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Multi-stage Nonlinear Optical Response in $BaTiO_3$ NPs

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Introduction

- Barium titanate ($BaTiO_3$) is a promising material **[1]** because of its strong intrinsic ultrafast optical nonlinearities, electro-optic behavior and physical tolerance. These properties provide a platform for realizing ultrafast optical control in optoelectronic devices, allowing various architectures for communications and signal processing applications..
- Nonlinear phenomena have been broadly investigated on the bulk form as well as at the nanoscale. However, a systematic study on the nonlinear optical responses of $BaTiO_3$ nanoparticles (NPs) is still lacking.
- Here, there has been an attempt to promote nonlinear optical properties of $BaTiO_3$ NPs by use of Aminomethyl phosphonic acid as an adsorbate. It could increase the stability of $BaTiO_3$ NPs with size~90-100 nm.
- Nonlinear optical properties of a highly stable $BaTiO_3$ NPs film using intensity dependent femtosecond Z-scan technique, were investigated. We found an exceptional nonlinear switching behavior in $BaTiO_3$ NPs (size ~90 -100 nm) from saturable absorption (SA) to reverse saturable absorption (RSA) through a distinct M-pattern at 800 nm which is near to the two-photon absorption band (3.2 eV).
- Further increasing the excitation intensity shows that the nonlinear absorption (NLA) behavior of the NPs is efficiently modified from M-pattern to pure RSA. The multi-stage NLA phenomenon is assigned to the interchange of simultaneous one photon-SA follows excitation absorption, pure two photon absorption and three photon absorption effects.
- We also observed broadband third order nonlinear optical properties of $BaTiO_3$ NPs achieved using spectral dependent Z-scan studies. The superior and switching NLO effects indicated that these materials might be utilized for potential applications, including multiphoton-based imaging, optical modulator, and all optical switching devices.

Experimental Setup and Nonlinear optical Mechanisms

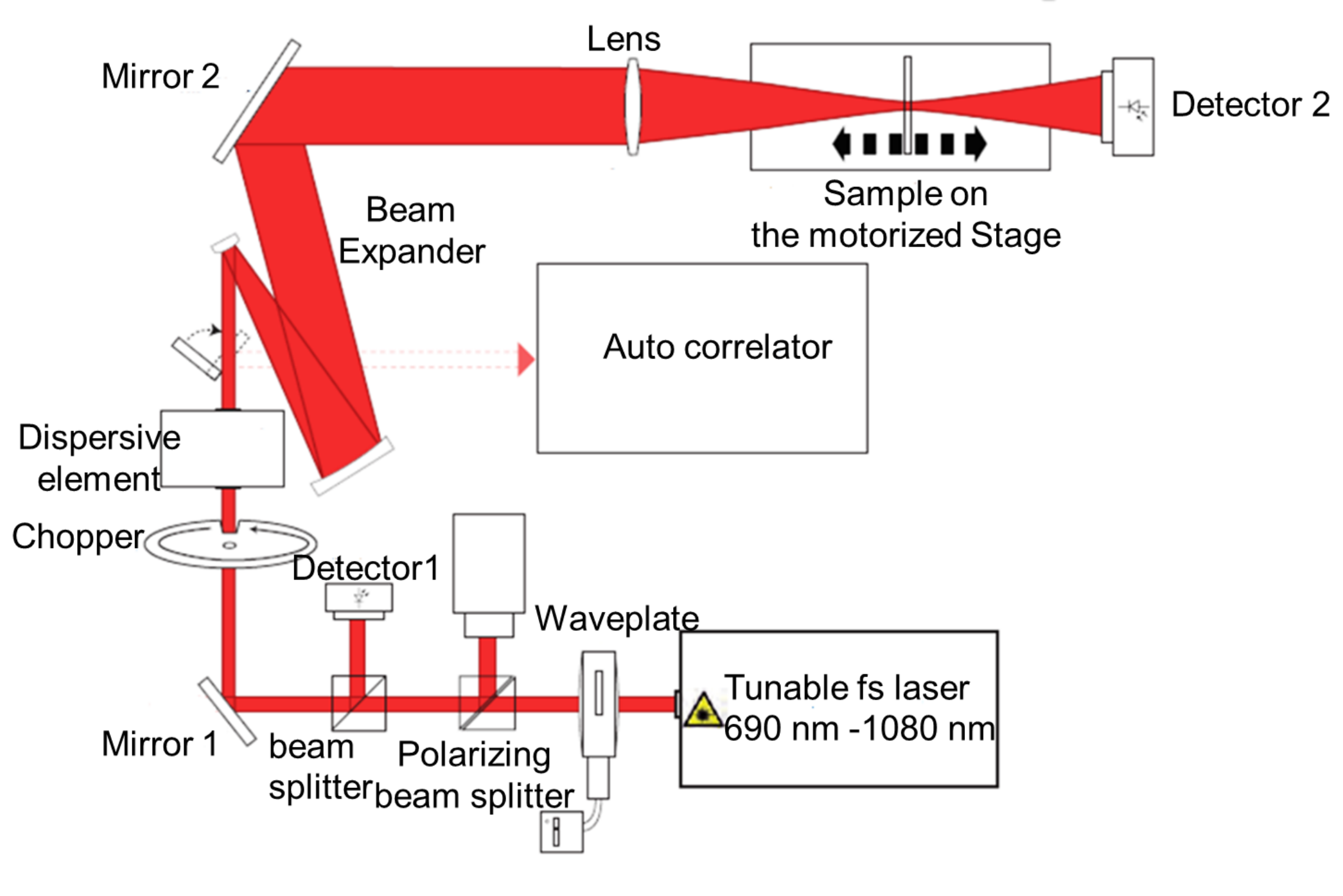

Figure 1 Z-scan experimental setup

- Z-scan setup and beam path from the tunable fs-laser to the sample. For more check **ref [2]**
- A waveplate and polarizing beam splitter attenuate the input laser power. Commercial beam expander (two parabolic mirrors) expand the beam by 4x and a lens focuses the beam on the sample.
- A motorized stage moves the sample in and out of focus.
- Two diodes record the measurement- and reference signal while a mechanical chopper allows to adjust the on/off duration of the signal.
- A flip mirror directs the beam to the autocorrelator to measure the pulse duration.

