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Sol–gel synthesis of silver nanocrystals embedded in sodium borosilicate monolithic transparent glass with giant third-order optical nonlinearities

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ABSTRACT

We report the preparation of uniform spherical shape silver nanocrystals doped sodium borosilicate monolithic transparent glass by sol–gel method. The characterization of the resulting Ag nanocrystals was accomplished by using X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, and energy dispersive X-ray spectrum. Surface plasma resonance absorption peaks of the silver nanocrystals glass at about 406 nm have been obtained from ultraviolet–visible absorption spectrometer and their intensity is changed with different heat treatment temperatures. We have investigated the nonlinear optical properties of silver quantum dots doped glass using Z-scan technique. Third-order nonlinear optical susceptibility $\chi^{(3)}$ of the glass was estimated to be 1.01×10^{-11} esu. In particular, a mechanism for the formation of Ag quantum dots glass is proposed. This work will significantly promote the obtained material applications in optical devices.

1. Introduction

Ultrafast all-optical switches have been demonstrated to play an important role in the next generation broadband optical networks [1,2]. In recent years, metal quantum dots glasses have been recognized as excellent candidate materials for fabricating all-optical photonic devices due to not only their ultrafast nonlinear response time and large third-order optical nonlinearities, but also their fast response speed and compatibility with the existing optical fiber systems [3–6]. Among the metal quantum dot dopants, Ag nanocrystals have attracted great attention in nanoscience and nanotechnology due to their fascinating chemical and physical properties, such as catalytic [7–9], optical [10], antibacterial [11,12], narrow plasmon band and high scattering efficiency [13]. What's more, the most conspicuous manifestation of confinement in optical properties are the appearance of the surface plasmon resonance (SPR) in the visible region that strongly enhances the third-order optical nonlinearity [14,15].

To date, a significant amount of research has been focused on Ag@SiO_2 core–shell structures materials because they combine the unique properties and promising applications of both the core materials and the shell materials [13,16–21]. In this case, the research on the third-order optical nonlinearity of Ag quantum dots glass has been lagging far behind. To the best of our knowledge, the third-order nonlinear susceptibility dispersion is for the first time measured for the case of Ag colloidal glasses around the SPR resonance in 1998 by Faccio et al. [22]. Later, Yang et al. [23] reported the preparation of Ag quantum dots glasses via ion-exchange method. The results indicate that the third-order susceptibility increases with the increasing of the annealing temperature, but the transmission electron microscopy (TEM) images indicated that Ag nanocrystals aggregation has a treelike structure. Recently, another interesting work [24] investigated the spectral dependence of both nonlinear refraction and absorption in lead–germanium oxide glasses containing silver nanocrystals, indicating that this material is suitable for all-optical switching at telecom wavelengths. However, in mostly

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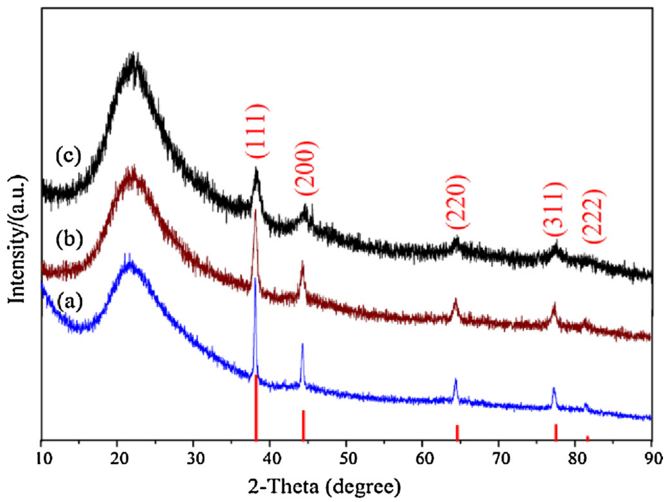

Fig. 1. XRD patterns of the Ag doped NBS glasses obtained after sintered at (a) 420 °C, (b) 450 °C and (c) 470 °C.The red lines show their standard patterns as in JCPDS card No. 65-2871.

previous studies, there always encountered a major problem that has a huge challenge to synthesize monolithic transparent metal quantum dots doped glass without fracturing, which significantly hinders their deep investigation and potential applications, particularly when used for manufacturing all-optical photonic devices. Furthermore, the high tendency to form aggregates induced by the high surface energy of the Ag nanocrystals, which causes deterioration of their chemical properties. Therefore, preparation of Ag quantum dots transparent glasses without fracturing and aggregating is essential in order to fully exploit their peculiar properties and unique applications.

