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RESEARCH PAPER

Surface second harmonic generation from coumarin 343 dye-attached TiO_2 nanoparticles at liquid–liquid interface

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Abstract The nonlinear optical properties of coumarin 343 (C343) dye-attached TiO_2 nanoparticles in the size range 5–8 nm adsorbed at the interface of water/1,2-dichloroethane have been studied by using the surface second harmonic generation technique. No second harmonic (SH) response was observed from the bare TiO_2 nanoparticles adsorbed at the interface, however, a strong SH response was measured from the dye molecules attached at the surfaces of the nanoparticles. The increase in the SH intensity with the increase of TiO_2 nanoparticle concentration in the aqueous solution of C343 is mainly due to the pre-alignment of the dye molecules at the surfaces of nanoparticles and is partly due to the third-order polarization contribution of the nanoparticles to the observed total SH response.

Keywords TiO_2 nanoparticles · Nonlinear optical properties · SHG · Liquid–liquid interface · C343

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Introduction

In recent years, wide band gap semiconducting nanoparticles, particularly TiO_2 nanoparticles have attracted a great amount of attention due to its wide range of applications such as in pollution control, catalysis, and solar energy conversion (Regan'O and Grätzel 1991; Fujishima et al. 1999). There are several reports about the measurement of nonlinear optical properties of metal nanoparticles (Louis et al. 2011; Bachelier et al. 2010; Galletto et al. 1999, 2007; Hao et al. 2002; Johnson et al. 2002; Vance et al. 1998a) taking the advantage of resonance of nonlinear signal with the plasmon band of the nanoparticles. However, the nonlinear optical properties of semiconducting nanoparticles remain relatively unexplored due to the difficulty in getting a nonlinear signal from the bare semiconducting nanoparticles, particularly from the TiO_2 nanoparticles.

When the size of the nanoparticles becomes smaller than the wavelength of the light, destructive interference takes place and the overall surface nonlinear polarization of the particle vanishes and no second harmonic (SH) response may be observed from such a particle. However, for particles with radius of curvature of the order of, or larger than the wavelength of incident light, the electric field cannot be assumed constant over the particle diameter. In this case, the compensation of the nonlinear polarization from the two opposite surface elements is not complete and consequently, SH response is observed (Wang et al. 1996). In fact, from the monodispersed bulk solutions

of nanoparticles, incoherent SH response, known as hyper-Rayleigh scattering (HRS), can still be observed (Johnson et al. 2002; Vance et al. 1998a; Sahyun 2002; Rassbach and Sahyun 2001). Sahyun (2002) have probed the photophysics of nanoparticulate TiO_2 using HRS spectroscopy. The estimated hyperpolarizability (β) is about 1×10^{-30} esu, which is three orders of magnitude smaller than observed for gold nanoparticles (Vance et al. 1998b) or CdSe nanoparticles (Jacobsohn and Banin 2000), and two orders of magnitude smaller than observed for AgBr and SiO_2 nanoparticles (Vance et al. 1998b). Further, it was observed that addition of carboxy-functional spectral sensitizing dye quenches SH generation (Sahyun 2002). HRS signals from gold nanoparticles were observed to exceed by factors of up to 10^5 those observed from suspensions of similarly sized wide band gap semiconductors (Lemon 1999).

One way to enhance the SH signal is to measure SH spectrum in resonance with the UV–visible absorption of the species adsorbed at the interface (Nagatani et al. 2002; Piron et al. 2000; Perrenoud-Rinuy et al. 2002) In order to make TiO_2 nanoparticles sensitive in the visible region, the absorption of bare TiO_2 nanoparticles, which is otherwise in the UV region, can be extended into the visible region by attaching dye molecules at the surfaces of TiO_2 nanoparticles (Fermin et al. 2003; Ghosh 1999).

