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Self-assembly of cadmium metasilicate nanowires as a broadband optical limiter

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ABSTRACT

Cadmium metasilicate nanowires ($CdSiO_3$ NWs) have been synthesized through a facile, eco-friendly, low-cost water–ethanol mixed-solution hydrothermal route. The transmission electron microscopy measurements of as-prepared samples indicate that the $CdSiO_3$ NWs with diameters in the range of 10–60 nm and lengths of more than 1 μm were constructed by self-assembly of 5–10-nm $CdSiO_3$ nanoparticles with good crystallinity. The monoclinic phase formation of the sample is studied in detail by X-ray diffraction, Fourier-transform infrared spectroscopy, and thermo gravimetric analysis. The results indicate that a pure monoclinic phase of $CdSiO_3$ can be obtained by a hydrothermal route without further calcinations and SiO_4 tetrahedra were the main constituents of the $CdSiO_3$ NWs. The nanosecond optical limiting (OL) effects were characterized by using an open-aperture (OA) *Z*-scan technique with 4-ns laser pulses at both 532 and 1064 nm. Theses $CdSiO_3$ NWs displayed an excellent OL performance at 532 and 1064 nm, which was better than carbon nanotubes, a benchmark optical limiter. Input-fluence dependent scattering measurements suggested than nonlinear scattering played an important role in the observed optical limiting behavior in $CdSiO_3$ NWs at 532 and 1064 nm. More significantly, the NLO performance in $CdSiO_3$ NWs incorporated solid silica gel glass has been improved in comparison to those dispersed in water. The unique structure and excellent OL property render these $CdSiO_3$ NWs competitors in the realms of optical limiting applications.

1. Introduction

Since carbon nanotubes emerged in 1991, one-dimensional nanostructures have received extensive academic and commercial interest owing to their potential applications in ultrahigh-density magnetic recording, ultrafast optical switching, microwave devices, and catalysis [1–5]. Up to now, many novel one-dimensional nanostructures have been successfully synthesized, including metal nanowires [6,7], semiconductor nanowires [8], II–VI and III–V nanowires/nanorods [9–13], semiconductor oxides nanobelts [14,15], WX_2 (W = W and Mo, X = S, Se) nanotubes [16–18], using the vapor–liquid–solid method, thermal evaporation, solution-based routes, and hydrothermal techniques.

Recently, the synthesis of inorganic nanostructures with novel morphologies has attracted increasing attention from chemistry and materials science researchers. Among these, silicates have been extensively researched because of their improved thermal and chemical stability, low material cost, and environmental friendliness. The basic unit of silicates is the [SiO_4] tetrahedron-shaped anionic group with a negative four charge (−4), which can be linked to each other in different modes and form single units, double units, chains, sheets, rings, and framework structures. The diversity of the silicate crystal structure renders such materials as potential candidates for constructing one-dimensional structures. However, under conventional conditions, only irregular particle structures can be obtained and the silicates' crystal structure, morphology and other parameters can't be effectively controlled. Therefore, exploration of new types of silicate nanostructures with unique and remarkable properties is of significant importance.

In the past decades, the search for potential optical limiters to protect human eyes and sensors from the threat of intense laser pulses has motivated many researchers to explore new materials that exhibit superior optical limiting (OL) performance. Generally, OL materials can effectively attenuate intense and potentially dangerous laser beams by allowing only a reduced transmission to the target area while exhibiting high-transmittance of low ambient light. They are capable of protecting human eyes and optical sensors from being damaged [19–22]. The output fluence is

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proportional to the input fluence at low input fluence but approaches a constant after the input fluence becomes greater than the limiting threshold. Up to now, many materials including metallophthalocyanines and porphyrins [13–25], fullerenes [26,27], graphene [28,29], carbon black and carbon nanotubes (CNTs) [30–32], metal and oxide metal nanoparticles (NPs) [33,34] have been widely studied as potential candidates for OLs. In many of these OL materials, one-dimensional nanostructured materials may play an important role. For example, CNTs exhibit unique broadband OL properties from the visible to the near infrared in the nanosecond regime, which arise from nonlinear scattering (NLS) because of the formation scattering centers consisting of solvent bubbles and ionized carbon microplasmas [31]. The OL properties of a series of metal nanowires (NWs) have also been studied and the results obtained at 532 and 1064 nm indicate that metal NWs have broadband OL capability and the OL metal NWs are comparable to or better than that of CNTs. It was found that the nonlinear response of metal NWs is dominated by NLS [33].

However, to the best of our knowledge, the OL properties of silicate NWs has not been reported, although silicates have been widely applied in the field of selective catalysis, zeolites, and gas adsorption and separation [35]. Besides the scientific interest in the mechanism of the nonlinear optical properties of such nanosystems, the study of the OL properties of silicate NWs may lead to cheap and efficient optical limiters. From the perspective of exploring new OL materials, we present here a water–ethanol mixed-solution hydrothermal method to self-assemble cadmium metasilicate nanowires. The OL properties of the cadmium metasilicate NWs are studied and their possible OL mechanisms are explored.

2. Experimental

2.1. Reagents

All the chemicals are of analytical grade and used as received without further purification. Deionized water was used throughout. Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$), sodium silicate ($Na_2SiO_3{\cdot}9H_2O$), sodium hydroxide, and ethanol were all purchased from Sigma-Aldrich.

