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Effect of silver nanoparticles on fluorescence and nonlinear properties of naturally occurring betacyanin dye

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ABSTRACT

We present the linear and nonlinear optical studies of a natural dye betacyanin extracted from red beet root in the presence of silver nano particles in colloidal solution. We synthesized silver nano particles and characterized by XRD and HRTEM. We show how appropriate concentration of silver nanoparticles can enable tuning of dye fluorescence efficiency. Nonlinear properties are studied using open aperture Z scan technique with Nd:YAG laser (532 nm, 7 ns, 10 Hz). We show modification of nonlinear properties for the dye to the desired level can be achieved in the presence of silver nanoparticles. High nonlinearity we also demonstrated in PVA/Ag nano/Betacyanin composite films. Theoretical analysis is performed using model based on nonlinear absorption of materials and scattering of metal nanoparticles.

1. Introduction

The optical material having large reverse saturable absorption (RSA) and nonlinear refraction can produce irradiance dependent transmittance and phase shift, which can limit the throughput fluence (optical energy per unit area). In the present age of advancement of optical technology there is a great importance of such materials in optical limiting related applications [1]. Now we also know that combinations of saturable absorber (SA) and reverse saturable absorber (RSA) type materials can be used for pulse compression, mode locking and different other pulse shaping schemes for high power laser amplifiers [2,3]. SA property and other third order nonlinear properties are also being exploited very highly precise techniques such as frequency combs [4]. Passive all optical diode using asymmetric nonlinear absorption is also demonstrated in recent past [5]. This SA and RSA properties can be used in optical computing and various similar applications such as spatial line modulators (SLM) [3]. So it is evident that the optical materials with large nonlinearity can be used as key component in modern photonic technologies such as optical computing, fluorescence imaging and different applications of optical limiting.

There is also a need of optical materials which are easy to synthesize, stable in high power applications, cost effective and hazardless in the safety grounds. Not only pigments like chlorophyll and carotenoids Indian subcontinent is full of natural dye containing plants [6]. Authors of this article believe that these cheap dyes can be good solution as new generation optical materials. One of the common natural pigments is betalain and quite extensively is being investigated for the application in Dye-sensitized solar cells (DESC) [7–9]. Betalain pigments are commonly found in red beet root and can easily be extracted by diffusion in room temperature or hot extraction method. The betalain pigments consists of the red–purple betacyanins (See Fig. 1), betanin (**I**) and betanidin (**II**), with maximum absorptivity λ_{max} about 535 nm and 542 nm respectively. The yellow betaxanthins (most commonly Indicaxanthin) have λ_{max} near 480 nm [10]. It would be worth mentioning that the amount of each pigment present in the extracted dye can actually shift the absorption spectra and emission spectra of the dye. Hence, observing the peaks of the sample it can easily be identified the purity of the sample.

If with the increase of intensity, excited states show saturation for their long lifetimes, the transmission will show SA characteristics and if the exited excited state has stronger absorption compared to the ground state it will show RSA characteristics. So, it becomes very important to identify the nonlinear absorption effects with determination of saturation intensity for SA material and two photon absorption (TPA) coefficients for two photon absorbing material. The RSA property of silver composite is also being tested recently [11]. It is also reported in recent works that

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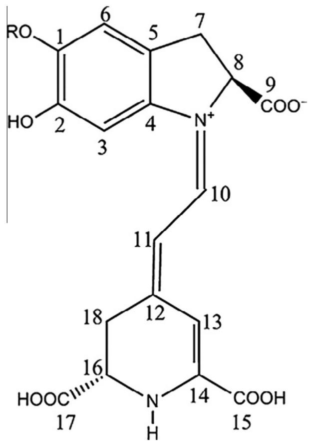

Fig. 1. Structure of betacyanin.

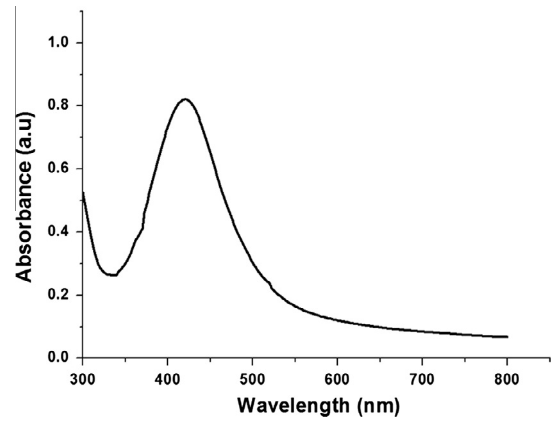

Fig. 2. Ag NP absorption spectra.

silver nanostructures can be used as plasmonic fluorescence enhancement for the dyes [12]. One of the other recent studies indicates scattering of metal nanoparticles can be used for light trapping and such principle can be used for plasmonic solar cells (PSC) [13,14]. One of the other challenges is improvement of fluorescence efficiency in present generation optical materials. In this article we will try to address all above requirements with our dye under test and silver nanoparticles.