Preparation of stable BaTiO3 NPs solution and Film

- Disperse 0.980 mg of $BaTiO_3$ NPs in 4mL of Aminomethyl phosphonic acid (1.25 mM) for the particle concentration of 10^{10} nanoparticles/cm3. After 24 hour of stirring process, we Pour the Colloidal NPs on the glass slide and make them dry (Reference: **Chia-Lung Hsieh, et al Three-dimensional harmonic holographic microcopy using nanoparticles as probes for cell imaging, Optics Express 17, 2880, 2009)**

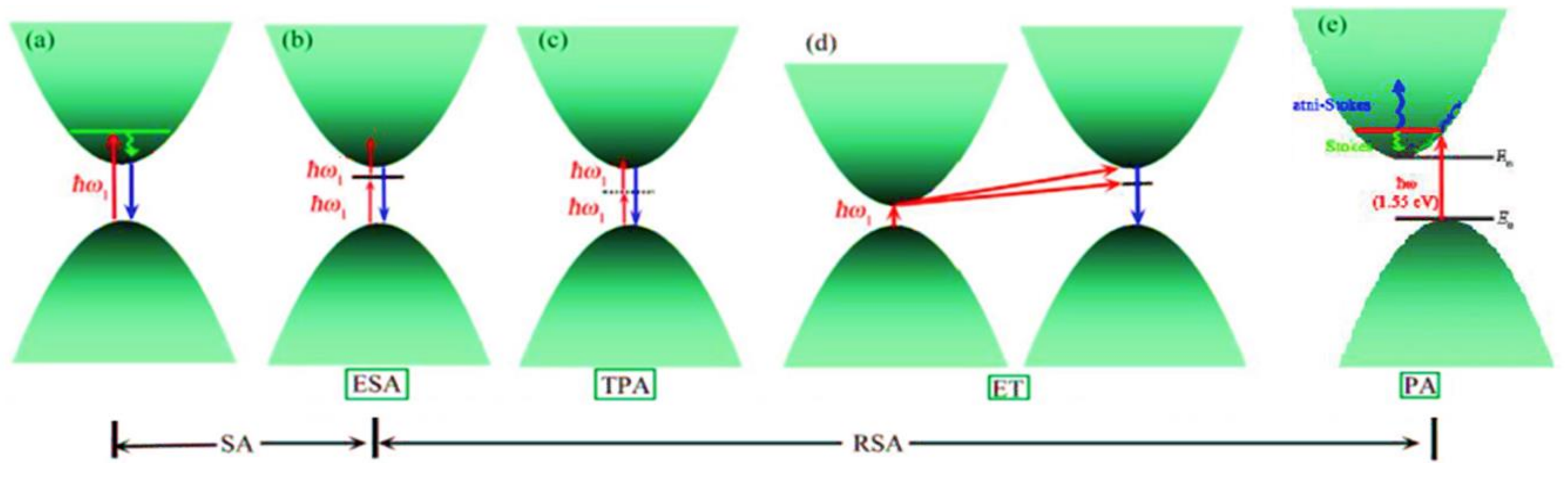

Figure 2 Electron transition schematics. a) Saturable absorption (SA). Reverse saturable absorption (RSA) includes: b) excited states absorption (ESA)-induced up conversion process via a real electronic state to absorb two photons. c) Two-photon absorption (TPA)-induced upconversion through virtual electronic state to absorb two photons. d) Energy-transfer (ET)-induced up conversion via a real intermediate state to excite a higher energy carrier. e) Phonon-assisted (PA) anti-Stokes through the absorption of photons and phonons to generate a higher energy carrier. (This figure is adapted from **ref [3]**)