In this article, we present the surface second harmonic generation (SHG) measurements of C343 dye-attached TiO_2 nanoparticles. The carboxylate group in C343 efficiently attaches with the TiO_2 nanoparticles (Ghosh 1999). Thus, the dye-attached TiO_2 nanoparticles become sensitive to the visible laser beam within the absorption spectrum of the attached C343 dye. No detectable SH response was observed from the bare nanoparticles, whereas a strong signal was observed from the dye-attached TiO_2 nanoparticles. Up to a certain concentration of TiO_2 nanoparticles, the SH response increases, whereas a sudden decrease is observed in the SH signal on further increasing the concentration of the nanoparticles.

Experimental

TiO_2 nanoparticles were prepared by the hydrolysis of $TiCl_4$ at low temperature followed by dialysis as reported by Moser and Grätzel (1983).The size distribution of the particles was 56 Å. At pH lower than 4, the TiO_2 particles were quite stable in the solution and no aggregation was observed within several days. All the reagents employed were of analytical grade. Water was purified by reverse osmosis followed by ion exchange (Millipore, Milli-Q SP regent system). The 1,2-dichloroethane (DCE) (Merck, extra pure) and C343 (Aldrich) were used as received. The C343 dye was dissolved in aqueous phase. The pH of C343 dye solution in the presence of TiO_2 nanoparticles was adjusted to 3 by adding HCl solution, and in this case there was no diffusion of dye molecules to the organic phase.

The optical setup for SHG measurements have already been described in detail (Nagatani et al. 2002; Piron et al. 2000). The fundamental beam at frequency ω is provided by an optical parametric oscillator (OPO) (Spectra-Physics MOPO 710) pumped with the third harmonic of a Q-switched Nd^{3+}:YAG laser. The fundamental wavelength was tuned from 760 to 1400 nm. Pulses at the repetition rate of 10 Hz with 5 ns duration were delivered by the laser source. The fundamental beam was impinging at the water/DCE interface under the total internal reflection (TIR) condition with an angle of about 70°. The TIR configuration greatly enhances the intensity of the SH signal from the interface. The energy per pulse at the fundamental frequency ω at the interface was about 2.8 mJ at 900 nm. The SH signal at the frequency 2ω generated at the interface was detected by a photomultiplier tube through a monochromator after passing through band pass filters to cut the fundamental beam. The data were finally acquired with a boxcar integrator. To take into account the wavelength dependence of the fundamental beam energy, about 2% of the output from the OPO was split by a beam splitter and detected by a power meter and the collected SH signal was normalized by dividing the SH intensity by the square of the laser energy. The fundamental beam was s-polarized unless otherwise noted. The polarization measurements to estimate the orientation parameters of the interfacial species were achieved by rotating the fundamental with an achromatic half-wave plate.

Results and discussion

The photocurrent measurements (Jensen et al. 2002) from the bare TiO_2 nanoparticles at the liquid–liquid

interface were clear indication of the adsorption of nanoparticles at the interface. The adsorption of nonlinear active nanoparticles or molecules at the interface is a first and foremost condition for detecting the coherent SH signal from the particles or molecules. Thus, the SH signal from the bare TiO_2 nanoparticles adsorbed at the neat liquid/liquid interface was expected. However, in our SHG measurements, bare TiO_2 nanoparticles showed no detectable signal. The experiments were done both for p- and s-polarization of the fundamental beam, but the signal was undetectable in both the cases, may be the SH response was too low to be detected with our experimental setup. Thus, signal enhancement was required in order to measure the SH response from the TiO_2 nanoparticles. We have attached TiO_2 nanoparticles with C343 dye molecules and a strong SH response was measured from the dye-attached nanoparticles.

The UV–visible spectrum of C343 in TiO_2 solution is presented in Fig. 1 along with the corresponding SHG spectrum at the water/DCE interface. In TiO_2 solution, the maximum of the absorption spectrum of C343 is around 450 nm and this is in agreement with the reported values (Ghosh 1999). In bulk water, the absorption spectrum of C343 is around 428 nm (Pant et al. 2004). The red shift of about 20 nm in the dye-attached TiO_2 nanoparticles compared with bulk water solution indicates attachment of dye molecules with the nanoparticles. The surface spectrum of C343 dye-attached TiO_2 nanoparticles adsorbed at the water/DCE interface is further shifted about 20 nm toward red from the absorption spectrum of C343 in TiO_2 solution and the maximum is around 470 nm.

