Nonlinear optical properties of cubic cuprous oxide with different sizes

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Abstract: Cubic cuprous oxide (Cu₂O) crystals with various sizes are successfully synthesized under room temperature by a simple solution-phase route. The surface morphology, structure properties and optical absorption spectrum of Cu₂O crystals are characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-visible absorption spectroscopy. The optical limiting (OL) properties of Cu₂O crystals are investigated using a nanosecond laser at 532 nm. The experimental results show that the OL properties of Cu₂O crystals do not only come from nonlinear scattering, but also might be due to nonlinear absorption.

Key words: Cuprous oxide, Cubic, Nonlinear optical properties

1. Introduction

In the past few years, metal oxide with well-defined shapes and sizes often exhibit unique thermal, chemical, physical, optical and catalytic properties of materials, considerable efforts have been devoted to synthesis this kind of metal oxide. Cuprous oxide (Cu₂O), as a p-type semiconductor with a direct band gap of 2.17 eV, has been intensively applied in a variety of fields, such as solar energy conversion [1], catalysis [2], gas sensors [3], negative electrode material for lithiumion batteries [4], and

1 template [5]. Due to the properties of Cu₂O crystals are related to their structures, sizes
2 and morphologies, much excellent work has been devoted to tuning the structure on a
3 specific morphology, which has been one of the research object of Cu₂O crystals in
4 recent years.
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9 Four-wave mixing, Z-scan technique and optical Kerr effect are used to investigate
10 the nonlinear optical properties of the materials [6-8]. Optical limiting (OL) is an
11 important application of nonlinear optics, which is used to the protection of human eyes,
12 optical sensors from high power laser radiation. As one of the representative of
13 transition-metal oxide, the nonlinear optical properties of Cu₂O crystals have been
14 widely investigated. For example, the optical nonlinearity in Cu₂O thin film has been
15 researched using the Z-scan method by femtosecond laser excitation [9]. The TPA
16 coefficient and nonlinear refractive index have been investigated for a single crystal
17 bulk Cu₂O sample using a balance-detection Z-scan single beam technique [10]. Many
18 groups also reported the nonlinear optical properties of Cu₂O crystals under different
19 experimental conditions [11-15]. The OL properties of different morphologies of Cu₂O
20 nanopowders were reported using open aperture Z-scan technique [15]. To the best of
21 our knowledge, the literature makes very few references to the OL properties of Cu₂O
22 crystals with various sizes. Nevertheless, a more detailed investigation on the OL
23 properties of Cu₂O crystals with various morphologies and sizes would be discussed.
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46 In this paper, cubic Cu₂O crystals with various sizes have been synthesized under
47 room temperature by a simple solution-phase route, and then we investigate the
48 nonlinear optical properties of the as-prepared samples using a nanosecond laser. The
49 experimental results show that the cubic Cu₂O crystals have strong OL behavior. The
50 nonlinear scattering experiment indicates that the larger sizes of samples have the
51 higher linear parts of scattering light, the nonlinear scattering is main mechanism for
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the OL properties of cubic Cu₂O crystals, while the nonlinear absorption could play an important influence on the OL behavior.

2. Experiments

Cubic Cu₂O crystals with different sizes had been synthesized by solution-phase route under room temperature, the preparation process was similar to Ref. [16]. In a typical procedure for the synthesis of different sizes of Cu₂O cubes, 50 mL deionized water were respectively added to sample vials labeled a, b, c. Then 1 mL of 0.1 M CuCl₂·2H₂O solution was added into the beaker. After 5 min, 1, 3 and 4 mL of 0.4 M NaOH solution were added into vials a, b and c, respectively. After stirring for 5 min, 1, 2 and 2 mL of 0.1 M ascorbic acid solution were added into vials a, b and c, respectively. The vials were stirred for 30 min to obtain the desired products at room temperature, and then the samples were centrifuged at 12000 rpm for 2 min (XIANYI TG16-WS centrifuged). The precipitates were collected and washed with deionized water and anhydrous ethanol many times. Finally the products were dried at 60°C for 6 h in a vacuum oven.

The solid products were characterized by transmission electron microscopy (TEM, JEOL JEM-2100), X-ray diffractometer (XRD, Bruker-AXS D8 Advance) and UV-visible absorption spectroscopy. The cubic Cu₂O powders were dispersed in ethanol by ultrasonication for 5 min, then the samples were filled in 5 mm thick quartz cells, and the linear transmittances of the samples were adjusted to 60%. All the samples were prepared for OL measurement. The OL performances of the Cu₂O crystals with different sizes were investigated, and the experiment condition is the same as the preliminary experiment case [17, 18].

