Materials Letters 116 (2014) 1–4

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Nonlinear optical behavior of silver nanopentagons

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ARTICLE INFO

Article history:
Received 21 September 2013
Accepted 25 October 2013
Available online 31 October 2013

Keywords:
Optical materials and properties
Nanoparticles
Saturable absorption
Reverse saturable absorption
Shape-dependent

ABSTRACT

Novel silver nanopentagons were prepared by a liquid-phase method. Their nonlinear optical properties were investigated by open aperture *Z*-scan technique using 8 ns laser pulses at 532 nm. The silver nanopentagons exhibited intensity-dependent transformation from saturable absorption (SA) to reverse saturable absorption (RSA). The SA behavior may be attributed to the bleaching of ground-state surface plasmon resonance absorption. By contrast, the RSA may have resulted from high excited-state free carrier absorption and nonlinear scattering. The transformation from SA to RSA is also found to be highly dependent on the shape and morphology of the silver nanoparticles.

1. Introduction

Noble metal nanoparticles, including Au, Ag, Pt, and Pd, have received increasing attention primarily because of their excellent properties and various applications in optics, catalysis, electronics, sensing, biomedicine, and information storage [1–3]. These metal nanoparticles produce strong surface plasmon resonance band in the visible to near-infrared regions of the electromagnetic spectrum. This phenomenon is due to the electromagnetic field-induced collective oscillation of the free conduction electrons, which results in a highly nonlinear optical enhancement. Noble metal nanoparticles possess ultrafast nonlinear optical response times, facilitating their application in optical communication, all-optical switches, and nonlinear optics [4–6]. Most importantly, the nonlinear optical properties of noble metal nanoparticles are experimentally found to be strongly dependent on the size and shape of the nanoparticles [7–9]. The size and shape of the noble metal nanoparticles can be controlled to customize and design their nonlinear properties to improve their performances.

In this paper, we report on the preparation of novel Ag nanopentagons using a liquid-phase method. Transmission electron micrographs and UV–visible extinction spectra were employed to characterize the Ag nanopentagons. The nonlinear optical behavior was investigated using open aperture *Z*-scan technique with 8 ns laser pulses at 532 nm.

2. Experimental

Ag nanopentagons were synthesized in the presence of polyvinylpyrrolidone (PVP), which has been successfully applied in the preparation of Ag triangular nanoplates [10]. In this method, the hydroxyl end groups of PVP can serve both as a very mild reductant for kinetically controlled synthesis of Ag nanoplates and stabilizer. Furthermore, the molecular weight of PVP has significant influence on the morphology of silver nanoparticles. And to obtain silver nanopentagons, we altered the molecular weight of PVP in the reported preparation of Ag triangular nanoplates. Specially, 0.68 g PVP (Mw=8000; Alfa Aesar, MA) was dissolved in 20.0 mL of aqueous solution in a 250 mL vial and heated to 70 °C in air under magnetic stirring. Subsequently, 20.0 mL of aqueous $AgNO_3$ solution (0.2 M) was quickly added into the vial. The mass ratio of $AgNO_3$ to PVP was set to 1. After the vial was capped, the reaction was continued for another 60 min at a constant temperature of 70 °C. The mixture was magnetically stirred throughout the synthesis process. Acetone (5 × the total solution volume) was first added to the products prior to washing with water and ethanol. The products were separated by centrifugation to remove excess PVP and subsequently dispersed in ethanol to obtain suspensions for further analysis and open *Z*-scan measurements.

The morphology of the Ag nanopentagons was examined using a transmission electron microscope (TEM; JEM-2010) with an accelerating voltage of 200 kV. For the TEM observations, the sample was ultrasonicated in ethanol to ensure that the nanoparticles were well dispersed. Then, a drop of the dispersed sample was left to dry on a commercial carbon-coated Cu TEM grid. The UV–visible extinction spectrum of the obtained nanoparticles was

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http://dx.doi.org/10.1016/j.matlet.2013.10.101