The red shift in the surface spectrum of C343 attached TiO_2 nanoparticles compared with the absorption spectrum of the solution implies that the dye molecule attached nanoparticles at the interface sense different environment from the bulk solution and is an indication of the adsorption of dye-attached nanoparticles at the water/DCE interface. Similar red shifts in the surface spectrum have been observed for virtually every system that has been probed using SHG technique (Jacobsohn and Banin 2000; Vance et al. 1998b; Lemon 1999) and several different arguments have been provided to explain the red shift in the surface spectrum. In the present study, the observed red shift in the surface spectrum of C343 dye adsorbed TiO_2 nanoparticles from the linear absorption spectrum may be simply due to the strong interactions among the closely packed nanoparticles at the water/DCE interface. This is further supported by the Langmuir adsorption isotherm we have studied for the C343 dye molecules attached to the TiO_2 nanoparticles at the water/DCE interface and is discussed in the following paragraphs.

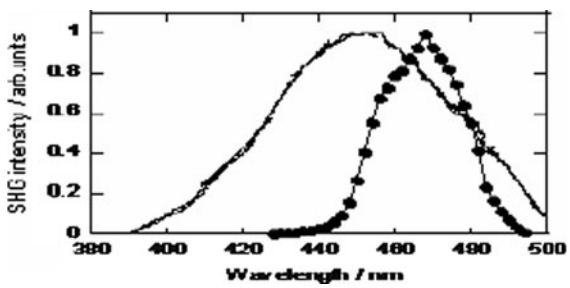

Fig. 1 UV–visible absorption spectra of C343 dye attached to TiO_2 nanoparticles (*solid line*) in aqueous solution, and surface SHG spectrum at the water/DCE interface for C343 (30 μM) dye attached to TiO_2 (1 g L^{-1}) nanoparticles (*solid line with filled circles*)

SH intensity at frequency 2ω under TIR conditions can be expressed by the equation (Brevet 1997):

$$I^{2\omega} = \frac{\omega^2}{8\varepsilon_0 c^3} \frac{\sqrt{\varepsilon_1^{2\omega}}}{\varepsilon_1^{\omega}\left(\varepsilon_m^{2\omega} - \varepsilon_1^{\omega}\sin^2\theta_1^{\omega}\right)} |\chi|^2 (I^{\omega})^2 \quad (1)$$

where ε and θ are the relative dielectric constant and the angle of incidence of the fundamental beam. The subscripts 1 and m relate to the incident medium and the interface, respectively. ε_m is the relative dielectric constant of the interface. For an isotropic surface or interface such as the water/DCE, the macroscopic quantity (χ) is a function of three nonzero elements of the second-order surface susceptibility tensor (χ_S)

$$\begin{aligned}\chi &= a_1\chi_{s,XZX}^2 \sin 2\gamma \sin\Gamma \\ &\quad + \left(a_2\chi_{s,XZX}^2 + a_3\chi_{s,ZXX}^2 + a_4\chi_{s,ZZZ}^2\right) \\ &\quad \times \cos^2\gamma\cos\Gamma + a_5\chi_{s,ZXX}^2 \sin^2\gamma\cos\Gamma \end{aligned} \quad (2)$$

where γ and Γ are the angle of polarization of the fundamental and the harmonic waves. The optical coefficients $a_1 \ldots a_5$ are determined from the relative dielectric constants of the different media and the angle of incidence. Finally, the macroscopic susceptibility tensor χ_S is related to the molecular quantities. It is the product of the total number of optically nonlinear active molecules adsorbed at the interface per unit surface N_S and the molecular hyperpolarizability, β of a single moiety

$$\chi_s^2 = \frac{N_s}{\varepsilon_0}\langle\beta\rangle \tag{3}$$

where the β tensor is taken as an ensemble average over all the possible orientation configurations.

