant is incorporated in the ZnSe matrix, rather than at the surface. The emission band of Cr^{2+}- doped ZnSe nanowires laser are shifted by 150 nm to the shorter wavelength in comparison with the bands of microsized powder random laser. The method we developed here may potentially open a new pathway for future optically and electrically pumped mid-IR lasers based on active-ion doped quantum confined structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional description of experimental details and results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: guoing_feng@scu.edu.cn.

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

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