# Tunable Nanosecond and Femtosecond Nonlinear Optical Properties of C–N–S-Doped TiO<sub>2</sub> Nanoparticles

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**Supporting Information** 

**ABSTRACT:** Third-order nonlinear optical (NLO) properties of undoped and C–N–S doped TiO<sub>2</sub> nanoparticles (NPs) were investigated using the Z-scan technique in the nanosecond (ns) and femtosecond (fs) regimes. Undoped TiO<sub>2</sub> NPs exhibited reverse saturable absorption (RSA) behavior with both ns and fs laser pulse excitation, whereas C–N–S-doped TiO<sub>2</sub> NPs demonstrated switch over from RSA to saturable absorption (RSA  $\rightarrow$  SA) behavior with fs excitation. Our detailed NLO studies have clearly demonstrated the tunable nonlinear absorption behavior of C–N–S-doped TiO<sub>2</sub> NPs. Such versatile tunability is important for various practical applications. The interesting nonlinear absorption (NLA) properties of these NPs are attributed to the interplay between ground and excited state absorption of the free carriers. The results obtained with ns laser excitation demonstrated that the nonlinear absorption coefficient ( $\beta$ ) and nonlinear refractive index ( $n_2$ ) for these materials varied with input irradiance,



thus indicating the possibility of higher order nonlinearity (free–carrier effect) occurrence rather than third-order nonlinearity alone. C–N–S-doped TiO<sub>2</sub> nanoparticles exhibited large magnitude for  $\beta$  and  $n_2$  with values of 2.1 × 10<sup>-10</sup> m/W and 15.4 × 10<sup>-17</sup> m<sup>2</sup>/W, respectively, with ns excitation. Further, the samples were tested for nonlinearity with continuous wave (cw) excitation as heat-induced refractive index changes were observed for the samples with cw laser excitation at 532 nm. The room temperature ferromagnetism (RTFM) was observed in both undoped and C–N–S doped TiO<sub>2</sub> NPs. Undoped rutile TiO<sub>2</sub> exhibited ~6.9-fold enhancement in RTFM as compared to the anatase phase of C–N–S-doped TiO<sub>2</sub> NPs.

### 1. INTRODUCTION

Light-matter interaction results in the observation of nonlinear effects in the strong field regime (focused ultrashort laser pulses). Two types of nonlinear optical (NLO) absorbers are well reported and understood (saturable and reverse saturable absorbers). For saturable absorbers, the absorption coefficient typically moderates with increasing input light intensity. This property is widely used in passive Q-switching technology to achieve short laser pulses. Materials exhibiting RSA are widely used for protecting sensitive optical devices at high power densities.<sup>1,2</sup> Organic molecules with strong  $\pi$ -electron delocalization have been assumed to be the best candidates for thirdorder NLO applications. Regrettably, the usage of organics for such applications is restricted due to their (a) low chemical durability and (b) poor thermal stability. The research activity on inorganic host matrices with an active organic phase as a dopant has intensified recently.<sup>3-6</sup> Wang et al. have reported the unique NLO behavior of nanohybrid of transparent thin films of TiO<sub>2</sub>-PMMA.<sup>7</sup> However, in the fabrication process of inorganic-polymer nanocomposites, it is challenging to control the morphology, the uniformity of assembled products and

particle size in the nanoscale regime. Thin films usually portray inferior optical limiting performance due to the absence of solvent enabling the formation of microbubbles as scattering centers. In comparison with organic NLO materials, inorganic semiconductor materials own the advantages of higher photochemical and photophysical stabilities. Therefore, they have been extensively investigated for NLO/photonic applications over the last few decades.<sup>8</sup> As the size of the semiconductor decreases, the third-order nonlinearity, usually, will be enhanced because of strong free-carrier production in the surface states. In semiconductors, a carrier-induced refractive index change is stronger than the Kerr effect, which makes it potentially more useful for optical limiting applications. TiO<sub>2</sub> is one of the interesting semiconductor materials investigated extensively due to its unique physical, chemical stability, and versatile optoelectronic properties. Anatase and rutile phases of TiO<sub>2</sub> have high refractive indices

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of 2.45 and 2.73, respectively. It also exhibits fast and reasonably large NLO response.<sup>9,10</sup> Furthermore, when metallic ions such as Au and Ag are doped in TiO<sub>2</sub> lattice, surface plasmonic resonance (SPR) plays a crucial role in determining the third-order optical nonlinearity.<sup>11,12</sup> Hari et al. have reported the two-photon absorption coefficient ( $\beta$ ) of Ag:TiO<sub>2</sub> nanocomposite (532 nm, 7 ns, 10 Hz) to be 51.6 cm/GW.<sup>13</sup> Rahulan et al. have observed an effective three photon absorption coefficient ( $\gamma$ ) of 10.8  $\times$  10<sup>-24</sup> m<sup>3</sup>W<sup>2-</sup> for Ag doped TiO<sub>2</sub> NPs.<sup>14</sup> These works clearly indicate that the nonlinear absorption and refraction can be tuned through controlled doping, which modify the energy level landscape through defect induced states. Additionally, there is also a possibility that (a) the time response associated with the nonlinearity in these doped nanoparticles can be tailored for specific applications of optical switching and (b) the emission properties can be modified to suit the optoelectronic applications. In the present work, the NLO properties in the background of free carrier-induced excited state absorption on nonmetal-doped TiO2 NPs are presented. The NLO coefficients were obtained using the Z-scan technique with 532 nm (ns), 800 nm (fs) and 532 nm (cw) laser excitations.

Many years of investigation on the origin of magnetism in semiconductors, both in the experimental and theoretical studies, have seldom yielded a clear understanding. In the beginning of diluted magnetic semiconductors, Mn-doped GaAs, InAs, etc., have been widely studied. The low Curie temperature of these materials is detrimental for spintronic applications which require ferromagnetism at room temperature. Semiconductor metal oxides (SMOs) doped with transition metals such as Co, Fe, Cr, and Nb have been widely analyzed.<sup>15-18</sup> In these materials, the room temperature ferromagnetism (RTFM) arises from ferromagnetic metal clusters or secondary phases, cation or anion vacancies. There still exists a controversy about RTFM in transition metal doped  $TiO_2$  as to whether it is intrinsic or due to the magnetic impurities. Shinde et al. reported that the ferromagnetic clusters of cobalt exhibited super paramagnetism in Co doped TiO2. Torres et al. studied doping of Fe in TiO<sub>2</sub> and reported that oxygen vacancies could increase the paramagnetic moment.<sup>2</sup> However, their studies also demonstrated that this did not induce ferromagnetism.<sup>20</sup> Zhang et al. observed that pure anatase and rutile phase of TiO2 exhibit paramagnetism while mixed phase shows ferromagnetism.<sup>21</sup> The magnetism in undoped metal oxide NPs is attributed to the oxygen vacancies present. RTFM has been studied in the nonmagnetic doped TiO<sub>2</sub> system. In these systems, ferromagnetism is attributed to the substitution of oxygen with the nonmetal element, the formation of spin polarized states, oxygen vacancies, and Ti<sup>3+</sup> defects. In the present investigation, a higher magnetization is observed in the rutile phase of TiO<sub>2</sub> due to its higher oxygen defect density. We have investigated the third-order NLO coefficients of these materials using nanosecond (ns) and femtosecond (fs) pulses, and continuous wave (cw) excitation. The mechanisms responsible for the observed behavior have been elucidated. Furthermore, the complete emission dynamics were also investigated.