In order to determine the adsorption properties of C343 dye molecules at the interface of water/DCE in the presence of TiO_2 nanoparticles in the bulk aqueous solution, the SHG intensity was monitored as a function of bulk aqueous concentration of C343. As it is clear from Eqs. 1–3, the SHG signal from the interface is proportional to the square of the number of molecules adsorbed per unit surface N_s, or to the square of the surface coverage, and hence the plot of square root of SH intensity against the concentration of C343 yield the adsorption isotherm of the molecule. Figure 2 shows the adsorption isotherm of C343 at water/DCE interface in the presence of TiO_2 nanoparticles in the aqueous phase. The measurements were performed at 470 nm with both the fundamental and SH waves p-polarized. The bulk aqueous concentration of C343 dye was varied from 0 to 0.2 mM while the concentration of TiO_2 nanoparticles was kept fixed at 1 g L^{-1}. The full monolayer coverage was obtained at a bulk aqueous concentration of about 100 μM of C343 dye.

From Fig. 2, it is clear that the simple Langmuir adsorption isotherm expression

$$\frac{N_s}{N_s^{max}} = \frac{a^w \exp(-\Delta G/RT)}{1 + a^w \exp(-\Delta G/RT)} \tag{4}$$

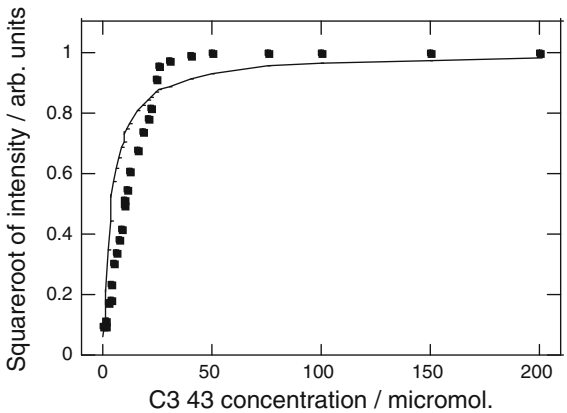

Fig. 2 C343 dye concentration dependence of surface SHG intensity at water/DCE interface. The concentration of TiO_2 nanoparticles is 1 g L^{-1} in aqueous phase and the SH measurements are done at 470 nm. The *solid line* is a fit to the isotherm of the form of Eq. 4

does not give excellent fit to the SH experimental data. This is because of the adsorption of the dye molecules at the surfaces of the nanoparticles and the strong interactions among them at the water/DCE interface. The simple Langmuir model does not include the depletion of the dye molecules due to the adsorption to the surfaces of the TiO_2 nanoparticles. Eisenthal and coworkers (Wang et al. 1998) measured the SH signals from the polystyrene sulfonate (PSS) microspheres of micron size diameter suspended in an aqueous solution containing SHG-active malachite green (MG). The dependence of SH response on to the concentration of MG followed the modified Langmuir isotherm, indicating that the adsorbed dye molecules at a single polystyrene particle were coherently interacting with each other. Similar adsorption behavior was observed for the MG adsorbed at the surface of oil in water emulsion consisting of sodium dodecyl sulfate (SDS) as a surfactant and 1-dodecanol as a coemulsifier (Wang et al. 1998).

The polarization dependence of SHG response provides information regarding the average orientation of dye molecules adsorbed at the interface. The s- and p-polarization curves for C343 attached to the surfaces of TiO_2 nanoparticles at water/DCE interface are slightly different from each other; particularly, the overall difference is in their intensities. The p-polarization is more intense than the s-polarization. Figure 3 shows the p-polarization curve as a function of fundamental polarization angle for C343 attached TiO_2 nanoparticles. In order to estimate the angle of molecular orientation, the s- and p-polarized output curves were analyzed by using Eqs. 1 and 2 and the values of three independent tensor elements $\chi_{s,XZX}$, $\chi_{s,ZXX}$, and $\chi_{s,ZZZ}$ have been obtained. Clearly, in the present system, the fitted curve deviates from the experimental intensity data points. This may be simply due to the pre-alignment of dye molecules at the surfaces of nanoparticles. Following the same procedure as we have described previously for the bulk C343 dye molecules adsorbed at water/DCE interface (Pant et al. 2004), the orientation parameter (D) and from that the average angle of orientation (θ) of the dye molecules was calculated using the equation

