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Nonlinear optical properties of crocin: From bulk solvent to nano-confined droplet

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ABSTRACT

Crocin has a strong Two-photon Absorption (TPA) capability that makes it suitable for medicine and photonic devices. To study the linear and nonlinear optical properties of crocin in solvent and Microemulsion (MEs), *Z*-scan instruments, Uv–Vis, and fluorescence were used. Nonlinear absorption coefficient (β), nonlinear refractive index (n_2), third-order susceptibility (χ_R), and second-order molecular hyperpolarizability (γ_R) values were extracted from the *Z*-scan instrument. The β and n_2 reduce with the increase in solvent's dielectric constant (ε). In crocin mixed with MEs, the nonlinear optical values depend on the size and concentration of the droplet at constant crocin concentration. The MEs can enhance the value of β as compared with other solvents. A red shift in absorption spectra of crocin was observed with an increase in ε. However, the absorption peak was constant in the MEs. The ratios of the excited state to the ground state of the dipole moments (μ_e/μ_g) of crocin in the solutions were determined by the quantum perturbation theory. It was shown that μ_e/μ_g has similar behavior with $1/\gamma_R$. The value of μ_g and γ_R are reduced with an increase in ε.

1. Introduction

The Z-Scan is a technique to study the nonlinear optical properties of dye. It is a method introduced by Sheikh-Bahaei et al. to measure Two-photon Absorption (TPA) and the Nonlinear Refractive Index (NLR) [1]. The nonlinear optical properties (NLO) of dye are taken into consideration because of its application in photonic devices and medicine [2–5]. The NLO of materials is usually observed at a high intensity of light. The new application of nonlinear optics in medicine uses TPA in Photodynamic Therapy (PDT) and is called Two-photon Photodynamic Therapy (TP-PDT) [6–9]. PDT uses a Photosensitizer (PS) under illumination to produce singlet oxygen and can destroy the cancer tissue [10–13]. One-photon Photodynamic Therapy (OP-PDT) is limited to the infiltration of light in the tissue. To develop the Photodynamic Therapy, TP-PDT is used to exited dye with two photon and higher wavelength or lower energy. Therefore, the materials with large TPA response have potential application in PDT.

Saffron comes from *Crocus sativus* Linnaeus flowers and it consists of crocins, picrocrocin, and safranal [14–19]. Saffron has strong nonlinear optical properties, which come from crocin. However, crocin is a type of water soluble carotenoid [20] that protects against cardiovascular diseases [21], inhibition of cancer cell proliferation [22], has neuronal protection [23–25], anti-inflammatory effects [26], and improves memory [27].

In this work, the effect of solvent and confined water (droplet) on crocin was studied to improve its NLO properties. The effect of solvent on NLO properties of materials was studied before. It was observed that the NLO properties of materials depend on solvent polarity. In this work, water ($\varepsilon = 80$), dimethylformamide (DMF, $\varepsilon = 36.7$), and dimethyl sulfoxide (DMSO, $\varepsilon = 46.7$) were used as the solvents of crocin. Moreover, the effect of size and concentration of confined water (droplet) was studied on NLO properties of crocin. Furthemore, it was compared with the results of the effect of solvent. The nano-confined water (droplets) is prepared with the mixture of water, oil, and surfactant (AOT). The size of the nano-confined water changes with the amount of water inside the continuous phase of oil, and the concentration of droplet changes with the amount of oil. The interaction of droplets changes by increasing droplet concentration and the medium of continuous phase. Dynamic light scattering is a method to study the interaction between droplets. For example, the interaction between droplets of $C_{12}E_5$ MEs changes from attractive to repulsive with an increase in tri-block polymer concentration [28]. The droplet of nano-confined water, prepared with AOT MEs, has repulsive interaction [29]. One of the interesting topics is the study of the effect of interaction of droplet (confined water) on NLO properties of materials. It was observed that nano-confined water can change the optical properties of dye [30–36]. It was also observed that the fluorescence intensity of rhodamine B, fluorescein sodium salt, and auramine O depends on the droplet size

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and concentration at constant dye concentration [32–35]. In this work, the effect of droplet concentration in NLO properties of crocin was studied and the results were compared with solvent effect.

In this study, several points are considered for scrutinization: Firstly, it was needed to find a way to enhance TPA in crocin. Therefore, its NLO properties, mixed with different types of solution, are studied in this work. The fact that different solvents have a different polarity (dielectric constant and refractive index) is well known, and it is very interesting to see the polarity effect on crocin. Secondly, the effect of droplet size and concentration in solutions was also studied. It is well-known that, with the increase of droplet concentration, electrostatic interaction between droplets also increases. Hence, it is very interesting to see the effect of electrostatic interaction between droplets on TPA and the nonlinear refractive index at constant dye concentration. Thirdly, the effect of dye on water concentration in nonlinear optical properties of MEs is studied in this work.