### 2. EXPERIMENT

**2.1.** Synthesis of C–N–S-Doped TiO<sub>2</sub> NPs. Double distilled water (40 mL) with thiourea (15 wt %) were mixed with the solution of titanium tetra isopropoxide (20 mL) and isopropyl alcohol (60 mL). The solution was stirred for 6 h at

room temperature of 30 °C. The mixed solution was then dried at 80 °C in a hot air oven. The undoped  $\text{TiO}_2$  NPs were synthesized using the same procedure, but thiourea was not added. Undoped (P) and C–N–S-doped (D) TiO<sub>2</sub> NPs were calcined at 500 °C (henceforth named as samples P3 and D3) and 600 °C (henceforth named as samples P4 and D4). The samples nomenclature followed our earlier works for consistency.<sup>22</sup>

**2.2. Characterization.** Powder X-ray diffraction (XRD) data were recorded using an X-ray diffractometer. The functional groups were identified using a FTIR spectrometer in the 400-4000 cm<sup>-1</sup> range. The Raman spectra were recorded with an Ar<sup>+</sup> laser (514.5 nm) (Witec Confocal CDM 200). X-ray photoelectron spectroscopy (XPS) measurements were performed using Shimadzu Axis Ultra XPS. EPR was recorded using an EPR magnetometer (JEOL, JES-X3 FA200) with the X-band frequency 9.451 GHz. The linear optical absorption spectrum was investigated using a UV-visible spectrophotometer (SHIMADZU UV-2450). Defects were identified using photoluminescence spectra (HORIBA Fluoromax-4 for the excitation wavelength of 320 nm). The FL decay time was measured with an excitation wavelength of 370 nm using JOBIN-VYON M/S Fluorocube Life Time System. FESEM images of the synthesized samples were obtained using a Quanta FEC 250 instrument.

2.3. NLO Studies Using the Z-Scan Technique. The NLO properties of undoped and C-N-S-doped TiO2 NPs were analyzed by both the open (OA) and closed (CA) aperture Z-scan technique with ns pulse, fs pulse, and cw laser excitations. A frequency doubled, Q-Switched Nd: YAG laser (532 nm, 9 ns, 10 Hz) was used for the ns Z-scan studies. A quartz cuvette (1 mm thick) was used for holding the sample in all the studies. The beam waist  $(\omega_0)$  in this case was estimated to be ~26  $\mu$ m. The transmittance was measured for the input energies of 100, 150, and 200 µJ. The NLO coefficients were also measured by a mode- locked Ti: sapphire laser (Chameleon, Coherent: 800 nm ~150 fs, 80 MHz). The laser pulses were focused with a lens of focal length 10 cm, and beam waist ( $\omega_0$ ) in this case was estimated to be ~33  $\mu$ m. The incident peak intensities were estimated in the range of 75-80  $MW/cm^2$ . The transmittance was monitored using a power meter (Field Max, Coherent). The Z-scan experiments with cw laser were carried out at 532 nm using a diode pumped Nd:YAG laser (50 mW) where the beam was focused with the lens of focal length of 3.5 cm. In all the Z-scan studies the criterion for the thin sample limit was fulfilled. The transmitted intensity was measured using a photodetector. Prior to all the Z-scan experiments the dispersions of these nanoparticles were sonicated for about an hour. The Z-scan experiments typically lasted 20-30 min and during this time we did not observe any precipitation of these dispersions.

#### 3. RESULTS AND DISCUSSION

**3.1. Crystal Structure.** XRD pattern of undoped (P3 and P4) and C–N–S-doped (D3 and D4) TiO<sub>2</sub> NPs calcined at 500 and 600 °C is shown in Figure S1. Pure anatase phase was observed for the calcining temperature of 500 °C, while the mixed phase (anatase and rutile phase) was observed for 600 °C. The weight percentage of anatase TiO<sub>2</sub> was 14% and 88% for P4 and D4, respectively. The anatase phase stability in the doped sample at higher calcination temperature is ascribed to the doping effect. Especially the sulfate ions delay the arrangement of an octahedron (TiO<sub>6</sub><sup>2–</sup>) thus preventing the

phase change. The average crystallite sizes (obtained using the size-strain plot method – SSP), were found to be ~28, ~32, ~4, and ~9 nm for P3, P4, D3, and D4, respectively. The characterization results are shown in the SI (Figures S1-S6). The complete details can be found in our earlier work.<sup>22</sup>

**3.2. Raman Analysis.** The Raman spectra of P3 and D3 samples revealed the presence of anatase phase in  $TiO_2$  (Figure S3).<sup>23</sup> A shift in the Raman bands toward higher wavenumbers was observed in the case of D3. The full width at half maximum (fwhm) and the intensity relatively increased as the particle size decreased for D3. The increasing of fwhm in the doped sample is attributed to the reduction in crystallinity. Campbell et al. have recently reported that a decrease in the particle size showed large shift and broadening of the Raman spectrum of silicon.<sup>24</sup> Choi et al. have demonstrated the effect of sizes in the Raman spectra of  $TiO_2$  NPs that show a red shift in the Raman modes with decreasing particle size.<sup>25</sup> The photon lifetime was decreased for the doped sample compared to the undoped one, as shown in Table 1. This is attributed to the particle size effect as discussed above.