Results

Switching behaviour from SA to RSA

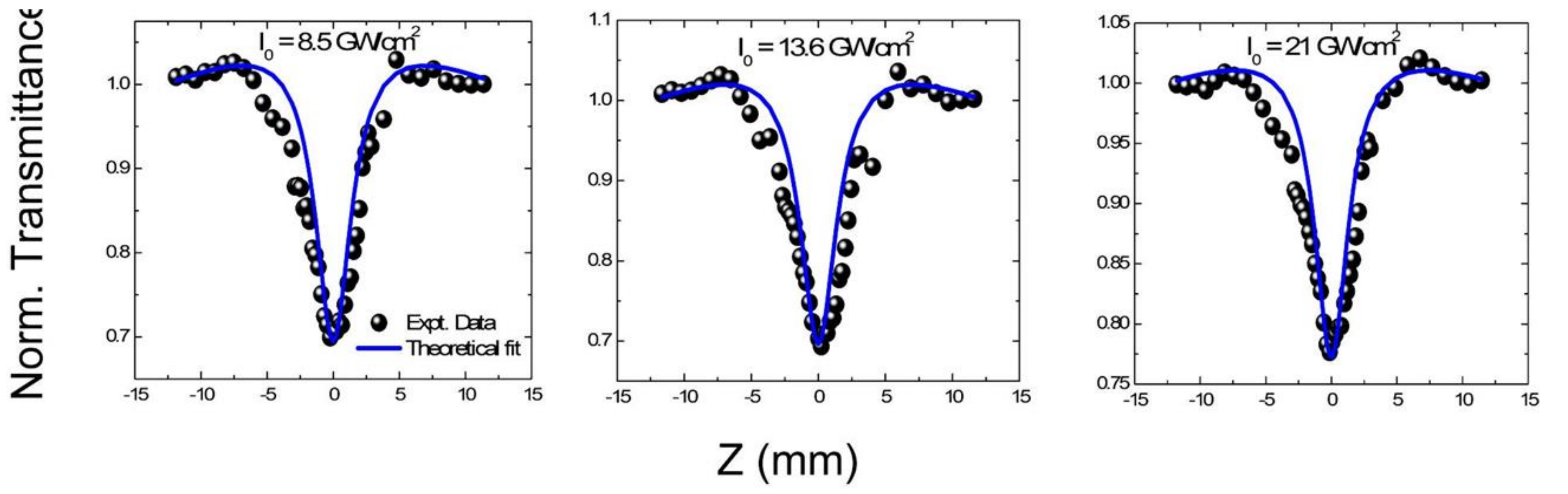

Figure 1 Open-aperture Z-scan curves of BaTiO3 NPs under the excitations with different input peak intensities, (a) 8.5 GW/cm2, (b) 13.6 GW/cm2, and (c) 21 GW/cm2. Results reveals NLO switching behavior from SA to RSA.

- Figure 1 demonstrated complex behaviour with switching from saturable absorption (SA) to reverse saturable absorption (RSA). A good fit was obtained for dominant effective two-photon absorption coefficient (β) with magnitude of the order of 10^{-7} cm/W and saturation intensity (I_s of ∼ of 10^7 W/cm^2) for various excitation intensities ranging from 8.5 to 19 GW/cm^2.
- The effective 2PA in the present case occurs via a one photon absorption induced excited state absorption mediated by real intermediate state because of residual absorption at 800 nm.