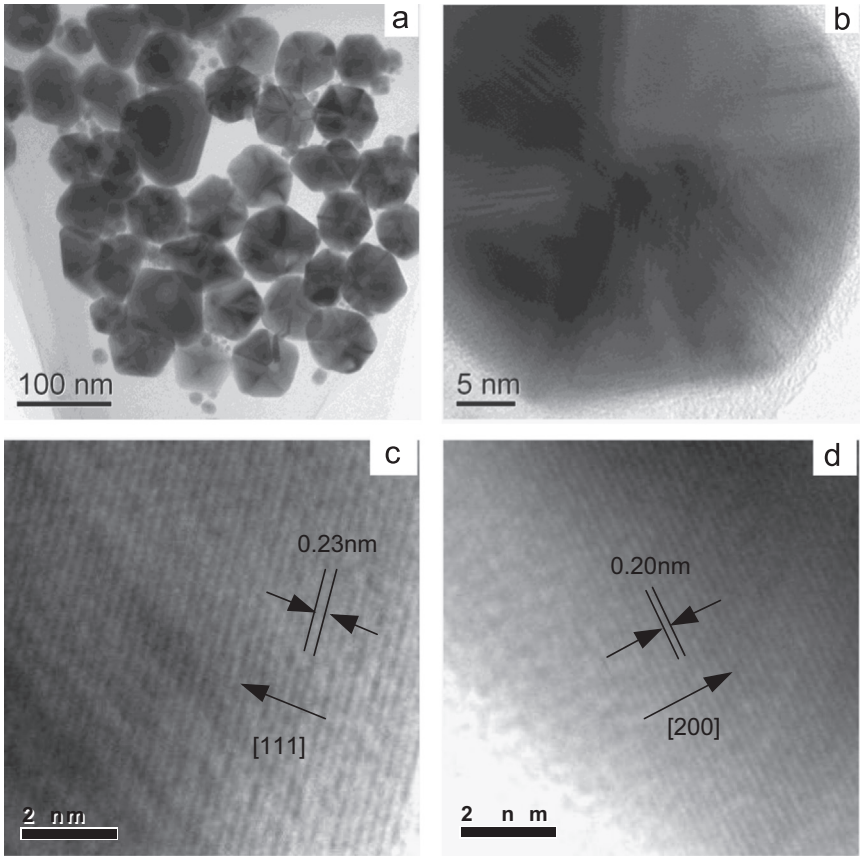

Fig. 1. Transmission electron micrographs of the Ag nanopentagons.

measured using a Shimadzu UV 2450 spectrometer. Finally, the Ag nanopentagons were put into 10 mm-thick quartz cuvettes.

The nonlinear optical studies were performed using an open aperture *Z*-scan measurement technique [11]. We used 8 ns pulses generated by a Q-switched Nd:YAG laser operating at a 1 Hz repetition rate and at 532 nm. The sample was dispersed in ethanol and put into 1 mm-thick glass cuvettes. The linear transmittance of the samples was adjusted to ~70%. The focal length of the lens was 300 mm, and the beam waist at the focus was 14.5 μm. The energy of a single pulse was set to 50, 100, 200, and 400 μJ. All measurements were conducted at room temperature.

3. Results and discussion

Transmission emission micrographs of the prepared Ag nanopentagons are shown in Fig. 1. The obtained product exhibits good monodispersity and primarily consists of nanopentagons with an average edge length of ~70 nm [Fig. 1(a)]. A high-resolution transmission electron micrograph (HRTEM) taken at the top edge of the nanopentagons further illustrates the morphology of the nanoparticles [Fig. 1(b)]. In Fig. 1(c) and (d), the fringe spacing of 2.3 and 2.0 Å can be indexed to the {111} and {200} reflections, respectively, of face-centered cubic (fcc) Ag. Combining with the HRTEM image shown in Fig. 1(b), we can conclude that these Ag nanopentagons were enclosed by a mix of {111} and {200} facets on the surface.

Three broad adsorption bands are observed in the optical extinction spectrum illustrated in Fig. 2. The pronounced band centered at 450 nm is attributed to the surface plasmon resonance, and its long-wavelength tail is caused by the *d–sp* interband

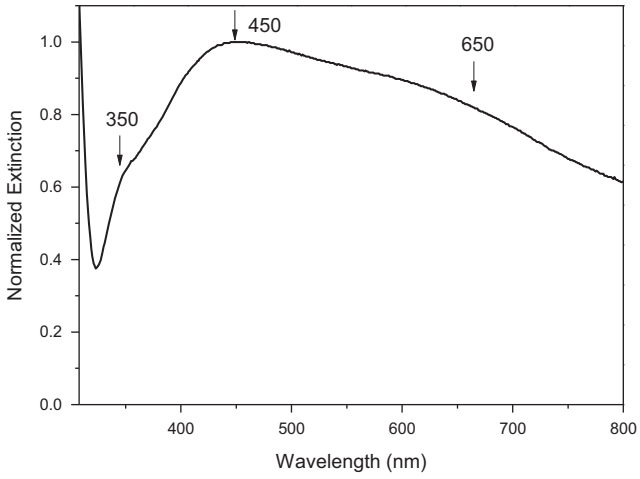

Fig. 2. Extinction spectrum of the prepared Ag nanopentagons.

transitions [12]. A weak band at 350 nm corresponds to the photon-induced Ag-bulk-plasmon emission [12].

The open aperture *Z*-scan curves of the Ag nanopentagons excited under four different single pulse energies are shown in Fig. 3. Unlike the open aperture *Z*-scan curves of conventional nonlinear optical materials, including fullerenes, phthalocyanines, porphyrins, and carbon nanotubes, the obtained *Z*-scan data of the Ag nanopentagons display unusual humps flanking the valleys at relatively low excitation intensity. The humps disappear with an increase in the excitation intensity, which indicates that the sample exhibits an intensity-dependent SA and RSA behavior. A very similar behavior was observed in gold nanorods [13], gold