Table 1. Raman Analysis of the Undoped and C-N-Sdoped TiO, Nanoparticles

sample	Raman line $(cm^{-1})$	fwhm $(cm^{-1})$	phonon life time $(\tau)$ (ps)
P3	142.3	25.3	0.21
D3	146.2	28.1	0.19

3.3. XPS Analysis. The peak of Ti 2p corresponding to the oxidation state of Ti4+ is confirmed. Undoped and doped samples depict the Ti  $2p_{3/2}$  and the Ti  $2p_{1/2}$  at 459.2 and 465 eV, respectively (Figures S4a,b,c). O 1s peak observed at 530.6 and 532 eV for undoped TiO<sub>2</sub> P3 (Figures S5a,b,c). However, it is slightly shifted by ~0.2 eV for C–N–S-doped TiO<sub>2</sub> (D3 and D4). It is mainly due to the presence of oxygen vacancies in the TiO<sub>2</sub> lattice. Figure 1 depicts the XPS spectra of D3 and D4 for the elements of carbon (C), nitrogen (N), and sulfur (S). C 1s peak [(a) and (b)] at 285.1 eV is due to C from the XPS measurement. A peak at 286.5 eV is accredited to a C-O bond, which confirms the substitution of Ti by carbon, and the peak at 289.3 eV is due to C=O. The N 1s peak (Figure 1c,d) at 399.8 eV is due to Ti-O-N or Ti-N-O. The peak at 401.2 eV reveals the interstitial position of N in TiO<sub>2</sub> lattice. The peaks at 169 and 170.1 eV are apportioned to S<sup>6+</sup> ions (Figure 1e,f).<sup>26</sup> Therefore, the replacement of Ti<sup>4+</sup> by S<sup>6+</sup> creates many oxygen vacancies on TiO<sub>2</sub> surface. As the calcining temperature increases, the binding energies of C, N, and S shifted to the lower angle side, which is due to the effective decomposition of thiourea. The atomic concentration of the doped elements in TiO<sub>2</sub> lattices are summarized in Table S1.

**3.4. EPR Studies.** Room-temperature EPR measurement of undoped and C–N–S-doped TiO<sub>2</sub> NPs is shown in Figure 2. Commonly expected point defects in TiO<sub>2</sub> semiconductor are (i) titanium vacancy  $(V_{\rm Ti})$ , (ii) titanium interstitial  $(i_{\rm Ti})$  (iii) Ti<sup>3+</sup>, (iv) oxygen vacancy  $(V_{\rm O})$ , (v) singly ionized oxygen vacancy  $(V_{\rm O}^{+})$ , and (vi) doubly ionized oxygen vacancy  $(V_{\rm O}^{2+})$ . EPR active defects are Ti<sup>3+</sup> and  $V_{\rm O}^{+}$ , which will be responsible



Figure 1. XPS spectra of D3 and D4: C 1s (a,b), N 1s (c,d), and S 2p (e,f).



Figure 2. EPR spectra of undoped and C–N–S-doped  $TiO_2$  nanoparticles measured at 300 K.

for the magnetism. The Lande g factor is evaluated through a well-known relation,

$$g = \frac{h\nu}{\mu_{\rm B}B} \tag{1}$$

where  $\nu$  is the applied microwave frequency (9451 MHz). In general, a resonant value at g > 2.0 is due to the  $V_{\rm O}$ , while g < 2.0 is for Ti<sup>3+</sup> defects. For the singly ionized oxygen vacancies, EPR reflects signals at 2.16, 2.48, 2.01, and 2.09 for P3, P4, D3,

and D4, respectively. P3 and P4 show quite high g value compared to a known g value (2.033) of free electron, indicating the distortion of the sample at room temperature. No other resonance due to Ti<sup>3+</sup> was noticed in both the undoped samples (P3 and P4), whereas the peaks at g1 = 1.99 and g2 = 1.97 in D3 indicate the existence of Ti<sup>3+</sup> ions. The incorporation of C–N–S in TiO<sub>2</sub> lattice creates the oxygen vacancies and hence Ti<sup>3+</sup> defects are formed by capturing an electron from such vacancies.<sup>27–30</sup> In the case of D4, Ti<sup>3+</sup> signals were not clearly distinguishable because of the low concentration of N and S at 600 °C calcination, which might have reduced the  $V_{\rm O}$ . The EPR data revealed that C, N, and S were inactive in the present case. However, the existence of the Ti<sup>3+</sup> signals in the doped samples reveals the creation of  $V_0$  defect centers.

3.5. VSM Measurements. The defect-induced magnetization is measured using VSM at room temperature with the applied magnetic field of  $\pm 12$  kOe. Figure 3 presents the field dependent magnetic measurement for undoped and C-N-Sdoped TiO<sub>2</sub> NPs. Undoped samples calcined at 500 (P3) and 600 °C (P4) show room-temperature ferromagnetism along with  $M_{\rm s}$  of 0.11 and 4.9 × 10<sup>-3</sup> emu/g, respectively. The origin of the observed ferromagnetism is mainly due to the oxygen vacancies, as it is strongly evidenced through PL and EPR measurements.<sup>31,32</sup> When compared to P3, P4 exhibited one order higher magnetization. Even though both the P3 and P4 are bare TiO<sub>2</sub>, the observed magnetism is strongly influenced by the crystalline phases of anatase and rutile. The present work reveals the single phase of anatase for P3, whereas 14% is revealed for P4. A lattice distortion in rutile TiO<sub>2</sub> induced by oxygen vacancies is the main cause for the strong ferromagnetism in P4 is owing to charge redistribution. In this connection, Santra et al. have discussed that the magnitude



Figure 3. Room temperature M–H curves of undoped and C–N–S-doped TiO<sub>2</sub> nanoparticles.

of the  $M_s$  in rutile phase (0.109 emu/g) is four times higher than that in anatase  $TiO_2$  (0.061 emu/g).<sup>33</sup> In addition to this, the hysteresis of P4 seems to be unsaturated hence it is assigned to the combination ferromagnetic (at lower fields) and paramagnetic (at higher fields) contributions. In the presence of nonmagnetic dopants such as C, N, and S, the magnetization is significantly affected as they partly tune the concentration of oxygen vacancies. The saturation magnetization of D3 is dramatically reduced to  $0.065 \times 10^{-3}$  emu/g; however, D4 shows 11 times higher value of  $0.71 \times 10^{-3}$  emu/g. This is attributed to the mixed phases of anatase (88%) and rutile (12%), which increase the oxygen vacancies upon doping. The lower value of magnetization in P3 and D3 is associated with pure anatase phase, which normally possesses weak ferromagnetism compared to rutile phase and crystallinity is also less at a lower calcining temperature (500 °C), which reduces the saturation magnetization compared to P4 and D4.

