

Preparation and Third-Order Optical Nonlinearity of Self-Assembled Chitosan/CdSe–ZnS Core–Shell Quantum Dots Multilayer Films

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The self-assembled chitosan CdSe quantum dots (QDs) and chitosan CdSe–ZnS core–shell QDs films have been prepared by using layer-by-layer electrostatic technique. The well-ordered nanostructure and the layer-by-layer deposition of the QDs are revealed by AFM and exciton absorption spectra, respectively. The optical nonlinearity of the composite films were studied by using Z-scan technique with femtosecond pulses at the wavelength of 790 nm, the value of third-order susceptibility of core–shell QDs are measured to be about 1.1×10^{-8} esu, which is about 200% larger than that of CdSe QDs of 5.3×10^{-9} esu. This has potential applications in all-optical switches in optical information processing.

1. Introduction

Nonlinear optical (NLO) materials with large nonlinear optical response, ultrafast signal switching, good processability, and environmental stability are important in future high-speed telecommunication, optical data storage, and optical computing. Semiconductor quantum dots (QDs) with dimensions close to the exciton Bohr radius have received tremendous attention within recent years owing to their unique physical and chemical properties.^{1–3} The quantum confinement effects and dielectric confinement effects make QDs a promising class of third-order NLO material with large third-order nonlinear susceptibilities and fast response time. Colloid synthesis allows the fabrication of monodisperse semiconductor quantum dots with sub-10-nm size. The nonlinear refractive index and nonlinear optical absorption of a few colloidal semiconductors (PbS,⁴ CdS,⁵ CdSe,⁶ ZnS,⁷ and Fe₂O₃⁸) were estimated to be several orders of magnitude larger than those of bulk materials. A significant challenge for this kind of nanoparticle is to incorporate them into a matrix while preserving the size distribution and quantum yield. It is well-known that semiconductor doped glasses (SDG) exhibit promising NLO response. Justus et al.^{9,10} investigated the nonlinear optical properties of quantum-confined GaAs and InP nanocrystals deposited in glass, and significant enhancement of nonlinear optical response was observed. But SDG materials typically lack a desired processability. Nanoparticle/polymer composites (NCs) combining the nonlinear optical properties of QDs and flexible reprocessability of polymers have attracted interest.^{11–14} Recently, Lin et al.¹¹ have reported a large optical Kerr coefficient of -8.4×10^{-14} cm²/W for CdS NCs in poly-(methyl methacrylate) (PMMA) with femtosecond laser pulses at 815 nm. Etienne M et al.¹² reported a large third-order nonlinearity of CdS NCs embedded in dendrimer films. Capped

CdS NCs in polydiacetylene¹³ and polystyrene¹⁴ were also reported for enhanced nonlinearity in comparison with bulk materials. Problems of nanoparticle/polymer composite materials are associated with achieving high QDs filling factors, which are essential for enhancing optical nonlinearities and obtaining large gain magnitudes. To realize the large third-order NLO of QDs in a device, it is necessary to have a relatively thin, homogeneous film containing a high loading of QDs and preserve high third-order nonlinear susceptibility $\chi^{(3)}$ for subsequent device fabrication.

The layer-by-layer (LBL) self-assembly technique is used to generate ultrathin film with molecular order and stability through electrostatic interaction. By this technique, it is possible to control, in a very precise manner, the thickness, composition, and surface structure of the bilayer building block.^{15–16} Fascinated by the advantages of this method, several research groups have employed it to construct second-order optical nonlinear films.^{17–19} Recently, Li et al. fabricated (porphyrin derivative/polyethylenimine)²⁰ and (Ag–His/BH–PPV)²¹ multilayer films and measured their third-order nonlinearity by using an 8 ns pulse at 532 nm. Nanostructured films containing fullerenes²² with large third-order optical nonlinearity were also developed by using LBL technology. The researches demonstrated that the NLO films made by LBL technology have greater thermal and temporal stability than other systems. It is may be more valuable to combine inorganic nanomaterials with high optical nonlinearity (e.g., QDs) into LBL films. To date, a mount of thin films fabricated through LBL assembly QDs (CdSe, SiO₂, TiO₂, iron oxide, etc.) with polyelectrolyte have been widely applied in areas such as biosensor, biomedical devices, and light-emitting diodes.^{16,23–25} Tailoring QDs colloids with active components by LBL self-assembly will result in special chemical properties and increased filling rate of nanoparticles, which are essential to NLO devices. However, until now, little attention has been attributed to the nonlinear optical applications of QDs LBL film.