Intensity dependent NLO coefficients

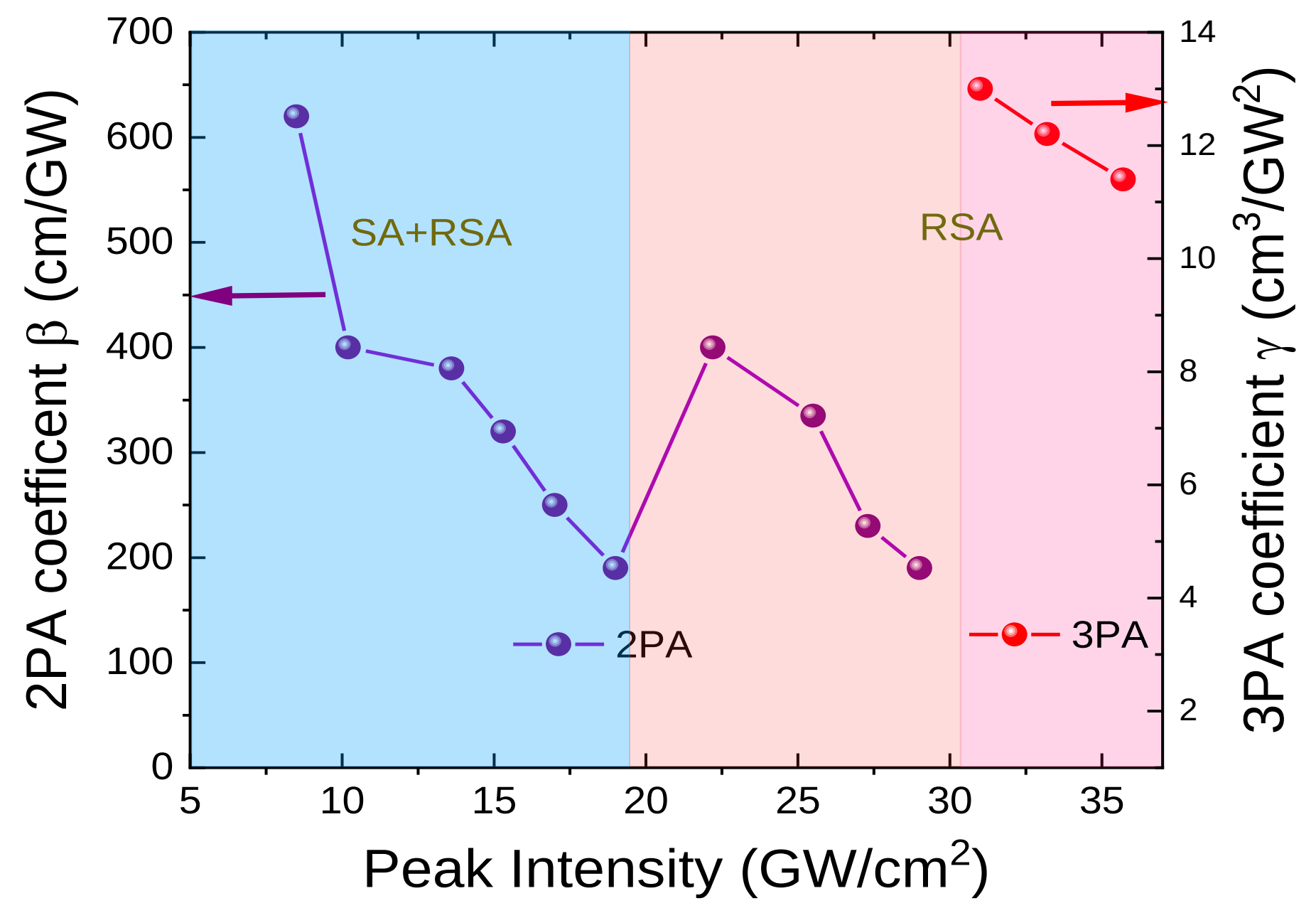

Figure 5 Intensity dependent nonlinear absorption coefficients of BaTiO3 NPs measured at the excitation wavelength of 800 nm. Purple squares, and red color circles represent β (2PA) and γ (3PA) coefficients, respectively

Optical Limiting

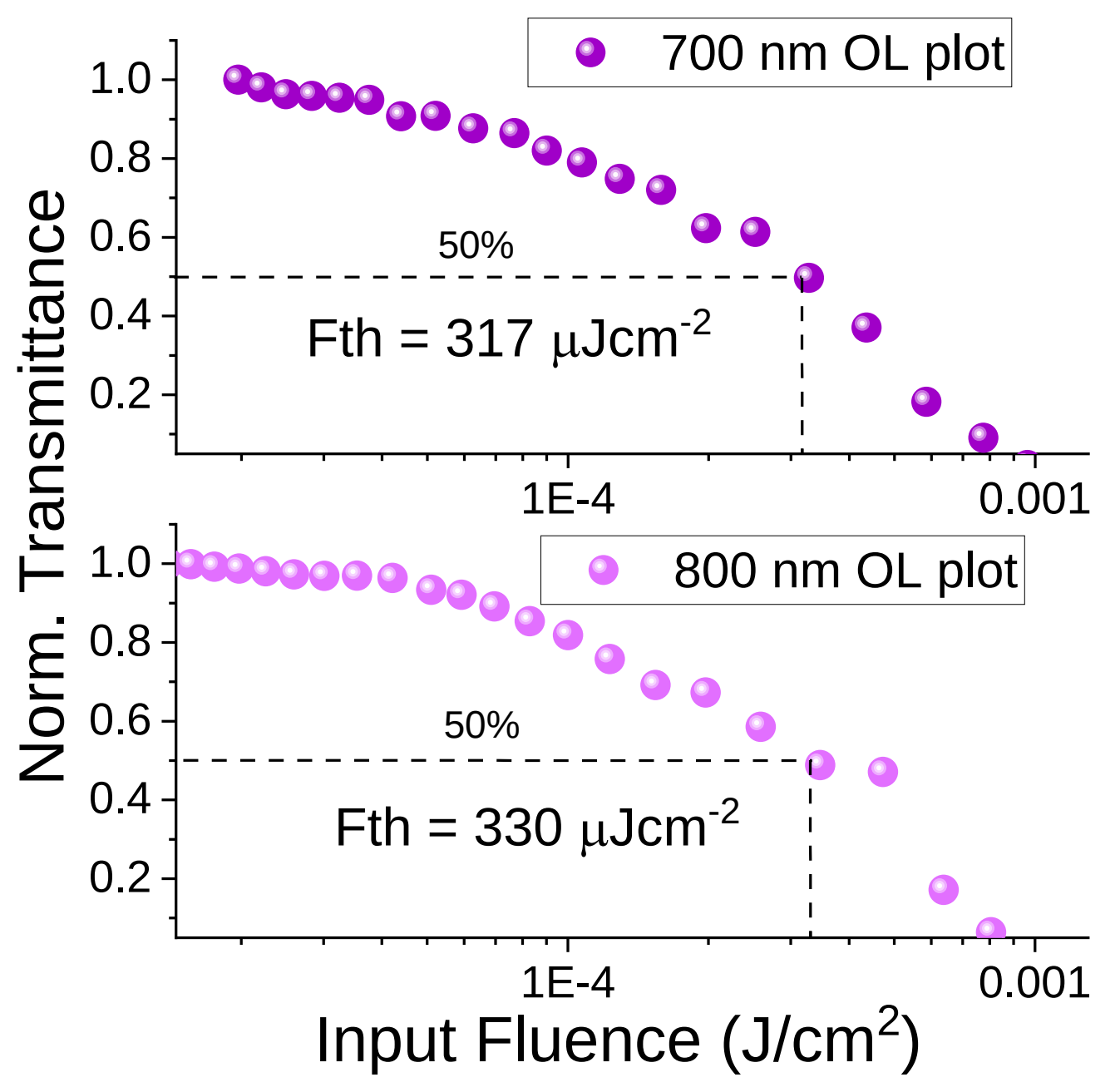

Figure 6 Optical limiting behavior of BaTiO3 NPs at (a) 700 nm and (b) 800 nm wavelengths