2. Experiments

We have used polyol method [15] for synthesis of silver (Ag) nanoparticles (NPs). In this method ethylene glycol (EG) (99% pure) is heated at 120° centigrade. At this temperature silver nitrate (pure) and polyvinyl pyrrolidone (PVP) ($Mw = 10{,}000$) (99%) (Sigma–Aldrich) is added. PVP is added to prevent agglomeration in AgNPs. We maintained 12:1 M ratio between $AgNO_3$ and PVP. The solution is allowed to heat for next thirty minutes to have following reactions:

$$OH{-}CH_2{-}CH_2{-}OH \rightarrow CH_3{-}CHO + H_2O \tag{1}$$

$$2(CH_3{-}CHO) + 2AgNO_3 \rightarrow (CH_3{-}CO{-}CO - CH_3) + 2Ag + 2HNO_3 \tag{2}$$

Particles are deposited using centrifuge and washed with ethanol. We have taken absorption spectra of both AgNP and beetroot extraction using spectrometer (Jasco V-570 UV/VIS/IR).

We got 420 nm as absorption peak for silver nano sample (Fig. 2). We have extracted dye from fresh cut beet root by diffusion process of extraction where EG is used as solvent. Absorbance of the extracted dye is shown in Fig. 3(a). The sample has peak absorption of 2.38833 near 542 nm, so we can easily conclude with this peak and shape of the spectra that the pigment present is betacyanin dye with betanidin as main component [10]. Fig. 3(b) shows variation of absorbance with introducing different concentrations of Ag NP in the dye. The fluorescence studies are done for the dye and dye with the presence of Ag NP in different concentration using a Cary Eclipse fluorescence spectrometer (Varian). Ag NPs were characterized using high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). TEM was taken on JEOL 3010. XRD was taken on AXS Bruker D% diffractometer using Cu Kα-radiation ($\lambda = 0.1541$ nm).

We have checked the third order optical characteristics of samples using single beam Z-scan technique as proposed by Sheik-Bahae et al. [16]. The transmission characteristics that changes near the focal point during the process of sample translation were measured in open aperture (OA). We used Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) as light source. 20 cm converging lens is used to focus the laser beam. The beam radius w_0 was calculated to be 35.5 µm. The Rayleigh length, $Z_0 = \pi w_0^2/\lambda$ was calculated as 7.4 mm. We have tested Z scan in following samples, B1 = Dye without Ag NPs, A1 = 3 mmole/l solution of Ag NPs in EG, C0 = Dye with 0.27 mmole/l concentration of Ag NPs, C1 = Dye with 5 mmol/l concentration of Ag NPs, C2 = Dye with 9.6 mmol/l of Ag NPs, C3 = Dye with 14 mmol/l of Ag NPs. Dye concentration was kept as $5 * 10^{-4}$ mM for all these samples. Sample C4 is a composite 70 µm film made of Ag NP, polyvinyl acetate (PVA) and dye. This film is made from 10 ml of dye, 10 ml water and 2 gram PVA. We added 2.7 mmol/l Ag nano in the same. Free standing film is generated by tape casting. For rest of the samples we used 1 mm thickness cuvette to make our sample thickness less than Rayleigh length. We have characterized our samples by calculating two photon absorption (TPA) coefficient (β), third order nonlinear optical susceptibility $Im[\chi^{(3)}]$ and optical limiting threshold.

3. Results and discussions

Fig. 4 is showing XRD results of a thin film made from our Ag NPs. In XRD we got peak at $2\theta = 39.147°$. We can easily calculate the spacing between planes (d) from the same with Bragg's law [17]:

$$2d \sin\theta = n\lambda \tag{3}$$

where θ is the scattering angle, λ be the wavelength of the X ray, and n is any integer. With this d becomes 2.2984 Å.

We take our lattice constant $a = 4.0867$ Å when face centred cube (FCC) is assumed [18]. Using $(1/d^2) = (h^2 + k^2 + l^2)/a^2$ with Miller indices (h,k,l), we understand that our peak belongs to the plane (1,1,1). This also matches to the JCPDS data (file No. 04-0783).

With XRD data crystallite size can easily be determined by Sherrer's equation [19,20]:

$$B(2\theta) = K\lambda/L\cos\theta \tag{4}$$

where L is the particle size, $B(2\theta)$ is the half value breadth. Full width half maximum ($\delta\theta_{FWHM}$) is 0.29327°, so we get $B(2\theta) = 0.005119$. Assuming $K = 0.93$ with Eq. (4) XRD average this size becomes nearly 30 nm. We determined the particle size with HRTEM (Fig. 5). TEM images also confirm particles prepared by us are approximately spherical. The average particle size calculated from TEM image is 39.58 nm.