**3.6. Linear Optical Studies.** 3.6.1. UV-Vis Absorption Study. Undoped and C-N-S-doped TiO<sub>2</sub> NPs were dispersed in ethylene glycol and studied for UV-vis absorption. Figure 4



Figure 4. UV-visible absorption spectra of the samples studied P3, P4, D3, and D4.

illustrates the absorption spectra with a maximum at 330 and 360 nm for undoped and doped samples, respectively. The absorption peak is due to the electronic transition from valence band of  $O^{2-}$  antibonding orbital to the lowest unoccupied orbital of  $Ti^{4+}$ .<sup>34,35</sup>

3.6.2. Photoluminescence Study. The emission spectra of the samples are shown in Figure 5 (with 320 nm excitation). The spectra contain several emission peaks. Undoped and doped samples exhibit similar type of emissions. The reduction in PL intensity is observed for both the undoped and doped samples. For clear observation of the position of emission peaks, Gaussian fit was undertaken for one of the samples. Near



band edge (NBE) of TiO<sub>2</sub> anatase phase samples (P3, D3, and D4) occurred at 398 nm whereas the maximum weight percentage of the rutile phase sample (P4) revealed NBE at 410 nm. Violet emission at 429 nm, blue emission at 464 nm, green emission at 560 nm, and red emission at 610 nm observed for all the samples. The peak at 429 nm is ascribed to the self-trapped excitons (STE). STE's result from the spontaneous self-localization of photogenerated charges occurd in TiO<sub>2</sub> with strong electron–phonon coupling. Compared to rutile, anatase is characterized by longer Ti–Ti interatomic distances, lower TiO<sub>6</sub> octahedral coordination, and poorer symmetry. These characteristics favor STE formation according to the Toyizawa theory of self-localization. Whereas, in the case of rutile TiO<sub>2</sub>, the same peak at 429 nm is assigned to recombination of free excitons.<sup>36,37</sup>

The visible emissions at 464, 560, and 610 nm are related to the oxygen vacancies. The excess electrons (upon the removal of an oxygen atom in  $TiO_2$ ) cause the appearance of new electronic states in the bandgap of 0.7-0.9 eV (rutile) and 0.55-1.18 eV (anatase) range below the conduction band edge of titania creating a F-center. The creation of oxygen vacancies leads to the neutral  $(V_{\rm O}^0)$ , singly ionized  $(V_{\rm O}^+)$  and doubly ionized  $(V_{\rm O}^{2+})$  F-centers.<sup>38-40</sup> The emissions due to excitation of electrons from oxygen vacancy states to the valence band are typically in the visible spectral region. These electrons located in the oxygen vacancy states form a donor level, directly affecting the TiO<sub>2</sub> electronic structure. With increasing oxygen vacancies, these donor states can grow in both anatase and rutile titania and overlap with the CB in the case of highly deficient anatase phase. The electrons left in the oxygen vacancies can be localized in two well-identified specific Ti sites thus formally creating Ti<sup>3+</sup> spices. Detailed study about the oxygen vacancies by Janotti et al. stated that  $V_{\rm O}^0$  and  $V_{\rm O}^+$  were shallow donors and  $V_{O}^{2+}$  defect state presented lower energy than  $V_{\rm O}^{+}$  for all Fermi-level positions in the bandgap.<sup>41</sup> When an oxygen atom is removed, the closest Ti atoms tend to relax away farther from the vacancy so as to strengthen their bonding. Neutral oxygen vacancy  $(V_{\Omega}^{0})$  located below the CB hold the Ti atoms close to their nominal position by gaining the energy level of relaxation of the Ti atoms. However, for the case of  $V_{0}^{+}$ , the Ti atoms move away from the vacancy and shift up to higher energy than  $V_{\Omega}^{0}$ . It was, however, reported that the Ti atoms relax and rise even higher in the case of  $V_{\Omega}^{2+}$ . In  $V_{\Omega}^{0}$ , the out-of-plane titanium atoms relax slightly inward to increase the overlap of the 'd' state, while in the case of  $V_{\Omega}^{+}$  the out-of-plane Ti atoms relax slightly outward. Hence, the magnitude of displacement of the Ti atoms in the vicinity of  $V_{\Omega}^{0}$  and  $V_{\Omega}^{+}$  is small when compared to those around  $V_{\Omega}^{2+}$ . Zuo et al. expressed  $V_{\Omega}^{2+}$  serves as an acceptor as well as Ti<sup>3+</sup>, forming an unoccupied state below the bottom of the CB.42 From the above statements, the visible emissions at 464 and 560 nm is due to the recombination of neutral  $(V_{\Omega}^{0})$  and singly ionized  $(V_{\Omega}^{+})$ oxygen vacancy (shallow donors) with the trapped hole.<sup>42–44</sup> In this study, the PL was collected in the presence of water which acts as hole scavenger through the production of more number of OH group.<sup>45,46</sup> The red emission at 610 nm is due to the recombination of deep trap state  $(V_{\rm O}^{2+})$ , i.e., trapped electrons with the valence band holes (see the illustration provided in Figure 6).

3.6.3. Fluorescence Lifetime Measurements. The fluorescence lifetime decay has been measured for undoped and C–N-S-doped TiO<sub>2</sub> nanoparticles by suspending in ethylene glycol and excited at 370 nm are shown in Figure 7a–d. The



**Figure 6.** Schematic diagram of  $TiO_2$  PL mechanism. The dotted lines represent nonradiative transitions, while the solid lines represent radiative transitions.

fluorescence lifetime is dependent on the radiative  $(K_r)$  and nonradiative  $(K_{nr})$  decay process by

$$\tau = 1/(K_{\rm r} - K_{\rm nr}) \tag{2}$$



Figure 7. Fluorescence decay curves of undoped and C–N–S-doped samples.