Two/Three-photon absorption

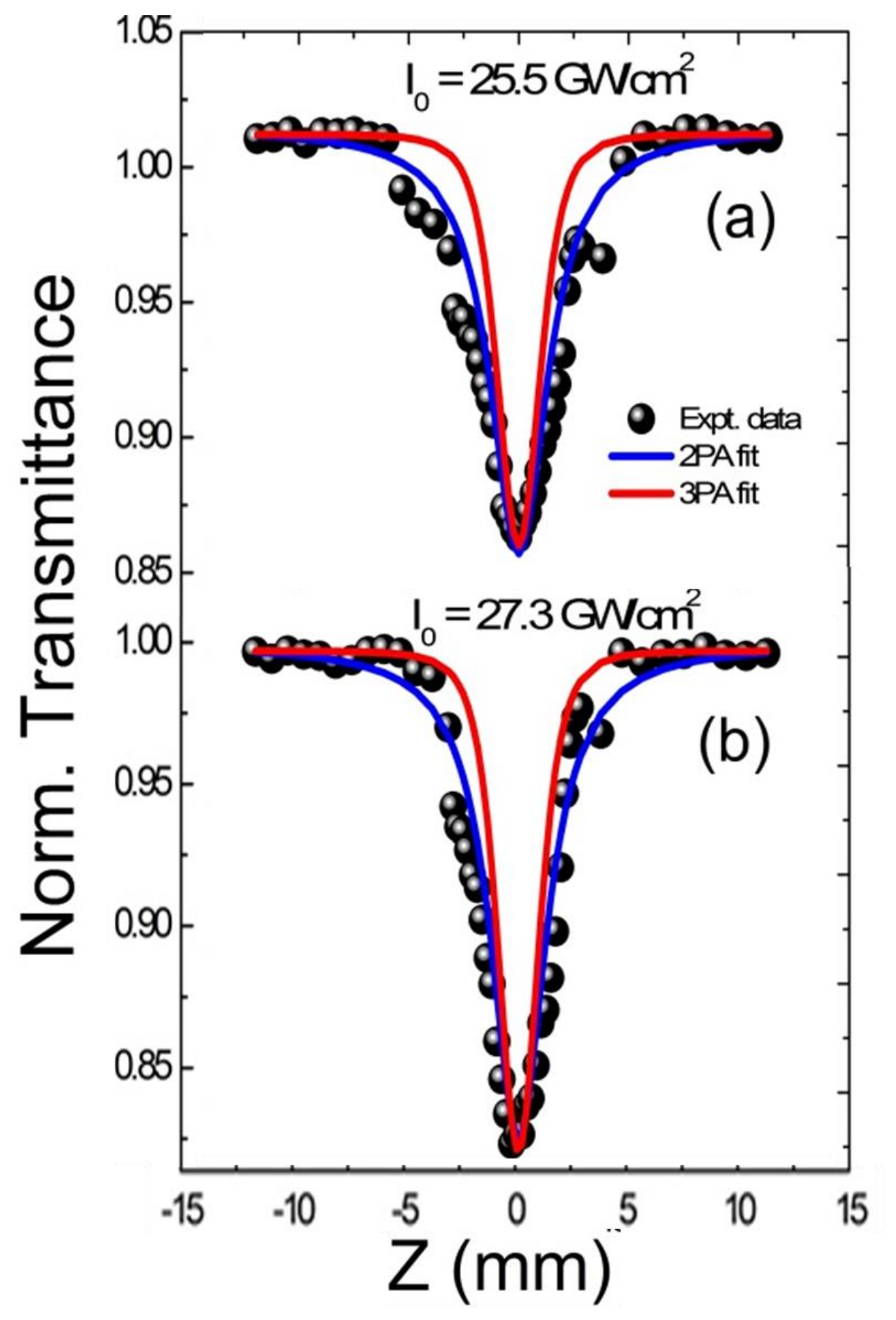

Figure 2 Open-aperture Z-scan curves of BaTiO3 NPs under the excitations with different input peak intensities, (a) 25 GW/cm2 and (b) 28 GW/cm2. Results demonstrate pure two photon absorption behavior at these intensities