$$D = \frac{2\chi_{s,XZX}^2 - 2\chi_{s,ZXX}^2 - \chi_{s,ZZZ}^2}{2\chi_{s,XZX}^2 - 4\chi_{s,ZXX}^2 - \chi_{s,ZZZ}^2} = \frac{\langle\cos^3\theta\rangle}{\langle\cos\theta\rangle} \tag{5}$$

The average value of θ determined in this manner is 27° for the dye molecules attached to TiO_2

nanoparticles, and is the angle between the molecular z-axis and the normal to the interface.

In the previous report (Pant et al. 2004), we have studied the orientation of bulk C343 molecules at the liquid–liquid interface and the angles of orientation were 32° and 42° at pH 6 and at pH 11, respectively. Clearly, the orientation of the dye molecules at the water/DCE interface for the C343 molecules attached to the TiO_2 nanoparticle is not dramatically different from the bulk C343 dye molecules adsorbed at the liquid/liquid interface. The observed small difference in the orientation angle of the C343 dye-attached TiO_2 nanoparticles from the bulk C343 dye molecules adsorbed at the water/DCE interface can be simply due to the pre-alignment of the dye molecules with the surfaces of nanoparticles via carboxylic acid group of C343 molecules.

In order to probe the contribution of TiO_2 nanoparticles to the observed total SH response, we measured SH intensity as a function of TiO_2 nanoparticle concentration for two different fixed concentrations of the C343 dye molecules in the solution (Fig. 4). Clearly, on increasing the concentration of nanoparticles, first the intensity of SH response increases nonlinearly up to a certain concentration of nanoparticles in the solution. On further increasing the concentration of TiO_2 nanoparticles, the intensity of the SH response suddenly starts decreasing. The SH intensity starts decreasing at higher concentrations of TiO_2 nanoparticles for the higher concentrations of the dye molecules in the solution.

The observed initial nonlinear dependence of the SH intensity on to the TiO_2 nanoparticle density in aqueous solution indicates that the nanoparticles interact coherently with each other, and rules out the HRS, since in the later case the SH intensity would vary linearly with the number density of the nanoparticles. The dye attached to the lateral sides of the nanoparticles now destructively interfere while the ones attached on the upper and lower surfaces, and normal to the interface, see a broken symmetry and are weighing more in the total output of the SH signal. Moreover, we believe the pre-alignment of the dye molecules at the surfaces of semiconducting nanoparticles is the main reason for the enhancement of SH intensity in the presence of nanoparticles in the solution.

We believe that in the presence of TiO_2 nanoparticles in the solution, the surface charges of the TiO_2 nanoparticles produce static electric field in the solution which is responsible for the third-order polarization contribution to the SH intensity. Eisenthal and coworkers (Ong et al. 1992, Zhao et al. 1993) used SHG technique to probe the silica/water interface. They observed that the SH signal at the charged silica/water interface was due to the electric field-induced polarization and orientation of water molecules in the electrical double layer region of the interface. Further,

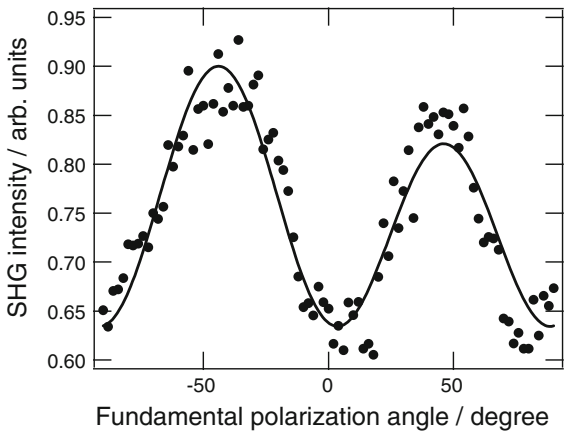

Fig. 3 Polarization curve for C343 (30 μM) attached TiO_2 nanoparticles (1 g L^{-1}) at water/DCE interface. The SH intensity was measured at 470 nm. The beam at the SH wavelength is p-polarized. *Filled circles* are the SHG data and the *solid line* is the fit to Eqs. 1 and 2