The life times were determined by fitting the kinetics to a multiexponential function. The multiexponential fit is considered for the NPs in a solution as it has more variety of trapping centers. The average lifetime of P3, P4, D3, and D4 is given in Table 2. It is longer for D4 ( $\sim$ 6.1 ns) and remaining samples

Table 2. Average Fluorescence Life Time of the Sample	Table	2.	Average	Fluorescence	Life	Time	of	the	Samp	les
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sample	$ au_1$ (ns)	$ au_2$ (ns)	$\tau_3$ (ns)	avg (ns)
P3	0.02	2.7	10.9	4.5
P4	0.03	2.4	11.6	4.7
D3	0.02	2.0	12.1	4.7
D4	0.1	2.9	15.3	6.1

shown the shorter lifetime (~4.7 ns). The shorter lifetime of the sample suggests that an increase in either the radiative or nonradiative relaxation rate. At 500 °C calcining temperature, undoped TiO<sub>2</sub> (P3) depicted a short carrier lifetime (~4.5 ns) but the doped sample (D3) depicted a higher carrier lifetime (~4.7 ns) due to the increase of shallow defects center (Ti<sup>3+</sup> and oxygen vacancies) as evident from the EPR analysis. At 600 °C calcining temperature, undoped and doped TiO<sub>2</sub> demonstrated increasing life times of 4.7 and 6.1 ns, respectively. On the contrary, as the calcining temperature increases, oxygen vacancies and grain boundary will decrease, causing the short carrier lifetime. However, in the case of the P4 and D4, the mixed phase of anatase and rutile is observed. In the mixed phase of TiO<sub>2</sub>, band bending occurs at the interface. Due to this, the carriers are separated increasing their lifetime. Choudhury et al. concluded that the in the case of mixed phase TiO<sub>2</sub> (anatase and rutile) the charge carriers possess a long lifetime, while a short lifetime was observed when rutile percentage increased.<sup>35</sup> Therefore, the increasing weight percentage of anatase in D4 shows a long-lifetime compared to P4. Apart from this, trap centers at the interface block the direct transition and, therefore, electrons take longer time to traverse in the mixed phases.<sup>47–49</sup>

3.7. Nonlinear Optical Measurements. The Z-scan technique permits the measurement of the nonlinear refractive index  $(n_2)$  and nonlinear absorption (NLA) of materials, and it provides the sign and magnitude of  $n_2$  and NLO coefficient  $\beta$ . Third-order nonlinear optical processes are divided broadly into two categories: resonant and nonresonant.<sup>50</sup> The resonance nonlinearity arises from the real transition and is slow (ns), whereas the nonresonant transition is virtual and fast (ps/fs). Resonant type nonlinearities are (a) saturable absorption (SA), (b) reverse saturable absorption (RSA), (c) excited state absorption (ESA), (d) free carrier absorption (FCA), (e) nonlinear refraction (NLR), and (f) nonlinear scattering (NLS). In principle, these nonlinearities depend only on the fluence of the incident pulse, whereas nonresonant nonlinearities are two-photon absorption (2PA) and multiphoton absorption (MPA) depend on the input peak intensity.

The observed energy dependent nonlinear absorption (Figure 8 data) can have contributions from the various mechanisms such as SA, RSA, 2PA, MPA, NLS, ESA etc. The plots of  $L_n(1 - T)$  versus  $L_n(I_0)$  ( $I_0$ : input intensity) at 532 nm have slopes of 0.5, 0.7, and 0.8 for 100, 150, and 200  $\mu$ J energies, respectively, indicating the coexistence of one and 2PA process (Figure S6).<sup>51,52</sup> However, for the fs laser excitation, the SA (a one photon absorption process) behavior was observed for the C–N–S-doped TiO<sub>2</sub> NPs (Figure 11 data). Hence, the OA Z-scan results at 532 nm were fitted using the equation<sup>53</sup>

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{q_0(z)}{(m+1)^{3/2}}$$
(3)

Where,

$$q_0(z) = \frac{\beta_{\rm eff} I_0 L_{\rm eff}}{1 + \frac{z^2}{z_0^2}}$$
(4)

The  $n_2$  is estimated by fitting the divided Z-scan traces of CA/OA.

$$T = 1 + \frac{4\Delta\phi_0 x}{(x^2 + 9)(x^2 + 1)}$$
(5)

$$\Delta \phi_0 = k I_0 \gamma L_{\text{eff}} \tag{6}$$

where  $k = 2\pi/\lambda$ , and  $\gamma$  is the nonlinear refraction coefficient. By contrast, for the fs laser excitation, the OA Z-scans were fitted by considering SA + RSA as follows:



**Figure 8.** Open aperture Z-scan measurements of undoped and C–N–S-doped TiO<sub>2</sub>. nanoparticles with 9 ns laser excitation for the energies of (a) 100  $\mu$ J, (b) 150  $\mu$ J, and (c) 200  $\mu$ J. Open symbols are the experimental data, while the solid lines are theoretical fits.

Table 3. Optical Limiting Value of Undoped and C-N-S-Doped TiO<sub>2</sub> Nanoparticles with Different Input Energy

	100 µ	ιJ	150 μ	uJ	200 µJ		
sample	$\beta  imes 10^{-10} \text{ m/W}$	OL J/cm <sup>2</sup>	$\beta \times 10^{-10} \text{ m/W}$	OL J/cm <sup>2</sup>	$\beta \times 10^{-10} \text{ m/W}$	OL J/cm <sup>2</sup>	
P3	$1.97 \pm 0.20$	$1.71 \pm 0.17$	$1.28 \pm 0.13$	$1.70 \pm 0.17$	$1.06 \pm 0.11$	$1.69 \pm 0.17$	
P4	$2.06 \pm 0.21$	$1.48 \pm 0.15$	$1.31 \pm 0.13$	$1.46 \pm 0.15$	$1.06 \pm 0.11$	$1.41 \pm 0.14$	
D3	$2.12 \pm 0.21$	$1.44 \pm 0.14$	$1.38 \pm 0.14$	$0.25 \pm 0.03$	$1.08 \pm 0.11$	$1.05 \pm 0.11$	
D4	$1.81 \pm 0.18$	$1.92 \pm 0.19$	$1.35 \pm 0.13$	$1.92 \pm 0.19$	$1.02 \pm 0.10$	1.89 ± 0.19	

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_s}} + \beta I \tag{7}$$

where  $I_s$  is a saturation intensity.

3.7.1. Nanosecond Pumping. Figure 8 shows the OA Zscan data at 532 nm (10 Hz) with pulse energies of 100 (a), 150 (b), and 200  $\mu$ J (c). The normalized transmittance decreases rapidly when the sample passed through the focal point (RSA). This demonstrated a typical optical limiting (OL) effect. Two important mechanisms resulting in OL are nonlinear absorption and nonlinear scattering (sometimes both).<sup>54</sup> Based on absorption mechanism of semiconducting materials, NLA can be divided into MPA, RSA, FCA, and ESA. Table 3 shows the variation of  $\beta$  with input pulse energy. This variation of  $\beta$  suggests that the actual mechanism of nonlinear absorption is an effective 2PA process (or sequential ESA involving real intermediate transition). As discussed earlier, genuine 2PA is a nonresonant nonlinearity that involves the virtual intermediate transition to promote an electron from its initial state to its final state. Hence genuine 2PA absorption coefficient is independent of incident laser fluence. In general,  $\beta$ depends on population in the ground state.<sup>55,56</sup> In the present case, a variation in  $\beta$  with input fluence was observed. A strong ESA depletes the ground state population strongly, thereby rendering ESA coefficient fluence-dependent.57,58 Therefore, the measured variation of  $\beta_{\rm eff}$  suggests that NLA seen for ns excitation has a critical contribution from ESA.59,60 Induced thermal scattering (ITS) has an important role in the OL of several semiconducting and graphene based nanomaterials with ns excitation.<sup>61</sup> For ultrashort (fs or ps) laser pulses ITS can be neglected since the thermal scattering centers form very slowly (ns). Typically longer pulse duration and lower surface tension of solvent favors the occurrence of ITS.<sup>62</sup> Interestingly, in the data presented here, we observed weak scattering, possibly due to (i) thermal homogeneous media (wherein the heat generated will be lost to the surroundings very fast) will inhibit