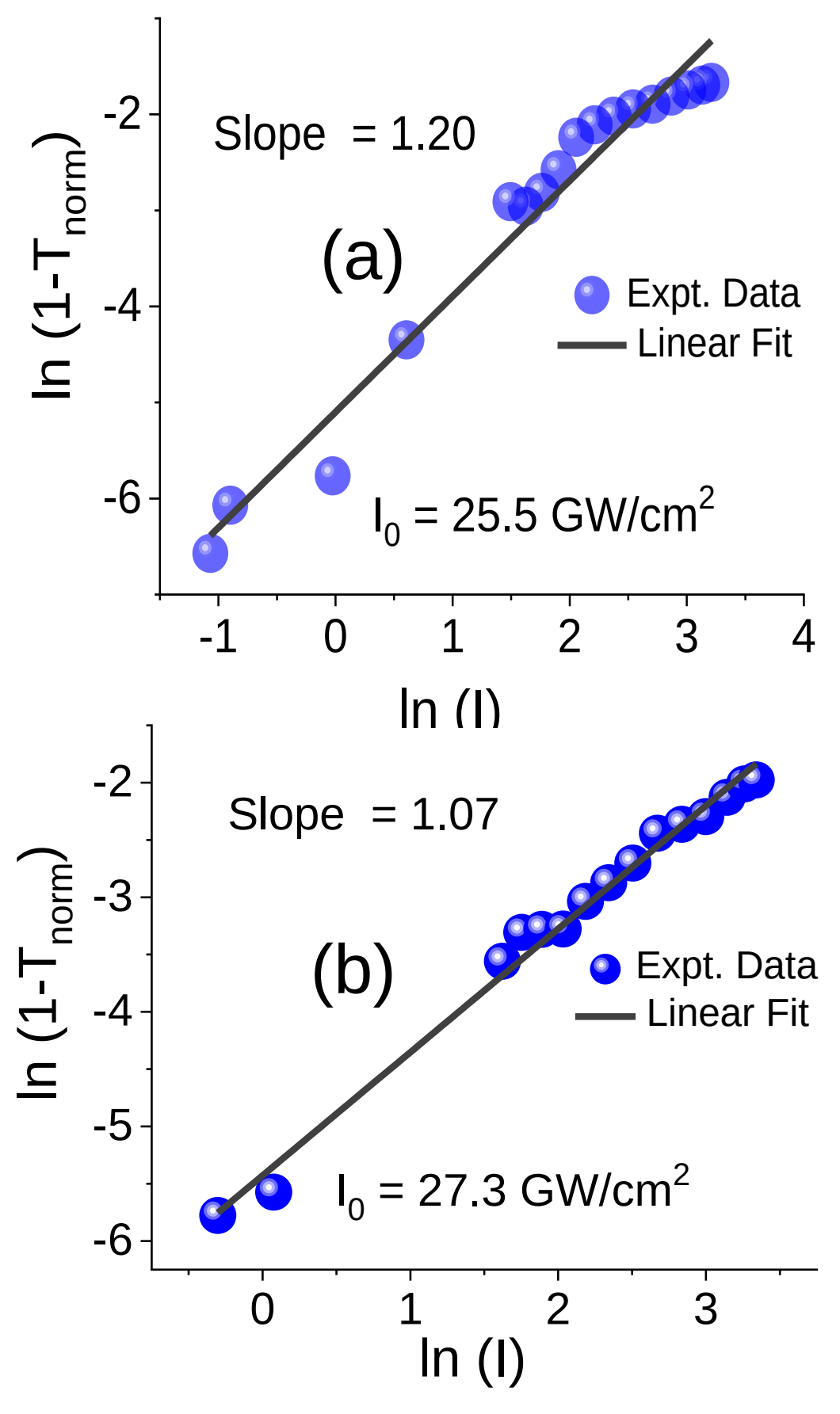

Figure 3 Two-photon absorption confirmation plots of BaTiO3 NPs under the excitations with different input peak intensities, (a) 25 GW/cm2 and (b) 27.3 GW/cm2.

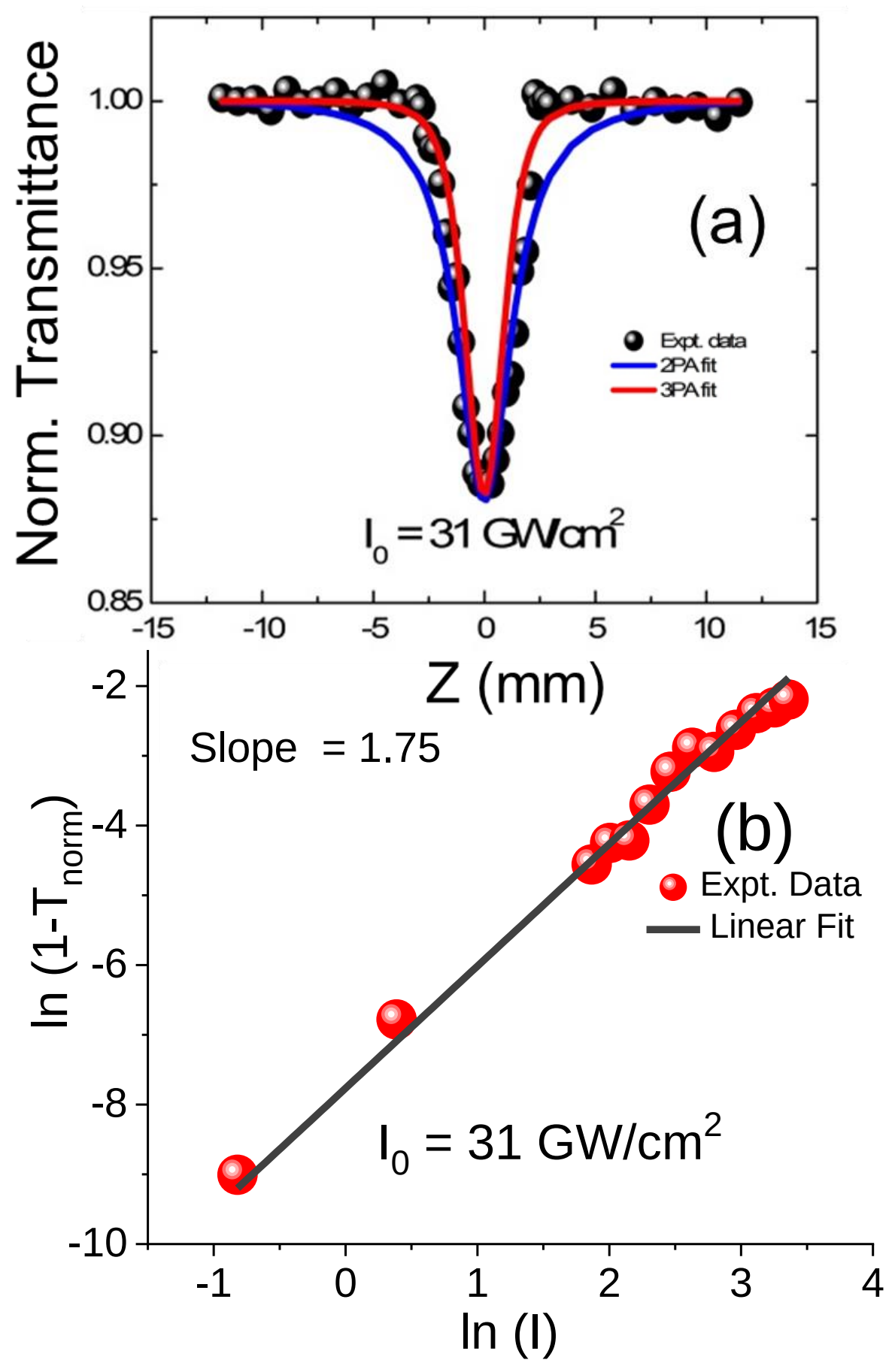

Figure 4 Three-photon absorption plot of BaTiO3 NPs under the excitations of input peak intensities, (a) 31 GW/cm2 and (b) 3PA confirmation plot

