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Nonlinear optical and optical limiting properties of ultra-long gold nanowires

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ABSTRACT

Ultra-long gold nanowires (NWs) were prepared and characterized. The gold NWs were predominantly formed from gold nanorods. The ultraviolet–visible absorption spectrum of the gold NWs contained two absorption bands. One corresponded to transverse surface plasmon absorption in the gold NWs, and the other to absorption by residual organic groups. The nonlinear optical and optical limiting (OL) properties of the gold NWs were characterized by the open aperture Z-scan technique, using 532-nm laser pulses with pulse duration of ~7 ns. The NWs exhibited strong OL effects for nanosecond laser pulses at 532 nm, and their OL performance was superior to that of carbon nanotubes; a benchmark OL material. Thus, the gold NWs could potentially replace carbon nanotubes in OL applications. Nonlinear scattering played an important role in the OL activity of the ultra-long gold NWs at 532 nm. The nonlinear behavior of the gold NWs altered from saturable absorption to reverse saturable absorption, with increasing excitation energy. This property can be exploited in optical pulse compressors, optical switching, and laser pulse narrowing.

1. Introduction

Lasers were invented in 1960 and have since been applied in energy weapons, optical communications, measurement, and chemical and materials preparation and processing. Protecting sensitive optical devices and human eyes from such high-energy optical sources is important. Optical limiters (OLs) can attenuate intense and potentially dangerous laser beams, by reducing their transmission to the target area, while still transmitting low ambient light. Thus, OLs can protect human eyes and optical sensors from damage [1–3]. The output fluence is proportional to the input fluence at low input fluence, but approaches a constant value when the input fluence increases above the limiting threshold. Metallophthalocyanines and porphyrins [4,5], metal and semiconductor nanoparticles (NPs) [6–8], quantum dots [9–11], fullerenes, carbon nanotubes (CNTs), and graphene [12–14] have all been widely studied as potential OLs. Two mechanisms typically contributeto OL behavior, including nonlinear absorption (NLA) (e.g., reverse saturable, excited-state, two-photon, multiphoton, and free-carrier absorption) and nonlinear scattering (NLS) [15]. Sometimes, these two mechanisms operate in the same system to more effectively enhance the OL properties.

Noble metal NPs such as those of gold and silver can exhibit significant nonlinear optical (NLO) properties and ultrafast response times. Their OL properties have been extensively studied by picosecond and femtosecond spectroscopy [16]. Developing OL materials using metal NPs is attractive, because gold and silver NPs are easily prepared, and are highly soluble and stable in aqueous and organic solvents. The linear and nonlinear optical properties of gold and silver NPs strongly depend on their size, shape, and dielectric environment. Considerable effort has focused on investigating the relationship between the OL and NLO properties and the NPs size and shape. Reported metal NPs include silver nanoprisms, silver nanowires (NWs), silver spheres, silver nanopentagons, gold spheres, and gold nanorods (NRs). Metal NWs are promising OL candidates because their OL response spans the visible to near-infrared wavelength range, which is generally attributed to NLS and NLA [17]. To the best of our knowledge, there are no reports on the NLO and OL properties of gold NWs, despite such one-dimensional nanostructures having important applications in biotechnology, optoelectronics, and photonics.

In this study, we prepared ultra-long gold NWs in aqueous solution. Generally, one-dimensional nanostructures can be classified as ultra-long materials as their aspect ratio of is larger than 100. Their morphology and linear optical properties were characterized by transmission electron microscopy (TEM) and ultraviolet–visible (UV–vis) absorption spectrophotometry, respectively. Their NLO and OL properties were characterized by open-aperture (OA) Z-scan measurements, using 532-nm laser pulses with pulse duration of ~7 ns. The gold NWs exhibited strong OL

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effects for nanosecond laser pulses at 532 nm. Their OL performance was superior to that of CNTs; a benchmark OL material. The OL mechanism of the gold NWs was also investigated.

2. Experimental

Gold NWs were produced following a modified reported method [17]. First, 100 mL of aqueous 0.001 mol/L $HAuCl_4$0.01 mol/L cetyltrimethylammonium bromide(CTAB) was prepared in a conical flask. Next, 6.00 mL of ice cold 0.001 mol/L $NaBH_4$ solution was quickly added under stirring. The solution immediately turned pink, indicating the formation of gold NPs. The particles in this solution were used as seeds within 2 h of preparation. Second, 20 mL of 0.001 mol/L $HAuCl_4$ and 40 mL of 0.1 mol/L CTAB were mixed. Then, 0.40 mL of 0.1 mol/L $AgNO_3$, 0.32 mL of 0.1 mol/L fresh ascorbic acid, and 0.80 mL of 1 mol/L HCl were added to the solution in turn. Finally, 10 mL of the seed solution was added under stirring, to obtain a homogenous solution. The color of the solution changed to intense pink within 30 min, indicating the formation of gold NWs.

The morphology of the gold NWs was investigated using TEM (JEM-2010, JEOLLtd., Tokyo, Japan), at an accelerating voltage of 200 kV. Samples were first ultrasonically dispersed in ethanol, a drop of which was allowed to dry on a commercial carbon-coated Cu TEM grid. UV–vis absorption spectra were recorded using a spectrophotometer (UV-2600), with quartz cells of a path length of 10 mm.