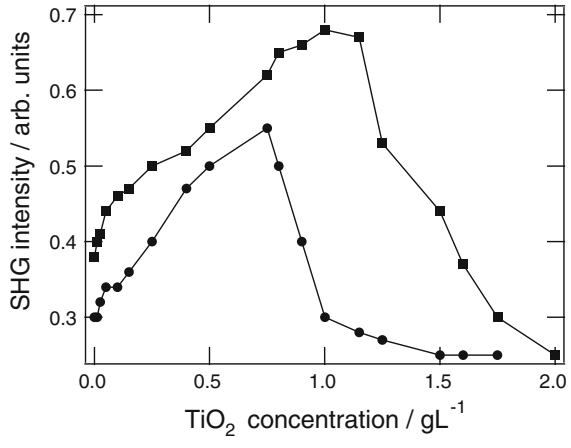

Fig. 4 TiO_2 nanoparticle concentration dependence of SH intensity at water/DCE interface for two different C343 concentrations: 30 μM (*solid circles*) and 100 μM (*solid squares*). The *solid line* is for guiding the eye through the data points

they have shown (Zhao et al. 1993) that the SH signal from the charged monolayers at air/water interface was linearly related with the interface electric potential and this was attributed to the polarization of water molecules in the electrostatic field of the charged monolayer.

In the absence of TiO_2 nanoparticles in the solution, the SH electric field $E_{2\omega}$, generated by the second-order polarization $P^2_{2\omega}$ can be expressed as

$$E_{2\omega} \propto P^2_{2\omega} = \chi^2 E_\omega E_\omega \tag{6}$$

where E_ω is the incident optical field at frequency ω. However, in the presence of TiO_2 nanoparticles in the solution, the static electric field due to the surface charge of the particles can induce a third-order nonlinear polarization $P^3_{2\omega}$. The SH electric field generated by the third-order polarization $P^3_{2\omega}$ can be expressed as

$$E_{2\omega} \propto P^3_{2\omega} = \chi^3 E_0 E_\omega E_\omega \tag{7}$$

where χ^3 is the third-order nonlinear susceptibility of the solution, and E_0 is the static field due to the surface charges of TiO_2 nanoparticles. The total SH signal due to the second- and third-order polarizations is given by (Ong et al. 1992)

$$E_{2\omega} \propto P^2_{2\omega} + P^3_{2\omega} = \chi^2 E_\omega E_\omega + \chi^3 E_0 E_\omega E_\omega \tag{8}$$

The χ^2 contribution, the major source for SHG, is from the adsorbed C343 molecules at the interface and is independent of electric field, whereas the χ^3 contribution is both from the interface and the bulk species. The increase in TiO_2 nanoparticle concentration in the solution means an increase in the total charge density, consequently, the SH intensity increases with the increase in concentration of TiO_2 nanoparticles. Pant and Levinger (1999) have calculated potential at the ZrO_2 water interface as a function of distance from the interface, and it was observed that the largest change in the potential occurs near the interface, within the distance between 0 and 5 Å from the interface. As the surface chemistry of TiO_2 is similar to the ZrO_2, thus we expect maximum change in potential for TiO_2 nanoparticles also near the interface only. Therefore, the observation of SH response from the bulk dye molecules near the interface becomes possible in the presence of charged TiO_2 nanoparticles in the aqueous bulk solution. The χ^3 contribution from the bulk solution to the total SH response is smaller compared with the SH response from the C343 attached nanoparticles adsorbed at the water/DCE interface.