- In **Figures 2**, and 4, Z-scan data of $BaTiO_3$ NPs film clearly exhibits RSA at 800 nm We analyzed this RSA phenomenon by plotting ln (1-T_{OA}) versus excitation intensity ln (I_0), confirming the two-photon absorption (2PA) at 25.5 GW.cm^2 (figure 3 a) and 27.3 GW.cm^2 (figure 3 b) and, three photon absorption (3PA) from above 31 GW.cm^2 (figure 4 b)
- Three-photon absorption phenomena at 800 nm is attributed to the combination of two-photon absorption and excited state absorption or free carrier absorption process. The two- and three-photon absorption coefficients are estimated to be ≈400 cm/GW and ≈13 cm^3/GW^2, respectively, which are two order of magnitude larger than those of bulk crystals and lower sized $BaTiO_3$ NPs.
- In general, there could be distortion of crystal structure in the large sized NPs, which could affect NLO properties and photoluminescence. In our case, the adsorbed phosphonic acid on the surface of $BaTiO_3$ NPs could made these NPs more stable and may also offer strong bonding network to the metal oxides that leads to charge transfer effects and enhance NLO coefficients.

Spectral dependence Z-scan studies

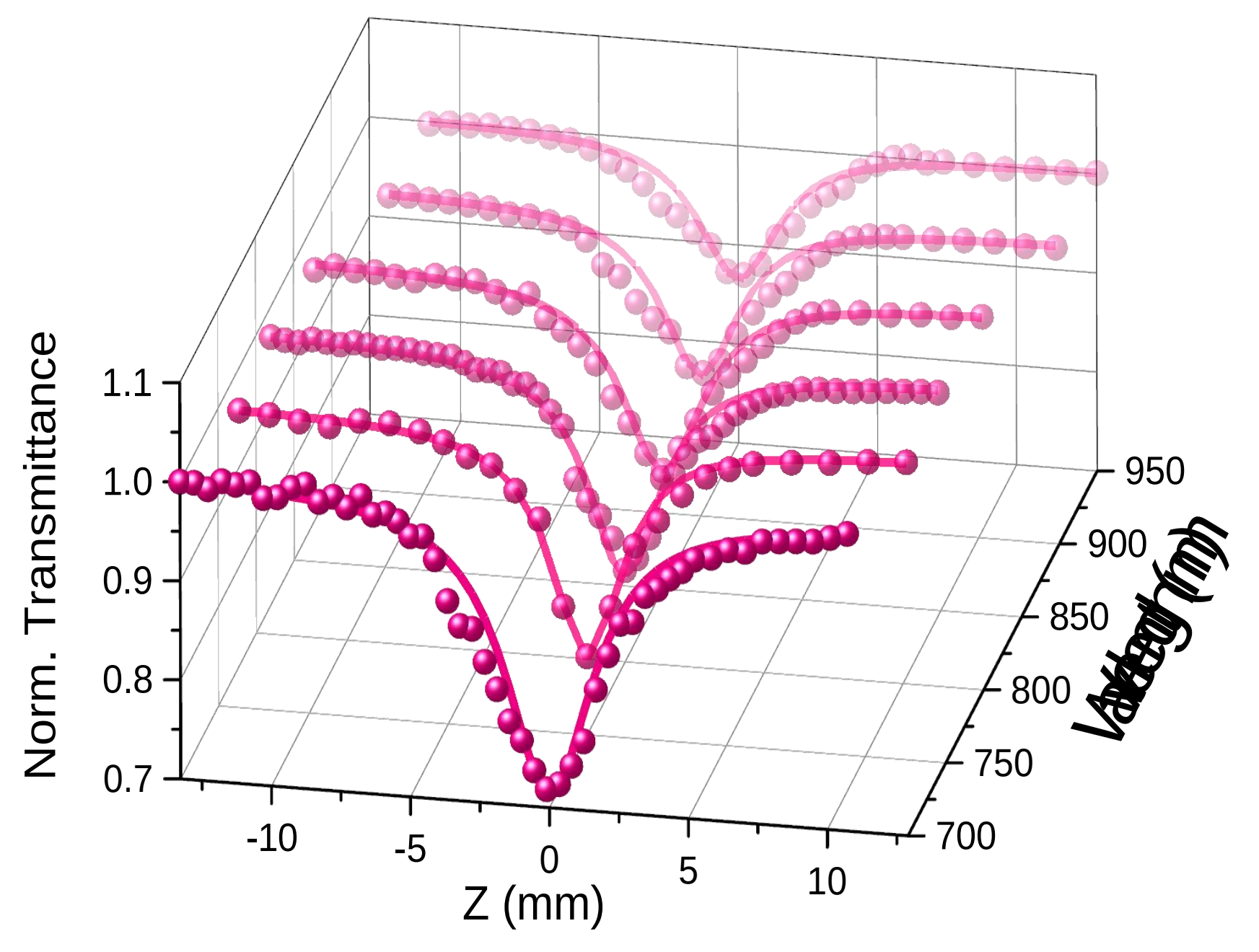

Figure 7 Wavelength dependent 2PA curves of BaTiO3 NPs measured in the spectral range of 700 nm -950 nm.