the formation of scattering centers (ii) very low repetition (10 Hz) laser pulses were used. Therefore, the contribution from scattering has been neglected from the calculations. From fluorescent lifetime decay measurement the carrier lifetime was found to be in the ns range. Hence, within this time all the excited molecules will relax back to the ground state and any generated heat will be dissipated completely.<sup>63–65</sup> The optical limiting thresholds for different samples (P3, P4, D3, and D4) at 100 (a, b, c and d), 150 (e, f, g, and h) and 200  $\mu$ J (i, j, k, and l) energies are illustrated in Figure 9. The OL threshold value was significantly less for D3 compared to P3, P4, and D4 (Table 3), which is due to the higher concentration of oxygen vacancy as evidence from EPR and PL studies.

From the closed-aperture, Z-scan data presented in Figure 10, a deviation from a symmetrical response was observed. This is probably attributed to higher order nonlinearities and incomplete accounting for the strong NLA at the detector.<sup>66</sup> These effects can distort the Gaussian beam profile, thereby introducing artifacts in the CA profiles. Thermal nonlinearities contribute to the negative nonlinear refraction. All our closedaperture Z-scan data were collected at lower peak intensities to minimize thermal effects. In the present study, the samples behave differently with varying energies [Figure 10, (a) 100  $\mu$ ], (b) 150  $\mu$ J, and (c) 200  $\mu$ J] as a self-focusing and selfdefocusing lens. Free-carriers also contribute significantly to the phase changes in the sample.<sup>67</sup> The physical origin of  $n_2$  could be electronic, molecular electrostrictive, or thermal, etc. Divya et al. have reported the morphology-dependent sign change of  $n_2$  of TiO<sub>2</sub> at 532 nm (388 MW/cm<sup>2</sup>).<sup>68</sup> Negative nonlinear refraction was observed for nanowires and nanoflowers of TiO<sub>2</sub>, whereas positive nonlinear refraction was observed for nanosheets and nanospheres. For the negative nonlinearity, the electron-phonon interaction is dominant, which is a nonradiative process leading to thermalizing the lattice because of the change of refractive index. However, the probability of phonon-phonon interaction is more in the case of positive



**Figure 9.** Optical limiting curves for input energies of 100 (a, b, c, and d), 150 (e, f, g, and h), and 200  $\mu$ J (i, j, k, and l) for P3, P4, D3, and D4 with 9 ns laser excitation. Open symbols are the experimental data, while the solid lines are theoretical fits.

nonlinearity. Hence, the onset of electronic nonlinearity is due to the high surface to volume ratio of nanosheets and nanospheres. In the present case (Figure 10 data), we evaluated the distance between the peak and valley  $(\Delta Z_{p-v})$  for all the samples was it found to be 2–7 mm except for P3 at 100  $\mu$ J (12 mm) and 200  $\mu$ J (9 mm). This satisfies the condition ( $\Delta Z_{p-v} \sim 1.7 \times Z_0$ ) of pure electronic third order nonlinearity for all the samples except P3 (thermal origin).<sup>69</sup>

From Table 4 data it is evident that the value of  $n_2$  is higher for P3 and D3 compared to P4 and D4. The XRD pattern of P3 and D3 demonstrated pure anatase phase (Figure S1). In general, anatase phase shows higher order nonlinearity compared to rutile phase of TiO<sub>2</sub>. Anatase phase has bound excitons with larger excitonic binding energy while rutile phase possesses free excitons with lesser binding energy. Weakly bound excitons have giant oscillator strengths compared to the oscillator strength of the free excitons.<sup>70</sup> NLO effects are enhanced when it has large optical oscillator strength. Long et al. have reported that the  $n_2$  for pure anatase phase to be -6.3 $\times 10^{-17}$  m<sup>2</sup>/W and rutile phase to be  $-2.7 \times 10^{-17}$  m<sup>2</sup>/W of the TiO<sub>2</sub> thin film (800 nm, 150 fs).<sup>71</sup> In the present study, P3 and P4 exhibited  $n_2$  values of  $18.3 \times 10^{-17}$  m<sup>2</sup>/W and  $12.8 \times$  $10^{-17}$  m<sup>2</sup>/W, respectively. On the other hand, the C-N-S dopant in TiO<sub>2</sub> enhances the oxygen vacancies leading to the defects on the surface of TiO<sub>2</sub>. This surface state provides the radiationless transition of photoinduced charge carriers. The surface states possess typical lifetime of nanoseconds (Table 2) favoring the trapped electrons, which are then transferred to the states (ESA).<sup>72,73</sup> Hence, the electronic nonlinearity is dominant for the doped material rather than the thermal origin for the refractive index changes. Table 4 shows the values of  $\beta_{\text{eff}}$  and  $n_2$  as a function of input energy. It is observed that as the energy is increased, the magnitude of  $\beta_{\rm eff}$  and  $n_2$ decreased.<sup>74</sup> This decreasing behavior is owing to their direct reliance on the charge carrier density as discussed earlier. Similar decreases of optical nonlinearities are observed in the



Figure 10. Closed aperture Z-scan measurements of undoped and C–N–S-doped TiO<sub>2</sub> nanoparticles with 9 ns laser excitation for the energies of (a) 100  $\mu$ J, (b) 150  $\mu$ J, and (c) 200  $\mu$ J. Open symbols are the experimental data while the solid lines are theoretical fits.

