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Optical limiting of flexible gold nanorods/organosilicon hybrid materials

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ABSTRACT

Due to the potential application of gold nanorods (GNRs) in tunable optical limiting materials, it is significant to develop GNRs/polymer hybrid materials. In this paper, GNRs were prepared using a seed-mediated growth method and coated with silica shells through hydrolysis of tetraethoxysilane under alkaline condition. The silica coated GNRs were then introduced into room-temperature vulcanized silicone rubber. Optical limiting property of the GNRs/silicone nanocomposites was investigated. The results indicated the GNRs doped silicone rubber sheets possessed good optical limiting performance and the optical limiting behavior was mainly attributed to the nonlinear absorption. The GNRs doped silicone materials would be good candidates for practical optical limiting applications.

1. Introduction

Gold nanoparticles have attracted considerable attention in recent years because of their ease-of-synthesis, chemical and thermal stability, unique nonlinear optical property and their potential application in photonic technology [1,2]. Gold nanoparticles were found to display strong optical limiting effect, and their optical limiting performances were size-dependent and enhanced by formation of aggregates [3–8]. Anisotropic gold nanorods (GNRs) possess enhanced surface plasmon resonance (SPR) absorption and Rayleigh scatting and optical limiting property study of GNRs colloids showed the assembled GNRs exhibited better optical limiting property than those well dispersed GNRs [9,10]. According to the theoretical calculation, there are two wave bands of optical limiting in the visible and near infrared region because of the morphological anisotropy of gold nanorods, and the longer wavelength optical limiting band corresponding to longitudinal surface plasmon resonance (SPR) may red-shift linearly by increasing the aspect ratio of gold nanorods [11]. The tunable optical limiting characters are suitable for designing optical limiting devices in a wide wavelength range. As we know, anisotropic GNRs possess two plasmon resonance peaks corresponding to transverse and longitudinal absorption bands, and the longitudinal plasmon resonance band is tunable throughout the visible and near-infrared region of the spectrum by changing the aspect ratio of the nanorods, surface charges, dielectric constant of the surrounding medium, and so on [12–14].

For gold nanorods, the optical limiting research was carried out mainly in solution, which greatly limited the application in practice. To exploit the application potential of GNRs in tunable optical limiting materials, it is significant to develop GNRs/polymer hybrid materials, especially the hydrophobic polymer doped with GNRs. But the organic phase synthesis of anisotropic GNRs is still a nascent area, because the synthesis of metal nanorods in organic solvents is rarely reported [15]. GNRs prepared via common seed-mediated sequential process are stabilized by CTAB bilayer in the aqueous phase [16–18]. Successful phase transfer of aqueous dispersions of anisotropic GNRs into organic phase and further preparation of transparent polymer samples remain a problem to some degree. Liu et al. adopted thio-terminated poly(ethylene glycol) (PEG) to surface modified the GNRs and further dispersed them in poly(methyl methacrylate)(PMMA) film [19]. They found the optical properties of GNRs in PMMA could be tuned through thermal reshaping. Another team deposited a uniform silica shell on the metal nanoparticles such as gold and silver nanospheres, as well as gold nanorods. The metal nanoparticles coated with silica shell were then doped into ureasils yielding flexible nanocomposites that retained the optical properties of the nanoparticles colloids [20,21]. The silica coating method provided an effective way to disperse the GNRs into hydrophobic polymer. Among the various kinds of polymers, silicone rubbers are important engineering materials because of their distinguished flexibility, low

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toxicity, good thermal stability, and electrical insulation. They have also received wide attention due to their excellent chemical stability and large operating temperature range (e.g. −100 to 250 °C) [22]. As soft matrix for optical limiting materials, silicone rubbers can provide excellent chemical and thermal stability in the course of operation.

In this paper, GNRs were prepared using the seed-mediated growth method and coated with silica shell by hydrolysis of tetraethoxysilane under alkaline condition. The silica coated GNRs were then introduced into room-temperature vulcanized (RTV) silicone rubber, yielding flexible nanocomposites. Optical nonlinearity and optical limiting property of the polymer nanocomposites were investigated. The results showed that the GNRs doped RTV silicone rubber sheets exhibited good optical limiting performance and could be candidates for practical optical limiting applications. The optical limiting behavior was mainly attributed to the nonlinear absorption.

2. Experimental section

2.1. Preparation of GNRs

Gold nanorods were prepared by the seed-mediated growth method. First, hexadecyltrimethylammoniumbromide (CTAB) solution (2 mL, 0.20 M) was mixed with 2.0 mL of 0.50 mM $HAuCl_4$. To the mixed solution, 0.48 mL of ice-cold 5 mM $NaBH_4$ solution was added under vigorous stirring to obtain a brownish yellow seed solution. Then CTAB (10 mL, 0.20 M) was added into a certain volume of 4 mM $AgNO_3$ solution at 27 °C. To this solution, 10.0 mL of 1.0 mM $HAuCl_4$ and 120 μL of 0.10 M ascorbic acid were added to obtain growth solution. Finally, 24 μL of the seed solution was added to the growth solution with gentle stirring. The temperature of the growth medium was kept at 27 °C for 12 h. The new-made GNRs colloids were centrifuged at 10,000 rpm for 10 min, decanted, and resuspended in 20 mL of 2 mM CTAB solution to decrease the content of free CTAB.