2. The experiment

2.1. Materials and preparation

Crocin, sodium bis(2-ethylhexyl) sulfosuccinate, AOT (purity >99%), dimethylformamide, dimethyl sulfoxide, and hexane were purchased from Sigma–Aldrich. In this work, two types of samples were prepared: (1) The mixture of crocin with three types of solvent (water, dimethylformamide, and dimethyl sulfoxide) at different crocin concentrations in solutions (C); (2) The mixture of crocin with water and confined water (nano-droplets). The droplets were prepared by weight, in terms of surfactant to water molar ratio of $X = [H_2O] / [AOT]$. The size of droplet change with water molar ratio and the droplet concentration change with the mass fraction of nano-droplets $\{m_{fd} = (m_{H2O} + m_{AOT}) / (m_{Total})\}$, where $m_{Total} = m_{H2O} + m_{AOT} + m_{Dec}$. The droplet was prepared at two water to AOT molar ratios (X = 5, 10 and 20). According to previous studies, handling water/AOT/hexane, it was observed that by increasing water to the surfactant molar ratio (X), the three different phases (monomeric, transient, and oligomeric phase) appear for MEs [37]. Moreover, MEs with X ≤ 8 has a monomeric phase [37]. The MEs in this phase is optically transparent without turbidity. In our samples, the AOT/water/oil/crocin is optically transparent without any turbidity. The nano-confined water mixed with crocin was prepared by weight in terms of the mass of crocin to water $Y = m_C / m_{H2O}$, in which m_C is the mass of crocin in water. The concentration of dye inside the nano-droplet is specified with the mass of dye to water ratio (Y = 2, 3 and 4 mM). The concentration of dye inside the MEs is defined with a mass of dye to MEs ratio (C).

2.2. Instruments

The *Z*-scan technique is used to study the nonlinear optical properties of the samples. A Gaussian beam with the CW diode laser (λ_z = 532 nm, with 80 mW) was used in the Z-scan instrument. The beam of laser was focused by a 5.0 cm lens. The beam radius (ω_0) and Rayleigh

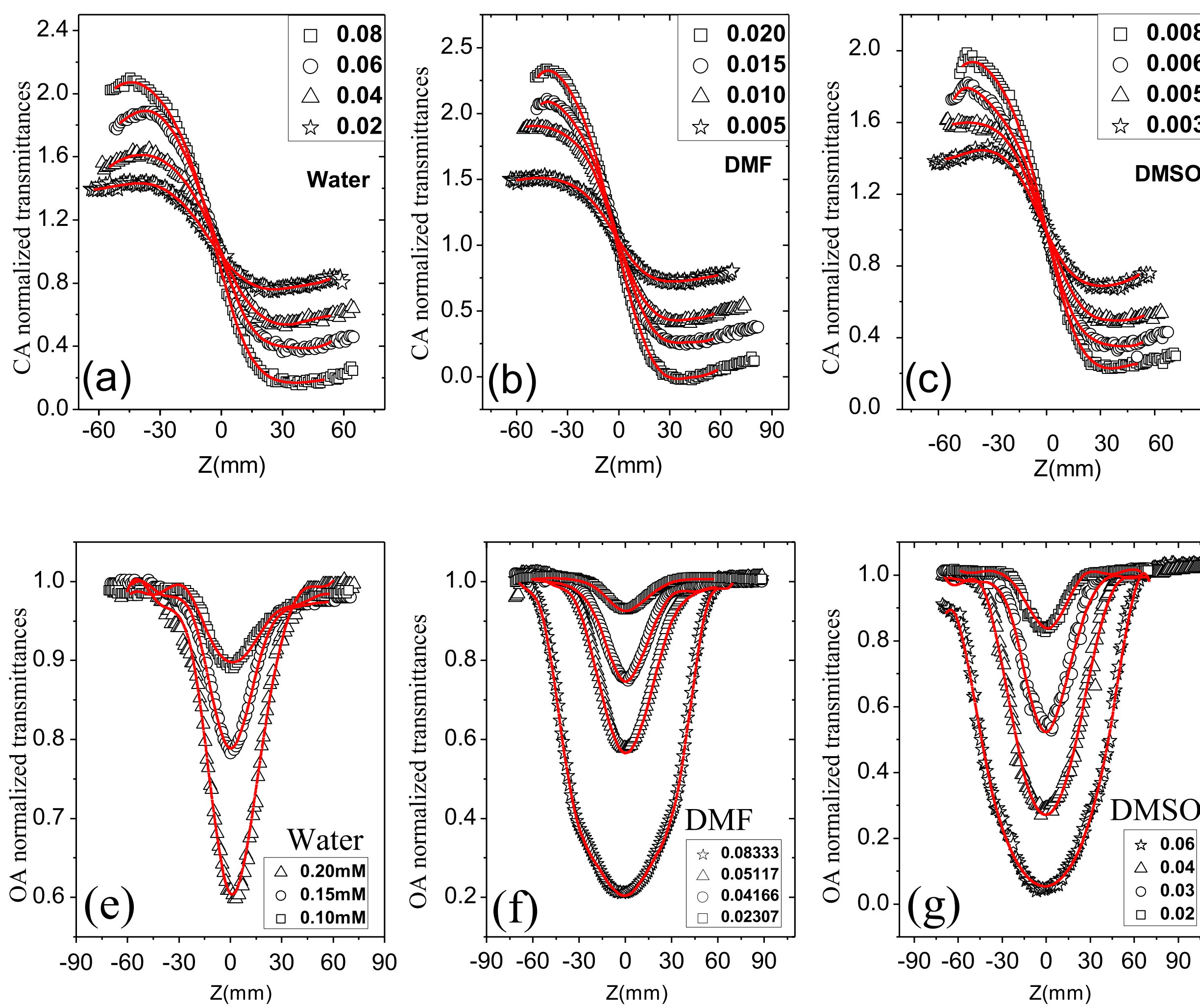

Fig. 1. Z-scan closed aperture (a,b,c) and open aperture (d,e,f) of Crocin in water, DMF and DMSO in different crocin concentration.