In this report, we employ CdSe–ZnS core–shell quantum dots to fabricate ultrathin multilayer films with chitosan through

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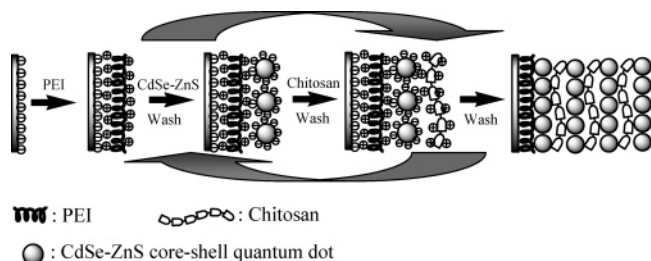


Figure 1. Schematic representation of the fabrication of multilayer film assembly of chitosan/CdSe–ZnS core–shell QDs.

LBL technology. The “bare” CdSe quantum dots and chitosan were assembled into multilayer film in the same way. Chitosan, a copolymer of (1 → 4)-2-amino-2-deoxy- β -D-glucan (GlcN) and (1 → 4)-2-acetamido-2-deoxy- β -D-glucan (GlcNAc), is the partial N-deacetylation product of chitin, which is one of the most abundant, easily obtained, and renewable natural polymers, second only to cellulose. Because of strong electrostatic repulsion between protonated amino groups, chitosan adopts an extended conformation in dilute solution. Chitosan can adsorb strongly onto a negatively charged surface, and the adsorbed chitosan layer adopts a flat conformation that provides a stable film on which charged QDs can be adsorbed. Our results indicate that the nanocomposite material has great third-order nonlinearity, well-controlled architecture, high optical stability, and high QDs filling rate, all of which make it a potential candidate of nonlinear optical device for photon communication.

2. Experimental Section

A. Sample Preparation. Nearly monodispersed CdSe QDs can be obtained according to the protocol reported by Peng.³ By using simple salt– $\text{Zn}(\text{AC})_2$ substituting $\text{Zn}(\text{NH}_3)_2$ as the precursor of Zn, highly qualified CdSe–ZnS core–shell QDs were synthesized at 200 °C.²⁶ Afterward, tri-*n*-octylphosphine oxide (TOPO) ligands were exchanged with thioglycolic acid (TGA) as in the literature²⁷ to obtain water-soluble QDs with negative charges. Chitosan with a molecular weight of 290 and degree of deacetylation of 93% was purified before being dissolved in 1% HAc at a concentration of 1 mg/ml.

Immobilization of chitosan/CdSe–ZnS core–shell QDs LBL films was performed as follows. The glass substrates were immersed in boiled piranha solution (70:30, v/v, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) for 20 min, before being thoroughly rinsed with Millipore water. Then substrates were subject to ultrasonication in distilled water. One side of the freshly cleaned substrate was masked before being functionalized with poly(ethyleneimine) (PEI) to produce a positively charged surface.²⁸ The charged substrate was alternately immersed in aqueous solutions of oppositely charged TGA-capped QDs (negative) and chitosan (positive) for 5 min. Each immersion was followed by washing with pure water and drying with a cool stream of air. This procedure is shown in Figure 1. For each cycle, a bilayer film of chitosan/QDs was formed. The UV–vis spectra of the growing layers were recorded in air after each assembly cycle. An accurate concentration of the nanoparticle solution was not known, however,