It is interesting to note that at very high concentrations of TiO_2 nanoparticles, the SH intensity starts decreasing with the further increase in nanoparticle concentration. This is because at higher concentrations of TiO_2 nanoparticles, the dye molecules are driven away from the water/DCE interface in order to get adsorb at the surfaces of nanoparticles resulting in a reduction in the concentration of the dye molecules adsorbed at the water/DCE interface. Consequently, there is a loss in SH contribution from the bulk dye molecules at the interface, which was otherwise a major source of the SH intensity. The C343 attached nanoparticles which are not adsorbed at the interface of water/DCE, may not have χ^2 contribution to the SH intensity due to the symmetry of the molecules adsorbed at the opposite surfaces of the nanoparticles. Since the distance of opposite surfaces of the TiO_2 nanoparticles is less than the coherence length of the process and are locally centrosymmetric. Consequently, the nonlinear polarizations induced in these oppositely oriented molecules are of opposite phase with respect to each other and cancel each other; thus, no coherent SH response may be observed from the C343 attached nanoparticles dispersed in the bulk solution. However, the surface charge of the particles can still induce a third-order nonlinear polarization in the bulk solution as well as at the interface. The overall result is a decrease in the SH intensity with the increase of TiO_2 nanoparticles in the solution.

These measurements clearly show that the SH signal can be increased about 100% in intensity by simply introducing TiO_2 nanoparticles in the solution of C343 molecules at the liquid–liquid interface. We believe the enhancement in intensity is due to the pre-alignment of dye molecules attached at the surfaces of nanoparticles and these dye-attached nanoparticles coherently interact with each other at the interface resulting in a nonlinear increase in SH intensity with the increase in concentration of nanoparticles in the solution. On further increase of the concentration of TiO_2 nanoparticles in the solution, the dye molecules are driven away from the water/DCE interface and eventually bind to the bulk nanoparticles which will make the SH signal to drop since now less dye will be at the liquid–liquid interface which were otherwise a major source of SH signal.

Conclusions

We have measured nonlinear optical properties of C343 attached TiO_2 nanoparticles at the water/DCE interface. A large red shift is observed in the surface spectrum of TiO_2 nanoparticles compared with the absorption spectrum and is attributed to the strong interactions of the closely packed nanoparticles at the water/DCE interface. The angle of orientation of the dye molecules attached at the surfaces of nanoparticles is found slightly different from the orientation of bulk dye molecules at the liquid–liquid interface and is due to the pre-alignment of the dye molecules at the surfaces of the nanoparticles. The SH intensity as a function of C343 dye concentration does not follow a simple Langmuir adsorption isotherm due to the strong interactions among the particles at the interface. The SH intensity initially increases with the increase in nanoparticle concentration in the solution and on further increasing the concentration of the nanoparticles, a sudden decrease is observed in the SH intensity. The increase in SH intensity with the nanoparticle concentration is mainly due to the pre-alignment of dye molecules at the surfaces of nanoparticles and partly due to the third-order polarization induced in the bulk solution near the interface and at the interface due to the static electric field from the charged surfaces of the TiO_2 nanoparticles. The decrease in the SH response after a certain concentration of nanoparticles in the solution is due to the depletion of the bulk C343 dye molecules at the water/DCE interface resulting from the adsorption of C343 dye molecules at the TiO_2 nanoparticle surfaces.

This study presents interesting results which shall provide insight in the field of interfacial SHG and introduces a new method which might be applied for the optical characterization of nanoparticles at liquid–liquid interface. We have clearly demonstrated that the nanoparticles which bind with the optically active dye molecules play an important role in the enhancement of SH signal of the molecules at the interface. Moreover, the contribution of nanoparticles to the total SH signal of the molecules at the interface, including the bulk third-order polarizability contribution can be observed by attaching optically active dye molecules at the surfaces of the nanoparticles, which was otherwise undetectable from the bare semiconductiong nanoparticles at the liquid–liquid interface.

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