2.2. Surface modification of GNRs

To the GNRs colloids (10 mL, $4.8{*}10^{-4}$ M) were added, in turn, 3-mercaptopropyl trimethoxysilane (MPS) (0.1 mL, 10.8 mM) and 0.6 mL of 25.6% ammoniumhydroxide under vigorous stirring. 0.02 mL of tetraethoxysilane (TEOS) was added into the resulting dispersion (pH = 11.5) then allowed to stand for 12 h, which resulted in the deposition of silica shells on the GNRs. Finally, impurities, such as ammonia, water, and unreacted silane were removed by repeated centrifugation and ultrasonic dispersion cycles. The GNRs@SiO_2 colloids were then redispersed in ethanol.

2.3. Preparation of GNRs-silicone sheets

GNRs/silicone hybrid rubber materials were prepared as follow. SYLGARD 184 silicone elastomer was purchased from Dow Corning Silicone Trading Co., LTD. (Shanghai, China), which was composed of base gum and curing agent. Stoichiometric amounts of base gum (10 mL) and curing agent (1 mL) were mixed, and then certain amount of GNRs@SiO_2 colloids in ethanol was added under stirring. The mixture was vacuum degassed and allowed for slow vulcanizing within vacuum oven at 80 °C for 2 h or 25 °C for 24 h.

2.4. Instruments and optical property measurement

UV–vis absorption spectra were obtained using a PERSEE TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) with a resolution of 1 nm. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2100 electron microscope. Scanning electron microscopy (SEM) images were taken on a Jeol JEM-2100 microscope. The optical limiting property of GNRs/organosilicon rubber was measured with a Continuum Surelite Laser, which provided 5.0 ns laser pulses at 532 nm with a repetition rate of 10 Hz. The energy of incident laser was adjusted by a polarization analyzer. The beam was split into two beams by the beam splitter, and the reflected beam was used to monitor the incident energy. A lens with a focal length of 6 cm was used to focus the incident beam on the surface of the rubber sheet samples and the beam waist at the focus was 3 μm. The incident and transmitted laser pulses under synchronous pulse irradiation were monitored with two FieldMaxII-P laser energy meters (J-10MB-LE energy sensor, Coherent Inc. USA) respectively. For measuring the nonlinear optical properties, open aperture *z*-scan experiments were conducted on the rubber sample according to the literature [23]. A focused laser beam was used for exciting the sample, which was moved along the beam (taken as the *z*-axis) through the focal point to the other side of the focus. The laser pulse energy used in the experiment was 150 μJ/pulse. For each *z* position the corresponding transmission was measured.

3. Results and discussion

3.1. Surface modification of GNRs and preparation of GNRs-silicone sheets

Using the seed-mediated growth method, GNRs with aspect ratios ranging from 1.5 to 5 can be prepared successfully. In the experiment, two kinds of GNRs with different length and aspect ratios were synthesized by changing the dosage of $AgNO_3$. The average length of short GNRs was 37 nm and the aspect ratio was 2.5, while the longer GNRs had average length of 43 nm and aspect ratio of 4.1. Transmission electron micrographs of the two GNRs samples are given in Fig. 1, and it can be shown that the nanorods are rather monodisperse.

To obtain the GNRs/organosilicon hybrid materials, the GNRs dispersed in water should be first phase transferred into organic phase. But the direct transfer from aqueous phase to organic phase will lead to irreversible aggregation of GNRs, so the GNRs were first surface modified. In the experiment, silica coating was adopted to stabilize the GNRs to avoid the aggregation. Furthermore, the chemical nature of the silica shell was identical to that of siloxane units in organosilicon polymer. The silica coating procedure was carried out according to the Stöber–Fink–Bohn method and MPS acted as coupling reactant to deposite silica on the surface of the GNRs [24,25]. Active silica (TEOS at a pH of 11.5 allows for a slow polycondensation of alkoxysilane groups to form silica) promoted the formation of a thin and relatively homogeneous silica layer around the GNRs. The UV–vis absorption spectra of the GNRs before and after silica coating are shown in Fig. 2. The transverse absorption peak position remained unchanged basically, while the longitudinal plasmon resonance band red-shifted due to the refractive index increase of the surrounding media. In the case of the short GNRs, the shift was about 20 nm, while for long GNRs the shift reached 30 nm. The relative small change of shapes of the spectra confirmed the nonaggregated nature of the GNRs, and the enhancement of the transverse absorption might be ascribed to the appearance of local cluster of the GNRs.

The concentration of GNRs within the hybrid silicone materials could be adjusted by the dosage of the GNRs. Three different concentrations of the samples were prepared and the mass content of GNRs was about 0.003%, 0.005%, 0.008% respectively. UV–vis spectra of different GNRs@SiO_2 doped silicone rubber sheets are shown in Fig. 3. The increased concentration leaded to the higher absorbance at all wavelengths, which indicated that the