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Short communication

New insights into non-linear optical properties, photocatalytic activity, and applications of ZnSe:Cu nanoparticles prepared by microwave-assisted hydrothermal method

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Highlights

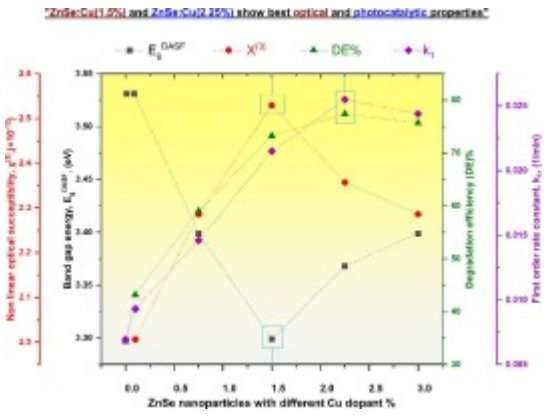
- >ZnSe:Cu NCs were provided by microwave-assisted hydrothermal method.
- Their optical, photocatalytic, photoluminescence and structural properties were studied.
- ZnSe:Cu (1.5 mol%) was the functional sample in optical applications as fibers.

- ZnSe:Cu (2.25 mol%) was the functional sample in photocatalytic applications.

Abstract

In the present work, semiconducting ZnSe:Cu (0, 0.1, 0.75, 1.5, 2.25 and 3 mol%) nanoparticles (NPs) were prepared by microwave-assisted hydrothermal (MAH) method at the fixed pH of 11.2. XRD patterns certified the formation of nanocrystals with the size of about 2.04–2.21 nm. Also, FESEM and TEM images confirmed the formation of round-shape NPs. UV–Vis spectra showed that the energy gap of nanoparticles decreased from 3.615 to 3.342 eV by the increment in copper impurity content. The exact value of the energy gap of NPs was determined by the absorption spectrum fitting derivative method (DASF). Results revealed that these NPs have a high potential in optical and optoelectronic applications; specially, the samples owing 1.5 and 2.25 mol% of Cu-impurity, as the best candidates for optical fiber applications, showed the highest third order non-linear optical susceptibility ($\chi^{(3)}$). Also, for all synthesized NPs, the optical characteristics such as the optical transition index (m), Urbach energy (E_{tail}), dielectric constant (ε) and the refractive index (n) at the absorption edge were determined. Moreover, the amount of metallization factor was also calculated, which decreases with the increase of impurity and microwave irradiation, indicating the increase of metal affinity of the samples. Photoluminescence (PL) spectra of ZnSe NPs demonstrated a general reduction in the intensity upon the introduction of Cu. This anticipated quenching further supports their heightened photocatalytic activity. The results of photocatalytic tests indicate that the sample containing 2.25 mol% of Cu exhibits the highest rate constant value (0.0255 min^{-1}) and achieves the maximum efficiency (75.7% after 60 min) for degrading the DB71, establishing it as the prime candidate for photocatalytic applications.

Graphical abstract



Introduction

In the recent years, semiconducting nanoparticles (NPs) have been the subject of many efforts, driven by their size-tunable optical and electronic properties. Among them, II–VI semiconducting NPs hold great importance and are widely used in light-emitting diodes, sensors, solar cell and catalytic agent [1], [2]. The increased attention to the synthesis and study of these NPs may also stem from their low toxicity [3], [4], [5], [6], [7], [8], which could lead to their expanded applications. Zinc selenide as one of the desired II-VI semiconductors has a wide bulk-energy band gap (2.7 eV) and a Bohr radius of 8 nm at room temperature [6], [7]; therefore, ZnSe is a suitable candidate for optical applications such as the production of blue-ultraviolet light, bio-imaging, bio-labels and photocatalytic applications [9], [10]; considering the toxicity of cadmium compounds and thus their induced drawback to their development, zinc-base agents, i.e. especially ZnSe NPs can be substituted as advantageous and preferable materials for different opto-biological applications; also ZnSe is one of the best hosts for dopants [2], [6], [8], [9].

Despite the existence of several synthesis methods such as the electrochemical, hydrothermal, wet chemical, sol–gel and chemical deposition, the microwave irradiation (MWIR)-assisted method was adopted due to its ability to yield NPs with a narrow and homogeneous size distribution, tunable size, rapid synthesis, ease of doping, and cost-effectiveness [11]. Therefore, leveraging the size-tunability feature of the MWIR method, the resulting NPs can be specifically engineered to harness optical advantages.

The linear and non-linear optical properties of semiconductors (especially II-VI and III-V bulk and quantum dots) are of great importance due to some their electro-optics aspects and their relevance to applications such as lasers, light-emitting diodes (LEDs), solar cells, optically bisatable memories, modulators, switches or oscillators [1], [2];

they are also important from the fundamental physics point of view [12]. Also, from the applied point of view, researchers have shown significant interest in the use of semiconducting NPs for photocatalytic remediation of environmental pollutants. The process of photocatalytic degradation is a highly efficient oxidation method for decomposing organic contaminants [7], [13]. During this process, electrons are excited and transited from the valence band to the conduction band of the photocatalyst by absorption of energy from an optical source, leading to the generation of highly reactive hydroxyl radicals for the oxidation and degradation of contaminants [14]. Metal oxides such as titanium oxide, zinc oxide, manganese oxide, and manganese dioxide have garnered considerable attention as photocatalyst [15]. It is while, a few researches have been reported in the case of the photocatalytic activity of the II-VI semiconducting NPs such as ZnSe.

