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Nonlocal nonlinear optical response of PEGylated superparamagnetic Fe_3O_4 nanoparticles

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ABSTRACT

PEGylated superparamagnetic Fe_3O_4 nanoparticles were prepared using co-precipitation method and analyzed by using X-ray diffraction (XRD), UV–Visible spectroscopy, Fourier-transform infrared (FTIR), Transmission electron microscopy (TEM), Dynamic light scattering (DLS), Vibrating sample magnetometer (VSM) and TG analysis. The XRD results showed that an FCC phase of the Fe_3O_4 structure was formed by an average lattice constant about 8.379 Å. From optical absorbance spectra, the linear absorption coefficient and the band gap of PEGylated Fe_3O_4 nanoparticles were measured 0.855 cm^{-1} and 2.27 eV, respectively. The magnetic characteristics indicated that the PEGylated Fe_3O_4 nanoparticles had the saturation magnetic moments of 61 $emug^{-1}$. The measurements of nonlinear optical (NLO) properties of PEGylated Fe_3O_4 nanoparticles have been performed using a nanosecond Nd:YAG pulse laser at 532 nm by the Z-scan technique. Both bare and PEGylated Fe_3O_4 nanoparticles clearly were exhibited a negative NLO index of refraction at 532 nm. A nonlocality in NLO response of nanoparticles was observed after PEGylation. The NLO absorption of PEGylated Fe_3O_4 nanoparticles is attributed to 2-photon absorption. A good NLO absorption was observed for both bare and PEG-coated Fe_3O_4 nanoparticles at 532 nm. Moreover, the nonlinear susceptibility of PEG-coated Fe_3O_4 nanoparticles was determined by the Z-scan technique of the order of 10^{-9} esu. The outcomes suggest that PEGylated Fe_3O_4 nanoparticles may be a promising candidate for the NLO applications.

1. Introduction

In recent years, nanoparticles have exhibited unique optical and magnetic properties so that combine with drug carriers and have introduced multi-functional applications in biophotonics and nanomedicine [1]. Often the surfaces of nanoparticles are covered with organic or inorganic layers during synthesis to transform nanoparticles into biosensing, catalysis, nanobiomedicine, biophotonics, and drug delivery applications [2].

Fe_3O_4 nanoparticles are used extensively for diverse biomedical applications. Fe_3O_4 nanoparticles are used for cell detection because of their unique features. Nevertheless, some research has shown that Fe_3O_4 nanoparticles decrease cell proliferation; induce apoptosis, inflammation, DNA damage, and oxidative stress in cells. The toxicity of Fe_3O_4 nanoparticles is severely related to their dose and coating. The problem of toxicity of Fe_3O_4 nanoparticles can be solved with the choice of more biocompatible materials to coat their surface with various polymers and biomolecules. Polyethylene glycol (PEG) that widely used in medicine is one of the candidate materials for coating magnetic nanoparticles. The researchers show that PEG has high bio-stability and very low toxicity [3–8].

Furthermore, PEGylated magnetic nanoparticles were also used as an efficient, cost-effective and environmentally friendly alternative for the oxidative cyanation of tertiary amines via C-H activation [9].

Although there are many reports about biomedical applications of PEGylated Fe_3O_4 nanoparticles, few reports have been published on NLO properties of these nanoparticles. To the best our knowledge, there is one report on the NLO properties of PEGylated Fe_3O_4 nanoparticles, which it was published only a few months ago [10]. However, the present work is important in two respects. First, the samples under investigation in this work exhibited the stronger NLO response. The second one is that the nonlocal NLO response for PEGylated Fe_3O_4 nanoparticles was observed after PEGylation, contrary to the previous work.

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This paper presents a glance of the NLO properties of PEGylated Fe_3O_4 nanoparticles prepared by using a co-precipitation method. UV–Vis absorption spectroscopy is utilized to calculate the optical band gap (E_g) and the linear absorption coefficient (α) of PEGylated Fe_3O_4 nanoparticles. X-ray diffraction (XRD) illustrates the formation of FCC structure for PEGylated Fe_3O_4 nanoparticles. Also, the fourier transform infrared (FTIR), transmission electron microscopy (TEM), dynamic light scattering (DLS) and thermo-gravimetric analysis (TGA) are performed. The vibrating sample magnetometer (VSM) is carried out to illustrate the superparamagnetic properties of PEGylated Fe_3O_4 nanoparticles. The NLO properties of PEGylated Fe_3O_4 nanoparticles are investigated using a single beam Z-scan technique at a wavelength of 532 nm. The measurements are performed for both Open and closed-aperture Z-scan setup.

2. Experimental details

2.1. Materials and methods

All materials were purchased from Merck Company. The Fe_3O_4 nanoparticles were prepared by co-precipitation of Fe(II) and Fe(III) chloride in alkali solution. In this regards, ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) were dissolved in deionized water with a 1:2 M ratio using a stirrer and deoxidized by nitrogen at room temperature. The resulting solution was stirred for 10 min at 75 °C. Then, under stirring pH reached in 11 by adding the ammonium hydroxide (25% NH_3 in H_2O) dropwise. Adding ammonium hydroxide gave rise to brown sediment, indicating the formation of Fe_3O_4 nanoparticles. The stirring of brown sediment was continued for more 1.5 h and followed by cooling to room temperature. The sediment was removed using a magnet and then washed several times with deionized water and ethanol to make the final products free of any residual salts, which was used during the co-precipitation. Then, the final sediment was washed two times with acetone and dried under vacuum at room temperature for 24 h. The obtained powder tagged bare Fe_3O_4 nanoparticles.