Table 4. Third-Order Nonlinear Parameters of Undoped and C–N–S-Doped TiO<sub>2</sub> Nanoparticles with Varying Input Energies for 9 ns Laser Excitation at 532 nm

		P3			P4			D3			D4	
energy (μJ)	$\begin{array}{c} \beta \times 10^{-10} \\ \mathrm{m/W} \end{array}$	$n_2 \times 10^{-17} m^2/W$	Т	$\begin{array}{c} \beta \times 10^{-10} \\ \mathrm{m/W} \end{array}$	$n_2 \times 10^{-17} m^2/W$	Т	$egin{array}{c} eta  imes 10^{-10} \ { m m/W} \end{array}$	$n_2 \times 10^{-17} m^2/W$	Т	$\begin{array}{c} \beta \times 10^{-10} \\ \mathrm{m/W} \end{array}$	$n_2 \times 10^{-17} m^2/W$	Т
100	$1.97\pm0.2$	$18.3 \pm 1.8$	0.6	$2.06\pm0.21$	$12.8\pm1.3$	0.86	$2.12 \pm 0.21$	$15.4 \pm 1.5$	0.73	$1.81\pm0.18$	$12.0 \pm 1.2$	0.80
150	$1.28 \pm 0.13$	$7.8 \pm 0.78$	0.9	$1.31 \pm 0.13$	$6.54 \pm 0.65$	1.06	$1.38 \pm 0.14$	9.1 ± 0.91	0.80	$1.35 \pm 0.14$	$9.5 \pm 0.95$	0.76
200	$1.06 \pm 0.11$	$7.5 \pm 0.75$	1.1	$1.06 \pm 0.11$	6.40 ± 0.64	0.88	$1.08\pm0.11$	$6.2 \pm 0.62$	0.94	$1.02 \pm 0.1$	5.8 ± 0.58	0.93

Table 5. Literature Comparison of a Two-Photon Absorption Coefficient with Its Energy/ $I_s$  with Different Laser Excitations

sample	laser	NLO response	$I_{\rm s}~{\rm GW/cm}^2$	energy $\mu J$	$\beta$ cm/W	ref
LG-PVA	532 nm, 5 ns	ESA	4.4	-	$30 \times 10^{-9}$	3
TNB-CdS	532 nm, 8 ns, 1 Hz	NLS + NLA	-	-	$1.84 \times 10^{-23}$	54
Cu <sub>2</sub> O	532 nm, 5 ns, 0.2 Hz	2 PA + ESA	1600	50	$6.4 \times 10^{-9}$	58
CdTe QDs	532 nM, 5 NS, 0.25 Hz	2 PA + ESA	-	200	$5.5 \times 10^{-10}$	60
P3HT-MoS <sub>2</sub>	532 nm, 4 ns	FCA + NLS	-	40	$5.0 \times 10^{-9}$	61
ZrS <sub>3</sub> /RGO	532 nm, 10 Hz	RSA	1430	32	$62.7 \times 10^{-9}$	74
N-doped graphene	532 nm, 40 Ps, 10 Hz	2 PA	-	12	$0.46 \times 10^{-9}$	77
GO NRS glasses	532 nm, 8 ns, 1 Hz	2 PA	9.1	150	$3.97 \times 10^{-10}$	81
	532 nm, 21 ps, 2 Hz	SA	114	1.02	$-3.19 \times 10^{-11}$	
lead iodide perovskite thin films	532 nm, 40 ns, 1 kHz	SA	0.0007	-	$-1620 \times 10^{-6}$	75
	514 nm, 200 fs, 1000 Hz	SA	60	-	$-0.23 \times 10^{-6}$	
C–N–S-doped TiO <sub>2</sub> NPs	532 nm, 9 ns, 10 Hz	2 PA + ESA	-	100	$2.12 \times 10^{-8}$	Present Work

case of lead iodide perovskite thin films.<sup>75</sup> The value of the figure of merit (*T*) shows that undoped and doped materials can be the best candidate for optical limiting applications. From the data in Table 5 it is observed that the absorption coefficient ( $\beta_{\rm eff}$ ) of C–N–S-doped TiO<sub>2</sub> NPs illustrate higher order magnitude compared to the other organic, graphene-based composites, quantum dots. The contribution of scattering effects to the nonlinearity in these experiments was observed to be insignificant.

3.7.2. Femtosecond NLO Studies. Undoped TiO<sub>2</sub> NPs (P3 and P4) exhibited RSA behavior, whereas C–N–S-doped TiO<sub>2</sub> (D3 and D4) show SA (Figure 11). The energy of 800 nm photon satisfies the criterion for observing two–photon absorption (TPA) process (1/2  $E_g < h\omega < E_g$ ) for the undoped TiO<sub>2</sub>. However, in the case of C–N–S dopant, SA was observed.<sup>76</sup> SA is the consequence of 1 PA process. When an 800 nm photon excites the material, the VB of O 2p electrons transfer to the lower energy levels of CB of Ti 3d.

Hence, the electrons are eventually filled near the CB, and no more electrons can be transmitted due to the band filling effect. Due to Pauli's exclusion principle, the lower energy levels near the CB are fully populated, and no more electrons can be further excited to this energy state by absorbing energy from the laser, forcing the sample to exhibit transparency at higher intensities (SA).<sup>77,78</sup> The 1 PA contributing to the SA process is accredited to the localized defect states above the VB, which is induced by the introduction of C-N-S (dopant) in TiO<sub>2</sub>. From the XPS spectra (Figure 1), N 2p + S 2p forms the intermediate level above the VB of O 2p. This intermediate state enhances the absorption cross-section of the ground state. Hence, the SA occurs in the doped sample. That the SA observed was from the nanoparticles only was confirmed by closely observing the cuvette wherein we did not observe any diffusion/movement of the solute (nanoparticles) during the entire scan. By considering the presence of 2PA with SA (eq 7)of the materials the saturation intensity  $(I_s)$  has been calculated



Figure 11. Open aperture Z-scan measurements of undoped and C-N-S-doped TiO<sub>2</sub> nanoparticles at 150 fs laser excitation. Open symbols are the experimental data, while the solid lines are theoretical fits.

and summarized in the Table 6. The closed aperture Z-scan curves of undoped and C–N–S-doped  $TiO_2$  NPs are shown in

Table 6. Saturation Intensity of Undoped and C–N–S-Doped TiO<sub>2</sub> for 150 fs Laser Excitation at 800 nm

sample	$I_{\rm o}~{\rm MW/cm^2}$	$I_{\rm s}~{\rm MW/cm^2}$
P3	69	$10520 \pm 1578$
P4	79	$520 \pm 78$
D3	75	$180 \pm 27$
D4	79	446 ± 67

Figure 12. A peak–valley signature for P3 and D4 indicate a negative  $n_2$  and self-defocusing behavior. Whereas, P4 and D3 exhibited self-focusing behavior (valley–peak signature or positive  $n_2$ ). The nonlinear refraction through the heat effect is neglected in this experiment since the pulse duration is very short (~150 fs) compared to the rise time of thermal origin.<sup>79</sup> From our Z-scan data, it was established that  $\Delta Z_{p-v} \sim 1.7 \times Z_{o}$ , confirming the major contribution of electronic nonlinearity.<sup>80</sup> Due to the ease of generating free carriers in semiconductors, a large free carrier nonlinearity is possible. For longer excitation pulses, such as in the nanosecond regime, free carriers are the primary contributors to the observed optical nonlinearity, and



Figure 12. Closed aperture Z-scan measurements of undoped and C-N-S-doped TiO<sub>2</sub> nanoparticles at 150 fs laser excitation. Open symbols are the experimental data, while the solid lines are theoretical fits.