3. Results and discussion

Fig. 1 shows a set of typical TEM images of the Cu₂O crystals, the samples were

prepared by dropping a few milliliters of each sample on copper holey carbon grids. Fig. 1(a-c) indicate that the average sizes of the Cu₂O crystals are about 45, 96 and 140 nm, which referred to as Cu₂O-I, Cu₂O-II and Cu₂O-III throughout this paper, respectively. The average size of each nanocrystal is calculated from the center of a Gaussian distribution is shown in Fig. 1(d-f)

The phase structure of the as-prepared products was examined by XRD characterization. Fig. 2 displays the XRD patterns of as-prepared products with different sizes of Cu₂O crystals. All diffraction peaks of the samples could be matched well according to the standard structure of Cu₂O (space group: Pn3m, lattice constant $a = 0.427$ nm, JCPDS file NO. 05-0667). No impurity phase such as copper or cupric oxide could be detected in this pattern, indicating that a pure phase of Cu₂O crystals can be readily synthesized.

The optical characterizations of the as-obtained cubic Cu₂O crystals have been carried out by the UV-vis absorption spectrum which is demonstrated in Fig. 3. From the UV-vis absorption spectra, we can see that the absorption peak of Cu₂O-I around 460 nm, which considerably blue-shifted compared to the bulk Cu₂O crystals (~570 nm) possibly as a result of quantum size effects [19-21]. Another prominent feature in the absorption profiles of the larger cubic samples (Cu₂O-II and Cu₂O-III) is the appearance of one absorption tail in the red and near-infrared (NIR) regions. Interestingly, this band progressively red-shift to the NIR region as the cube diameters increase, and this broad band feature should be attributed to Mie scattering, which only occurs when the particles' size is comparable to the wavelength of incident light, and the same results were reported for the Cu₂O crystals in Refs. [22-24].

OL is a very important nonlinear optical phenomenon in protecting optical sensors and the human eyes. To study the OL mechanism of the Cu₂O crystals, we measured the

1 scattering light of our samples, and found that all the samples exhibit a strong nonlinear
2 scattering, which is shown in Fig. 4(a). The scattering rates are also nearly constant at
3 the low input energy density and then increase with the increasing incident fluence,
4 which means that the scattering light is a nonlinear process dependent on the incident
5 fluence. In comparison, the linear parts of scattering rates of Cu₂O-III are greater than
6 those of Cu₂O-I and Cu₂O-II crystals, which could be explained by the scattering origin.
7 The cubic Cu₂O crystals with larger size have the larger initial scattering centre size,
8 more effective heat transfer from samples to solvents, and hence the faster solvent
9 bubbles growth, resulting in the stronger scattering behavior. Cubic Cu₂O crystals with
10 various sizes are measured in the same experiment conditions, the influence of
11 morphology and experiment conditions could be excluded, so the particles size could be
12 the dominant reason for their scattering behaviors.

13 Fig. 4(b) shows the transmission as functions of the incident pulse energy density
14 for three dispersions. It can be clearly seen that the transmittance of these dispersions
15 decreased with increasing input fluence, exhibiting a promising OL behavior. Evidently,
16 cubic Cu₂O crystals with small average size showed a better OL performance than those
17 with big size. Compare to Fig. 4(a), it is found that Cu₂O-III dispersions show the
18 strongest scattering but result in the weakest transmitted loss. It is worth noting that, at
19 532 nm, the OL performances follow Cu₂O-I > Cu₂O-II > Cu₂O-III, while the scattering
20 signals follow Cu₂O-I < Cu₂O-II < Cu₂O-III, indicating that the OL behavior of the
21 Cu₂O dispersions is attributed to the combined mechanisms of nonlinear scattering and
22 nonlinear absorption.

23 4. Conclusion

24 In summary, the cubic Cu₂O crystals with different sizes are obtained under room
25 temperature. The nonlinear optical properties of Cu₂O crystals are studied via the
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fluence-dependent transmittance and the nonlinear scattering measurements. The experimental results show that the nonlinear scattering is the main mechanism for the OL properties, while the nonlinear absorption could play an important role in the OL behavior.

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Figure captions:

Fig. 1. TEM images (a-c) and Size distribution histograms (d-f) of Cu₂O products (a, d: Cu₂O-I, b, e: Cu₂O-II, c, f: Cu₂O-III).

Fig. 2. XRD patterns of the Cu₂O crystals with different sizes: (a) Cu₂O-I, (b) Cu₂O-II, (c) Cu₂O-III.

Fig. 3. UV-vis absorption spectra of the Cu₂O crystals: (a) Cu₂O-I, (b) Cu₂O-II, (c) Cu₂O-III.

Fig. 4. (a) Scattering signals with respect to the input fluence of cubic Cu₂O dispersions with different sizes, (b) Transmission as function of the incident pulse energy density for three dispersions at 532 nm. The linear transmittance is 60%.

Figures:

FIG1.TIF

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