To reach this aim, the use of sol–gel technique is often mentioned as a promising alternative. As we know, the sol–gel technique has the major advantages in obtaining the promising monoliths glass materials over conventional methods, such as significantly lower synthesis temperatures, the controllable composition and high chemical homogeneity of the materials, near-net-shape objects can be produced directly by casting and gelating of the sols in molds [25–27]. On the other hand, depending on how the stiff gel is sintered, the stability of the metal nanomaterials can greatly enhance and the aggregation of metal particles can be suppressed. In addition, various metal quantum dots (such as In, Cu, Bi) doped glasses [28–30] were successfully prepared by the facile sol–gel technique, and their nonlinear optical properties were carefully investigated in our previous reports.

Herein, inspired by noble metal quantum dots doped glass enhanced the optical nonlinearities, we have prepared Ag-doped sodium borosilicate (NBS) glass with Ag content (Ag/$Na_2O + B_2O_3 + SiO_2$) of 1.5 wt.% by sol–gel technique. The structure, absorption and nonlinear optical properties were carefully characterized and discussed. The most important study is that the formation mechanism of Ag quantum dots glass has also been discussed. And the results showed that the obtained materials are promising for applications in ultrafast all-optical switches and other optical devices.

2. Experiment

2.1. Stiff gels preparation

Fig. S1 is the photographs of Ag QDs NBS gel samples and Ag QDs NBS glasses obtained. The sodium borosilicate glass containing Ag nanocrystals (1.5 wt.%) was prepared by employing sol–gel method. All materials were analytical grade without further purification. The composition of the glass matrix was 5.74 Na_2O–21.38B_2O_3–72.88SiO_2 (in wt.%). Sodium borosilicate system glass containing silver nanocrystals was prepared by using tetraethyl orthosilicate (TEOS), boric acid (H_3BO_3), sodium ethylate (C_2H_5ONa) as precursors, methanol, 2-methoxyethanol, ethanol as precursor solvents, and hydrochloric acid as catalyst. The whole preparation procedure was

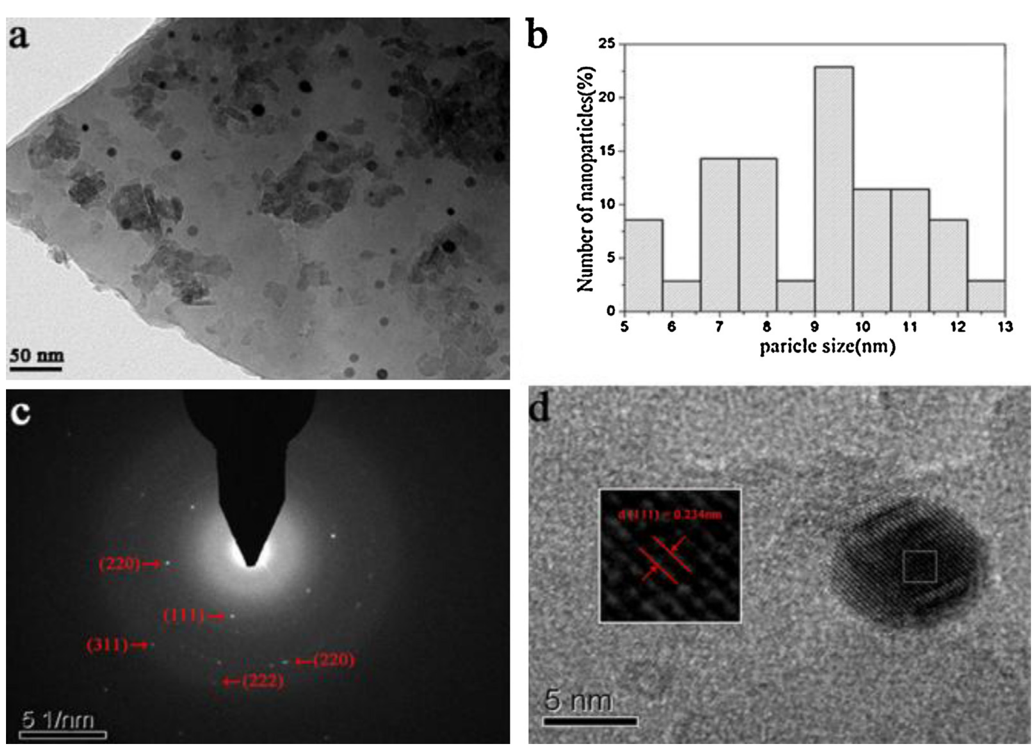

Fig. 2. TEM analysis of the Ag doped NBS glass (a) morphological image of TEM; (b) the size distribution image; (c) SAED image; (d) HRTEM image.