2.2. Synthesis

2.2.1. Synthesis of $CdSiO_3$ NWs

In a typical synthesis, 0.5 g $Cd(NO_3)_2{\cdot}4H_2O$ and 0.6 g $Na_2SiO_3{\cdot}9H_2O$ were each dissolved in 5 mL diluted water in a 50 mL beaker. The two solutions were then mixed under vigorous stirring to form a white precipitate, followed by the addition of 20 mL ethanol. Subsequently, NaOH or HNO_3 was added to adjust the pH of the reaction mixture, and the resulted pH is 10 and 3, respectively. For the purposes of comparing, the $CdSiO_3$ NWs was also prepared without NaOH or HNO_3 (pH = 7). And then, the obtained mixture was transferred into a 40 mL Teflon-lined autoclave and hydrothermally treated at 180 °C for about 24 h. The temperature and reaction duration is the optimized duration. If the temperature was lower than 180 °C, the NWs cannot form even we prolong the reaction time. Similarly, the NWs cannot be obtained at 180 °C if the reaction time was less than 24 h. After the hydrothermal treatment, the autoclave was allowed to cool to room temperature. The as-formed products were collected after being centrifugally filtered, washed with deionized water and then acetone, and dried at 80 °C in air.

2.2.2. Synthesis of $CdSiO_3$ NWs incorporated silica gel glass

$CdSiO_3$ NWs incorporated silica gel glass was fabricated through hydrolysis and polycondensation of tetraethyloxysilane (TEOS), 3-glycidoxy-propyltrimethoxysilane (GPTMS), and 3-aminopropyltriethoxysilane (APTES). The doping level of $CdSiO_3$ NWs was 9.6×10^{-3} (mass ratio of $CdSiO_3$ NWs to SiO_2). The molar ratio of (TEOS + GPTMS + APTES), ethanol, and distilled water in the precursor was 1:4:4; the molar ratio of TEOS, GPTMS, and APTES was 7:2:1. In addition, N-N′dimethyl formamide (DMF) was introduced as solvent and drying control chemical additive (DCCA) at a proportion of 0.6 DMF per ethanol volume ratio. Specifically, 8.0, 2.3, 1.2, 12.1, and 3.7 mL of TEOS, GPTMS, APTES, ethanol, and water were respectively mixed under ultrasonication for 30 min. Subsequently, 7.3 mL of DMF suspension containing $CdSiO_3$ NWs was gradually added to the mixture, which was continuously ultrasonicated for 4 h. The mixture was divided into several parts with equal volumes, individually casted into polystyrene cells, sealed, and left to age and dry for several weeks. All of the gel glasses were approximately 1.3 mm in thickness and 4 cm in diameter. The linear transmittances of the produced bulk gel glasses were found to be 61.8% at 532 nm and 62.3% at 1064 nm, respectively.

2.3. Characterization

The morphologies of $CdSiO_3$ NWs synthesized under different pH were confirmed by field-emission scanning electron microscopy (FESEM: JEOL JSM-6700, JEOL Ltd., Tokyo, Japan). For the SEM observations, Au was deposited onto the freshly fractured surface of the sample by sputtering. Meanwhile, the morphology of the obtained $CdSiO_3$ NWs under alkaline condition was further investigated using transmission electron microscopy (TEM; JEM-2010; accelerating voltage, 200 kV). The samples were ultrasonicated in ethanol to ensure dispersion. A drop of the dispersed sample was left to dry on a commercial carbon-coated Cu TEM grid. X-ray diffraction patterns were obtained using a BrukerD8 advanced diffract meter with CuKα radiation of k = 1.54056 Å. Fourier-transform Infrared (FT-IR) spectra were obtained using a ThermoNICOLET6700 spectrometer. The samples were prepared in the form of KBr pellets. Thermo gravimetric analysis (TGA) was performed using a NETZSCH STA449F3 thermal analysis instrument (heating rate of 10 °C/min, under a nitrogen atmosphere). Data were collected in the range of 25–1000 °C.

2.4. Z-scan measurements

The OL behavior of the $CdSiO_3$ NWs was evaluated using the open-aperture (OA) *Z*-scan technique [36]. The excitation light source was an Nd:YAG laser (Brio 640, Quantel, Les Ulis, France) with a repetition rate of 1 Hz. The laser pulses (period, 4 ns; wavelength, 532 nm) were split into two beams with a mirror. The pulse energies at the front and back of the samples were monitored using energy detectors D1 and D2 (PE25, Ophir Optronics Solutions Ltd., Jerusalem, Israel). The diameter of the laser beam was approximately 14.5 μm, and the energy of a single pulse was 200 μJ. All of the measurements were conducted at room temperature. Each sample was dispersed in ethanol and added to 1 mm glass cuvettes. The cuvettes were mounted on a computer-controlled translation stage that shifted each sample along the *z*-axis. The Z-scan system was calibrated by CS_2, one standard nonlinear optical material and presents pure nonlinear refraction, to ensure the accuracy of all experimental Z-scan results. The result showed that the nonlinear refraction index of CS_2 measured in the Z-scan setup applied in our lab was 0.47×10^{-11} esu, which match the reported value (1.2×10^{-11} esu) [37]. And the estimated uncertainly of extracted coefficient are about ±5% which mainly arise from the energy fluctuation.