Materials Science and Engineering B 121 (2005) 199–203

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Shape dependent resonance light scattering properties of gold nanorods

Jian Zhu [a,*], Liqing Huang [a], Junwu Zhao [a], Yongchang Wang [a], Yanrui Zhao [a], Limei Hao [a], Yimin Lu [b]

[a] *Institute of Modern Physics, School of Science, Xi'an Jiaotong University, Xi'an 710049, China*
[b] *Department of Physics and Astronomy, Cardiff University, Cardiff, UK*

Received 6 October 2004; received in revised form 12 March 2005; accepted 25 March 2005

Abstract

Suspended gold nanorods with mean aspect ratio 2.5 have been synthesized via electrochemical method. Resonance scattering properties have been studied. Two scattering peaks fixed at 400 and 640 nm are due to the scattering of the gold nanorods via coupling to the transverse and longitudinal surface plasmon resonance. The quasi-static calculation results indicate that with the increasing aspect ratio of the nanorods, the longer wavelength scattering peak red shifts linearly and the shorter wavelength peak blue shifts non-linearly. When aspect ratio $a/b = 1.0$, ellipse degenerate to sphere and the two peaks unite into one peak at 450 nm.

Keywords: Nanorods; Surface plasmon resonance; Scattering; Aspect ratio; Quasi-static

1. Introduction

Gold nanorods have received much attention in recent years due to their special electronic and optical properties [1–5]. In the letter of Cepak and Martin, gold and silver nanorods of diameter 40 and 90 nm and having a variety of aspect ratios (length/diameter) were prepared using the template synthesis approach [1]. In the letter of Yao et al., the two-dimensional arrays of various metal nanowires with diameters ranging from 15 to 70 nm have been fabricated by electrodepositing metals of Cu, Ag, Au, Ni and Co into the nanoholes of the anodic aluminum oxide (AAO) films, followed by partial removal of the film. The strong surface-enhanced Raman scattering (SERS) effects were observed from the metal nanowire arrays including Ni, Co metals that were normally considered to be non-SERS active substrates [2]. Electrochemical synthesis method and absorption spectral features of gold nanorods were reported by Yu et al., two surface plasmon bands corresponding to transverse and longitudinal resonance due to the anisotropy of the shape were observed [3]. The 'lighting' gold nanorods were reported by Mohamed et al., gold nanorods capped with micelles and having an aspect ratio of 2.0–5.4 are found to fluoresce with a quantum yield which is over a million times that of the metal [4]. Previous studies by Qi et al. have demonstrated that both ultrasonication and electrode polishing could influence the generation of gold nanorods [5]. If a solid particle is illuminated by electromagnetic wave, electric charges in the obstacle will be set into oscillatory motion. Accelerated electric charges radiate electromagnetic energy in all directions, this secondary radiation is called scattering. Rayleigh scattering is a light scattering phenomenon that electromagnetic radiation and material act each other and generate elastic collisions. If the wavelength of the incident beam is close to that of the absorption band of the molecular particles, Rayleigh scattering will deviate from the ordinary law and the intensity of some wavelengths will rapidly increase. This phenomenon is called resonance light scattering (RLS) [6–8]. In recent years, RLS as a new analytical technique has been applied to the study and determination of some biological macromolecules, ion-association complexes, trace amounts of metals, non-metals

* Corresponding author. Tel.: +86 29 267 2529; fax: +86 29 266 8004.
E-mail address: zhujian@mail.xjtu.edu.cn (J. Zhu).

0921-5107/$ – see front matter
doi:10.1016/j.mseb.2005.03.022

and so on [8–12]. Our previous studies have reported on the resonance light scattering from gold colloidal nanospheres and nanoshells, which is result from the surface plasmon resonance [12,13].

Many theories have been developed in describing the optical responses to noble metal nanoparticles. Mie [7,14] first described the phenomenon theoretically by solving Maxwell's equations for a radiation field interacting with a spherical metal particle under the appropriate boundary conditions. Martin and co-workers [15] have used and modified the Maxwell–Garnett theory to model the absorption spectra of gold nanoparticles. Simulation of the optical absorption spectra of gold nanorods as a function of the aspect ratio has been made by Link et al. [16,17]. Their calculations show that the absorption maximum of the longitudinal plasmon resonance depends on the aspect ratio in a linear fashion. Kelly et al. [18] have reported the progress in the theory of nanoparticle optical properties, particularly methods for solving Maxwell's equations for light scattering from particles of arbitrary shape in a complex environment. They discussed in detail the description of the qualitative features of dipole and quadrupole plasmon resonances for spherical particles; the analytical and numerical methods for calculating extinction and scattering cross-sections, local fields, and other optical properties for non-spherical particles.