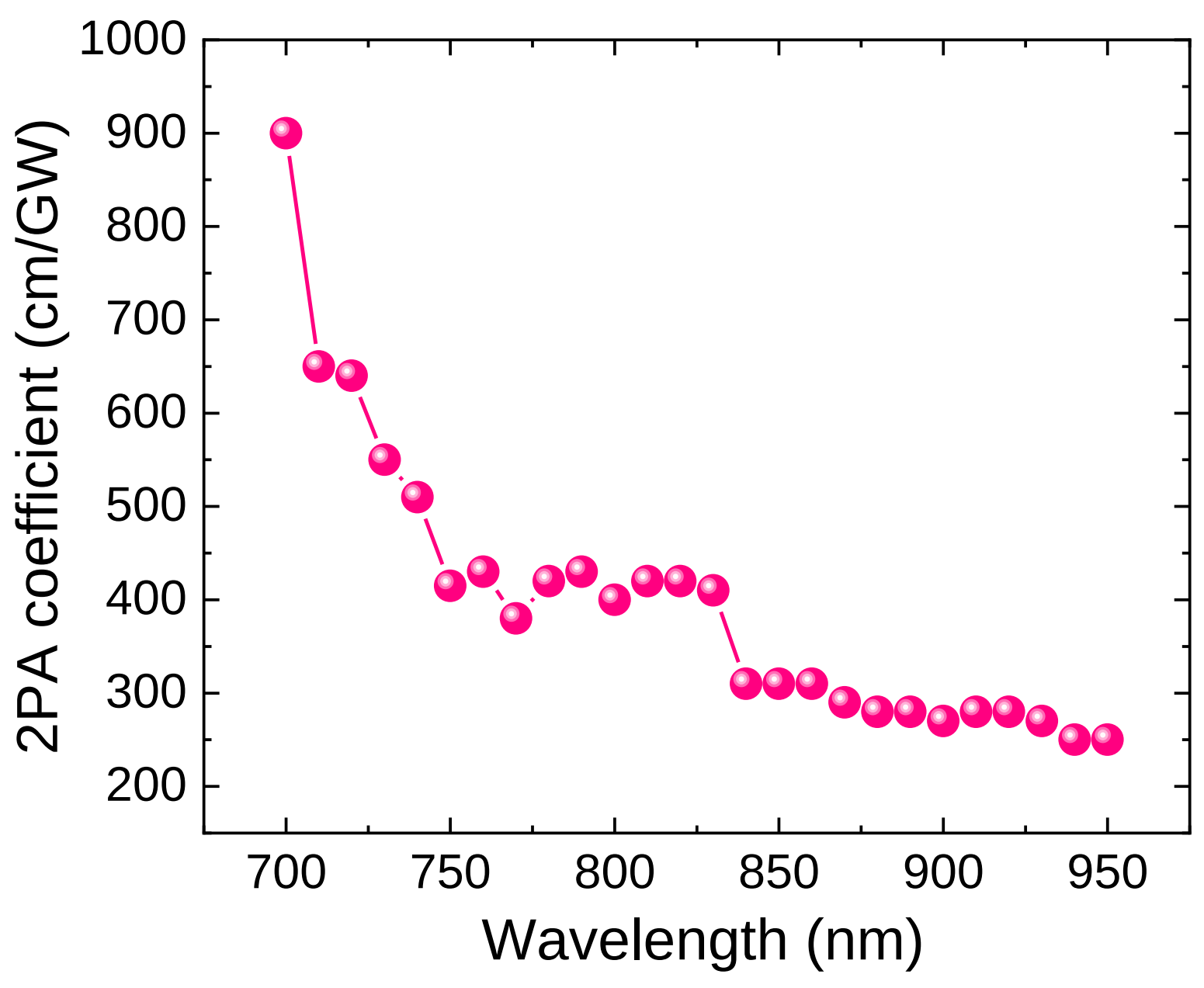

Figure 8 2PA cross-section spectra of BaTiO3 NPs.

Conclusion

- Duo to the effect of Aminomethyl phosphonic acid, the highly stable $BaTiO_3$ NPs exhibit strong and multi-stage NLO properties. A strong 2PA and 3PA coefficient were obtained with a magnitude of ≈400 cm/GW and ≈13 cm^3/GW^2 at 800 nm, which is superior to other bulk materials and smaller sized NPs
- These $BaTiO_3$ NPs exhibited a strong two-photon absorption cross-section ~10^7 GM in the 700 nm – 950 nm spectra region.
- These highly nonlinear nanomaterials may prove most beneficial as biosensors, phase conjugate nanomirrors, etc.

References

1. A. Karvounis et al, Barium Titanate Nanostructures and Thin Films for Photonics, Adv. Opt. Mater. 8, 2001249 (2020)
2. S. Wolfgang et al, Fully automated z-scan setup based on a tunable fs-oscillator, Opt. Exp. 9, 3567 (2019)
3. X. Tian et al, Reverse Saturable Absorption Induced by Phonon-Assisted Anti-Stokes Processes, 30, 1801638 (2020)