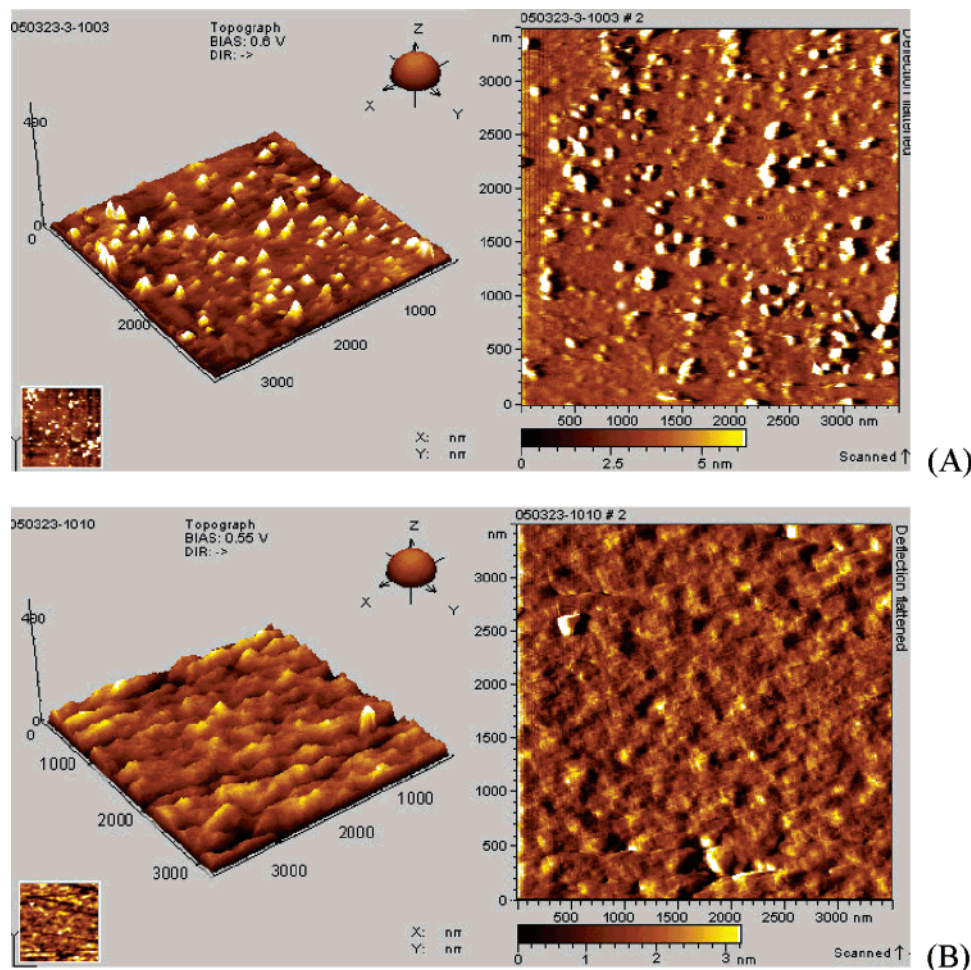


Figure 2. Tapping-mode AFM images of chitosan/CdSe–ZnS core–shell QDs films on glass slide in the 3500 nm × 3500 nm region: (A) image of top QDs layer with 6 deposition cycles and the corresponding 3D image; (B) image of chitosan layer with 1 deposition cycle and the corresponding 3D image.