In this paper, we report on the shape dependent resonance light scattering properties of gold nanorods. We have observed that when the average aspect ratio of the gold nanorod is about 2.5, not single but two scattering peaks enhanced from surface plasmon resonance display, which is different from nanosphere. Furthermore, we discuss in detail the relation between average aspect ratio and resonance light scattering characters.

2. Experimental

Gold nanorods have been prepared via electrochemical method [3–5]. A gold metal plate (20 mm × 10 mm × 0.5 mm) with purity 99.99% is used as the anode and a platinum plate (20 mm × 10 mm × 0.5 mm) with purity 99.99% is used as the cathode in the electrochemical cell. The space between anode and cathode is about 2 mm. The electrolyte solution consists of $AgNO_3$ (0.03 g), CH_3COCH_2 (100 μl), $C_{32}H_{68}BrN$ (0.026 g), $[CH_3(CH_2)_{15}]N(CH_3)_3Br$ (0.182 g), $Na_3C_6H_5O_7\cdot 2H_2O$ (0.028 g) and ultra-pure water (10 ml). A controlled current electrolysis is used throughout the process for a current of 10 mA and an electrolysis time of 25 min. The synthesis is conducted under an ultrasonication and a stationary temperature at 42 °C. The resulted solution has been aged at room temperature for 15 h and the color turns from brown to purple-grey. The transmission electron microscopic (TEM) images are obtained by using a JEOL JEM-200CX TEM, as shown in Fig. 1. Then, we obtained nanorods with mean aspect ratios 2.5 (average transverse diameters is about 15 nm and longitudinal length is about 37 nm). Their shapes are clearly distinguishable from the spheroidal shape.

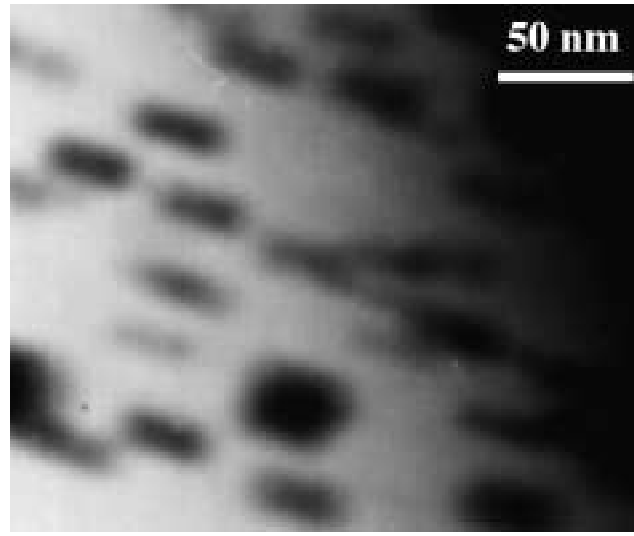

Fig. 1. TEM image of gold nanorods.

3. Results and discussion

The UV–vis spectrum of this gold nanorod sample with an average aspect ratio of 2.5 was recorded on a SHIMADZU UV-250IPC spectrophotometer. The band at 520 nm is referred to as the transverse plasmon resonance, while the one centered at 650 nm is called the longitudinal plasmon absorption, as shown in Fig. 2. The fluorescence emission spectra are recorded on a Perkin-Elmer LS 55 spectrophotofluorlometer. Fixed the detection wavelength equal to the exciting wavelength, we get the intensity of scattering light. Comparing the relative intensity of scattering peaks with different exciting wavelengths, we find that the resonance scattering peaks take place at 400 and 640 nm, as shown in Fig. 3.

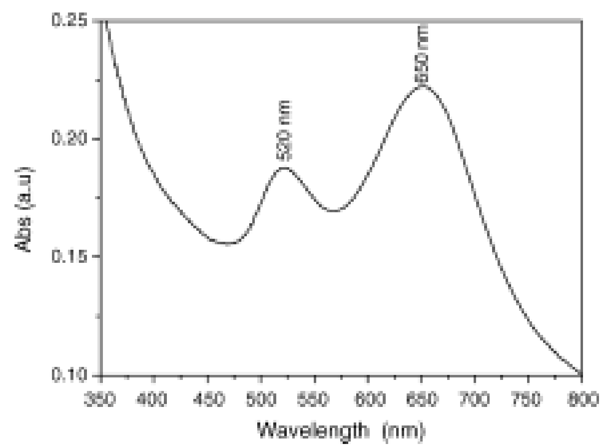

Fig. 2. UV–vis absorption spectrum of gold nanorods.