In the next step, 2.4 g of PEG was dissolved in 100 mL of deionized water. The obtained product was added to the wet magnetite nanoparticles and was allowed to stir for 1.5 min at room temperature. The PEGylated Fe_3O_4 nanoparticles were collected by centrifugation at 10000 rpm, followed by washing with deionized water and ethanol several times to remove unreacted PEG. The resulted material was dried in vacuum at room temperature for one day. The obtained black powder tagged PEGylated Fe_3O_4 nanoparticles.

2.2. Characterizations

The optical absorbance of PEGylated Fe_3O_4 nanoparticles was carried out with a high-resolution spectrophotometer, Camspec, Model M350. Fourier transform infrared spectra were taken in the range of 600–4000 cm^{-1} by jasco FTIR-410 spectrophotometer. The structural properties of the sample were analyzed by a Philips Xpert-MPD Model 3040 X-ray diffractometer (XRD) with Cu Ka radiation with $\lambda = 1.5406$ Å. Transmission electron microscope (Philips CM120 model) was applied to characterize the morphology of the nanoparticles. The magnetic properties of nanoparticles were determined by a vibrating sample magnetometer (VSM, MDK Company, Kashan). Moreover, the dynamic light scattering (DLS) analysis was performed using a Malvern Nano S (model red badg-632.8 nm). Thermal gravimetric analysis (TGA) was carried out using TGA Q50 V6.3 Build 189. The temperature of the sample gradually increased from 25 to 600 °C at a rate of 10 °C/min under nitrogen atmosphere.

2.3. Z-Scan technique

A simple and pleasant technique for measurement the NLO properties of materials is the Z-scan experiment, developed by Sheik-Bahae and co-workers [11]. The schematic experimental setup used for the Z-scan technique is presented in Fig. 1.

In the Z-scan experiment, a polarized Gaussian laser beam was focused using a lens. The sample was moved along the path of the laser beam between +z and −z positions and the transmitted intensity through the sample was measured. In the closed-aperture Z-scan setup, an aperture was placed in the far field and in front of the detector. During the moving the sample thru the focus of the beam at z = 0, self-focusing or self-defocusing phenomena alter the wavefront phase, therewith modify the detected intensity which recorded by detectors. In this work, Z-scan experiments were performed by using a Q-switched Nd: YAG laser (Ekspla NL640 model, 532 nm, 10 ns, 200 Hz). The laser beam was focused to a spot size of 80 μm and the Rayleigh length z_0 of 37.8 mm [12].

3. Results and discussion

3.1. X-ray diffractometry

X-ray diffraction pattern of PEGylated Fe_3O_4 nanoparticles is shown in Fig. 2. As can be seen from Fig. 2, the characteristic peaks at $2\theta = 18.28°$, 30.15°, 35.39°, 43.07°, 53.70°, 57.02° and 62.82° are consistent with (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflection planes of the face-centered cubic (FCC) phase of the Fe_3O_4 structure (JCPDS card No. 19–0629) [13]. The corresponding space between adjacent (*h k l*) lattice planes (d) is calculated from Bragg's law, $n\lambda = 2d\sin\theta$, which λ is the wavelength of the X-ray incident and n is the order of diffraction.

The lattice constant for cubic crystals was calculated from $a = d(h^2 + k^2 + l^2)^{1/2}$, wherein this formula *h*, *k*, *l* are Miller indices. The average lattice constant estimated about 8.379 Å. According to JCPDS file 19-0629 and JCPDS file 39-1346, the a-values for Fe_3O_4 and γ-Fe_2O_3 are 8.396 Å and 8.346 Å, respectively. Since the a-value in this work is between a-values belonging to the Fe_3O_4 and γ-Fe_2O_3 phases and at the same time closer to Fe_3O_4 lattice constant, it can be evidence for slight oxidation of Fe_3O_4 [14].

The average crystallite size was calculated from Scherrer's equation, $D = 0.89\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray, β is the full width at half maximum (FWHM) and θ is the Bragg angle [15–17]. The average crystallite size estimated 11.86 nm for PEGylated Fe_3O_4 nanoparticles.

3.2. Morphological observations

To investigate the morphology and particle size of PEGylated Fe_3O_4 nanoparticles, TEM analysis was done. Fig. 3 shows the TEM image of PEGylated Fe_3O_4 nanoparticles. As can be noted in Fig. 3, the determination of particle size and morphology is difficult

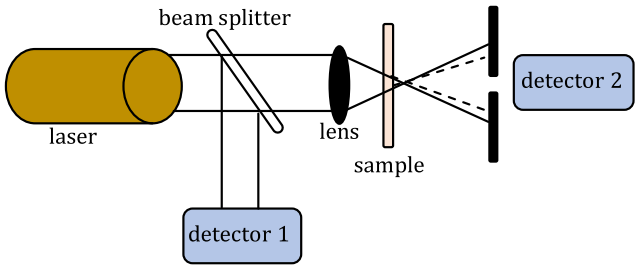

Fig. 1. Schematic diagram of the experimental setup for measurement of NLO parameters of PEGylated Fe_3O_4 nanoparticles.