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they can mask the faster responses from the bound electronic nonlinearity. This is in contrast with fs pulse excitation, where, at low excitation intensity, the dominant contribution to the nonlinearity is from the bound charge carriers. However, with the higher pulse intensity, the nonlinearity from the free carriers dominates the bound charge carriers.<sup>81</sup> Therefore, a change in the  $n_2$  in the CA Z-scan data is attributed to the bound charge carriers induced effects since the pump intensity was not enough ( $\sim$ 75 MW/cm<sup>2</sup>) to generate large carrier concentration that can induce a change in the refractive index of the materials. Kalanoor et al. have reported that a change in the sign of the nonlinear refractive index of lead iodide perovskite thin films under fs laser pumping with varying pump intensity and repetition rate.<sup>75</sup> The  $n_2$  of the P3, P4, D3, and D4 were established to be  $15.3 \times 10^{-17} \text{ m}^2/\text{W}$ ,  $-14.5 \times 10^{-17} \text{ m}^2/\text{W}$ ,  $-16.7 \times 10^{-17} \text{ m}^2/\text{W}$ , and  $5.9 \times 10^{-17} \text{ m}^2/\text{W}$ , respectively. The  $n_2$  value is higher for P3 and D3 (pure anatase phase) compared to P4 and D4, and it is due to the different oscillation strengths of anatase and rutile phase as discussed in the case of ns pumping. Typically, 10-15% errors are expected in all the values of NLO coefficients obtained in these studies due to errors in the estimation of spot size at focus, fitting errors, and input laser fluctuations.

3.7.3. *cw Z-Scan Measurements.* The magnitudes of  $\beta$ ,  $n_2$ , and real/imaginary parts of  $\chi^{(3)}$  were measured using cw radiation. The OA curve (Figure 13a) exhibited a normalized



Figure 13. Open (a) and closed (b) aperture Z-scan curves of undoped and C–N–S-doped  $TiO_2$  nanoparticles under cw laser irradiation.

transmittance peak, indicating the presence of saturable absorption, i.e., increase in transmittance with the input energy. In SA, the population in excited states saturate because of their long lifetime. In other words, the absorption cross-section is high in the ground state compared to the excited state. OA Zscan traces show the enhancement of nonlinear absorption coefficient with increasing calcining temperature and for the C–N–S dopants (Table 7). Thus, with increasing temperature, the grain size increased and could have possibly resulted in the observed size-dependent enhancement of  $\beta$ . The CA curves (data presented in Figure 13b) exhibited a peak-valley behavior. This signature indicates the self-defocusing property (negative  $n_2$ ) of the samples. The physical origin of nonlinear refraction could be due to any of the electronic, molecular, electorstrictive, or thermal effects. The peak-valley separation of D4 is  $\sim$ 3.3 × Z<sub>R</sub>. A peak-valley separation of >2.3 × Z<sub>R</sub> is a clear suggestion of thermal nonlinearity.<sup>82–84</sup> The excitation of cw laser light on the nonlinear medium will induce heat, which expands the medium. This expansion travels in acoustic form. causing the temperature and, thereby, density gradients within the medium that alters the refractive index. This is called the thermal lensing effect. In the cw laser, index change is proportion to changes in density of the liquid. Hence, in these cw Z-scan experiments, the origin of  $n_2$  is from thermooptic effect.<sup>85-88</sup> The calculated nonlinear parameters are summarized in Table 7. D4 sample exhibited high  $n_2$  and  $\beta$ values, which will be useful to the optical switching applications.

3.8. Conclusions. Oxygen vacancy related defects were identified for the undoped and C-N-S-doped samples through EPR and PL studies. Our detailed Z-scan studies using ns and fs pulses revealed that the NLO coefficients were enhanced through free carrier generation in the case of ns laser excitation with varying input energies. The dominant mechanism is the combination of 2PA and FCA resulting from the efficient charge/energy transfer from N 2p + S 2p intermediate state of the Ti 3d state, with the fs laser excitation that can be attributed to Pauli blocking effect. 2PA dominated with ns (532 nm) laser excitation, whereas SA is dominated with fs (800 nm) laser excitation for the C–N–S-doped  $TiO_2$ nanoparticles. Thermal nonlinearity was observed in these samples with low power cw laser excitation. A single phase of rutile and mixed phase with anatase depicted higher order magnetization than pure anatase TiO<sub>2</sub> nanoparticles.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b08778.

XRD, FTIR, micro-Raman, and XPS analysis of undoped and C-N-S-doped TiO<sub>2</sub>, FESEM images of P4 and D4, linear fit of  $L_n(1 - T)$  versus  $L_n(I_0)$  at 532 nm with the energy of 100, 150, and 200  $\mu$ J for D3, and atomic concentration table of doped samples from XPS measurement (PDF)

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Table 7. Third-Order NLO Coefficients of the Samples under cw Laser Irradiation

sample	$n_2 \times 10^{-8} \text{ cm}^2/\text{W}$	$\beta  imes 10^{-4} \ {\rm cm/W}$	Re $\chi^{(3)} \times 10^{-6}$ esu	Im $\chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
Р3	$8.40 \pm 0.84$	$0.25 \pm 0.03$	9.9 ± 1	$0.16 \pm 0.02$	$9.9 \pm 1.0$
P4	$9.60 \pm 0.96$	$0.38 \pm 0.04$	$7.9 \pm 0.8$	$0.24 \pm 0.02$	$7.9 \pm 0.8$
D3	$10.25 \pm 1.0$	$0.57 \pm 0.06$	$8.4 \pm 0.8$	$0.35 \pm 0.04$	$8.4 \pm 0.8$
D4	$10.99 \pm 1.1$	$0.92 \pm 0.09$	$7.0 \pm 0.7$	$0.57 \pm 006$	$7.0 \pm 0.7$

Notes

The authors declare no competing financial interest.

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