The OL behavior of the gold NWs was evaluated from OAZ-scan measurements [15]. The excitation source was an Nd:YAG laser (Brio 640, Quantel, Les Ulis, France), with a repetition rate of 1 Hz. The 532-nm laser pulses (4 ns period) were split into two beams using a mirror. The pulse energies at the front and back of the sample were monitored using D1 and D2 energy detectors (PE25; Ophir Optronics Solutions Ltd., Jerusalem, Israel). The laser beam waist was ~14.5 μm, and the energy of a single pulse was 200 μJ. All measurements were recorded at room temperature. Samples were dispersed in ethanol and transferred into 1-mm-thick glass cuvettes. Each sample was mounted on a computer-controlled translation stage, which shifted the sample along the *z*-axis.

3. Results and discussion

The morphology of the prepared gold NWs was confirmed by TEM. The TEM image in Fig. 1(a) shows gold NWs with a bent and twisted morphology, with diameters of ~20 nm and lengths of > 10 μm. The aspect ratio of resulted gold NWs is calculated to be more than 500, such nanostructures can be regarded as ultra-long NWs. The gold NWs were predominantly formed from gold NRs. A high-resolution TEM (HRTEM) image of the junction more clearly shows a single gold NW consisting of many gold NRs. The image shows a distinct crystal lattice spacing of 0.24 nm, which can be indexed to the (111) plane of face-centered-cubic gold. The HRTEM image indicated that the gold NWs were highly crystalline.

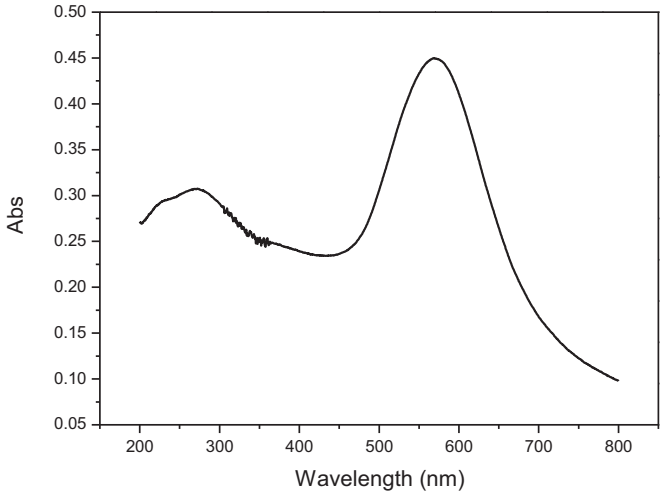

Fig. 2. UV–vis absorption spectrum of the gold NWs.

The linear optical properties of the gold NWs were studied by UV–vis absorption spectroscopy. The UV–vis absorption spectrum of the aqueous gold NWs is shown in Fig. 2, and contained two absorption bands. The strong sharp surface Plasmon resonances (SPR) peak centered at ~550 nm corresponded to the transverse mode perpendicular to the gold NWs. Compared to the spherical gold nanoparticles, whose SPR located at approximately 520 nm. The SPR of gold NWs occur slight red-shift. The SPR is due to the electromagnetic field-induced collective oscillations of the conducted electrons in the states near the Fermi level and significantly dependent with quantum confined effect. The size of gold NWs in radical direction is comparable to the electronic de Broglie wavelength, and therefore the motion of electrons in this dimension is limited. Subsequently, electronic states would quantize and the continuous band will be broken down into discrete energy levels. Such effects cause luminous efficiency decreases and the emission peak or absorption band would red-shift. The SPR of gold NWs was

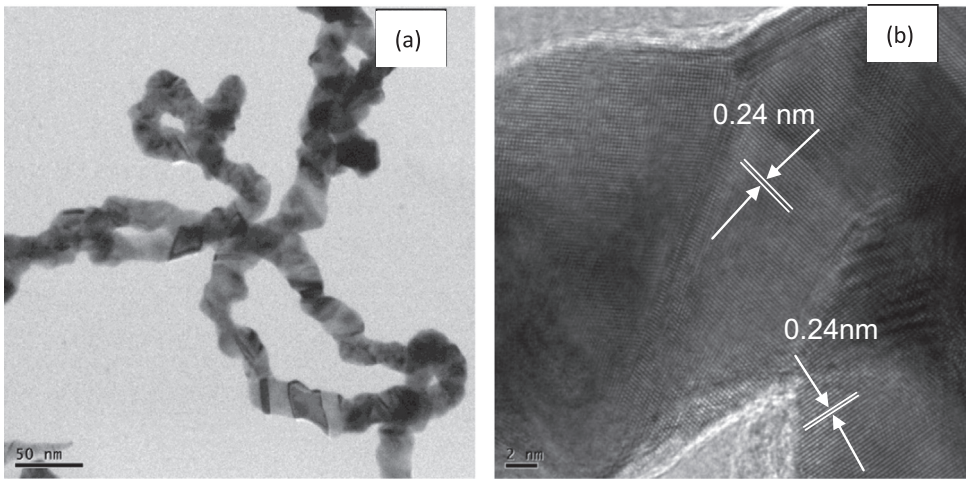

Fig. 1. TEM (a) and HRTEM (b) images of the gold NWs.