The present work deals with the synthesis and growth of the Cu-doped ZnSe NPs in a wider range of copper impurity (0–3 mol%) compared with the previous attempts (i.e. 0–1.5 mol%) [11], [16]. Preparing the NPs was done via the environmentally friendly MWIR-assisted hydrothermal method [17], [18], and linear/non-linear optical properties of the NPs were studied. In this regard, several characteristics of the NPs were determined; such as: the inverse of wavelength at the absorption edge ($\lambda^{-1}{}_g$), the DASF optical gap ($E_g{}^{DASF}$), the EMA-size of the nanoparticles, the Scherrer's size of crystallites, the optical transition index m (from DASF method), the Urbach energy E_{tail}, refractive index n, and the dielectric constant ε, as well as, the third order non-linear optical susceptibility ($\chi^{(3)}$), the light intensity dependent refractive index (n_2), the reflection loss (R_L), the electronegativity (χ^*), the metallization factor (M) and the transmittance (T). Furthermore, as another aspect of this work, the photocatalytic activity of the fabricated NPs was investigated considering the degradation of a three azo dye, called "Direct Blue 71 (DB71)" in the presence of UV-C light using a slurry batch photo-reactor. DB71 is a water soluble dye with a widespread application in cellulose, cotton, silk, leather, polyester and paper dyeing [19]. The application of azo dyes as the indicator for the photocatalytic process are common due to the presence of their absorption peaks in the visible rang [20], [21], [22]. In brief, this study targeted at the fabrication, structural and non-linear optical, photocatalytic (PC) and photoluminescence (PL) investigations of ZnSe:Cu NPs. It should be noted that there is no systematic report for these properties and capability of zinc selenide NPs e, especially in the field of non-linear optics. So, the synthesized NPs were quantitatively assessed for their properties. The significance and novelty of this work lie in introducing powerful nano-scale optical-photocatalytic materials. The contribution of such work in the field of optical and organic pollutant degradation application is in operational improvement of the agents in optoelectronic field as fibers. Then, their

aforementioned characteristics have been extensively studied. Also, since exploring the best materials in especial applications needs achieving the optimum crystalline quality and good optical features, the optimal sample has been introduced by determining PL, Urbach energy, energy band gap, nonlinear optical susceptibility and a target pollutant photocatalytic degradation efficiency. Moreover, there are few reports only on the third order non-linear optical susceptibility of pure and Cu-doped and Cu-Mn codoped ZnSe NPs [11], [16], [17]. So, due to the lack of reports on the aforementioned chemical and non-linear optical features on the present samples, the work was planned on the investigation of such features, along with the extension of Cu content to the amounts higher than those chosen in our previous works [11], [16] to achieve the functional sample(s) in the desired applications; as stated and would be discussed later, to explore the more efficient and functional sample in optical and photocatalytic aspects, Cu-dopant content was increased to an amount in which the highest dye degradation efficiency observed.

Section snippets

Materials

All reagents were used as received without further purification. Analytical reagent grades used in this research are: $CuSO_4$ (Merck 99.99%), Zinc acetate (Merck 99.99%), selenium powder (Merck 99.99%), sodium tetrahydroborate ($NaBH_4$: as reduction agent, Merck 99.99%), sodium hydroxide (NaOH: as pH regulator agent, Merck 99.9%) and thioglycolic acid (TGA: as surfactant, Merck >99%). The three azo dye DB71, $C_{40}H_{23}N_7Na_4O_{13}S_4$ (C.I. No.: 34140, CAS No.: 4399-55-7, M_W=1029.9g/mol), as the…

XRD analysis

The XRD diffractograms of prepared ZnSe:Cu NPs are shown in Fig. 3. All diffraction peaks can be accurately indexed to the cubic zinc blend structure (Ref: JCPDS file No. 88-2345). No additional crystalline phase was detected in the XRD patterns. The reflection lines corresponding to (111), (220), and (311) planes exhibit $2\theta_{hkl}$ values of 27.42°, 46.99°, and 53.21°, respectively. These values were utilized to calculate the crystallite size using Scherrer's formula, $D_{SCH} = k\lambda/\beta_{hkl}\cos\theta_{hkl}$ [3], …

Conclusions

From the present work, the following outcomes can be noted concisely:

- ZnSe:Cu (0, 0.1, 0.75, 1.5, 2.25, 3 mol%) nanocrystals (NCs) were synthesized successfully using the microwave-assisted hydrothermal method.…
- The band gap of NCs was found to be approximately 3.5 eV which is higher than the bulk case of ZnSe (~2.7 eV), indicating formation of nano sized crystals.…
- The microwave irradiation (for 6 min) and the copper impurity lead to an increase in the nanoparticles size and a decrease in the…

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CRediT authorship contribution statement

Erfaneh Moghaddasi Nezhad: Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization. **Dariush Souri:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Ali Reza Soleymani:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software,…

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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