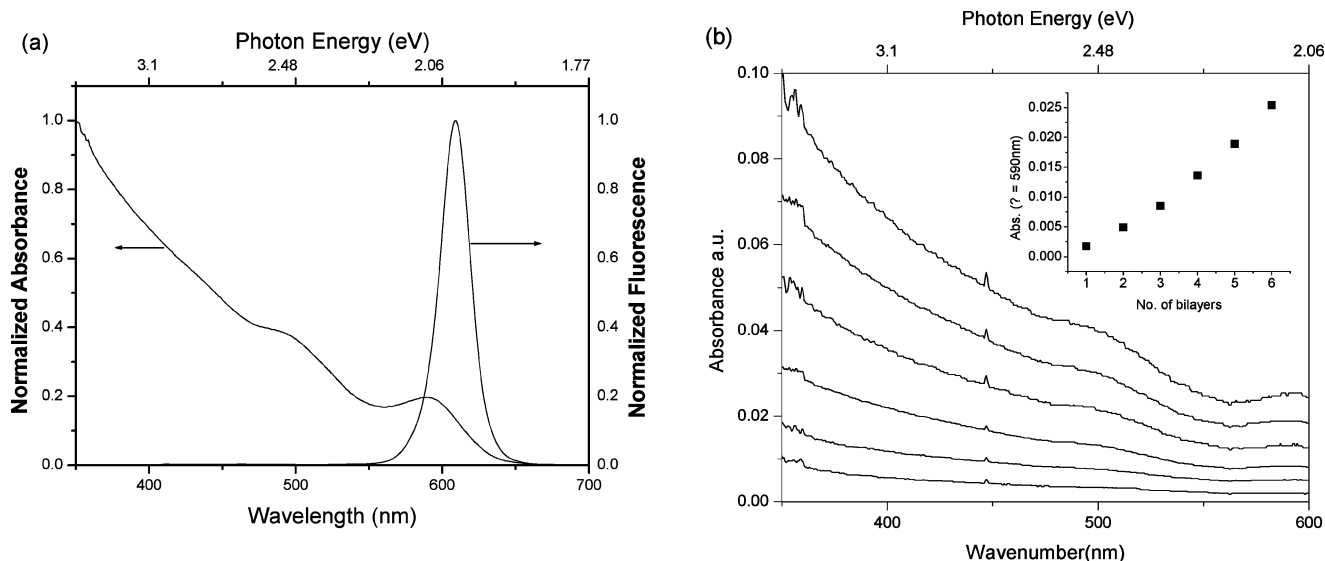


Figure 3. (a) Normalized linear absorbance and PL spectra of TGA-capped CdSe-ZnS core-shell quantum dots in solution. (b) UV-Vis spectra of chitosan/CdSe-ZnS core-shell QDs multilayer assemblies ($n = 1-6$). The inset shows the plot of absorbance at $\lambda = 590$ vs the number of bilayers.

the concentration was held constant through monitoring of the intensity of the absorption band at 590 nm.

B. Measurements. UV-Vis spectra and fluorescence spectra were recorded on a Shimadzu 1601 and a Hitachi F-4500, respectively. Thickness of films was measured by using a profilometer (Taylor Hobson Precision, Form Talysurf series 2). AFM measurements were conducted on a Picoscan AFM (Molecular Imaging Inc.) Images were acquired in "tapping mode" in air with a SiO₂ cantilever. The nonlinear absorption and nonlinear refraction of the multilayer composite film and the pure chitosan film were measured by using femtosecond Z-scan technique. The laser pulses used were generated by a mode-locked Ti:sapphire laser (Coherent, Mira 900), operating at a repetition rate of 76 MHz with a pulse duration of 150 fs and a wavelength of 790 nm.

3. Results and Discussions

A. Film Structure. The diameters of the prepared CdSe quantum dots and CdSe-ZnS quantum dots determined by TEM were 3.1 and 5.0 nm, respectively. The film thickness per bilayer (chitosan/CdSe-ZnS) obtained from several measurements in samples with different numbers of layers by using a profilometer was calculated to be around 8 nm. This is consistent with the average size of 5.0 nm for CdSe-ZnS QDs particles.

AFM images provide detailed information of the surface morphology of the film. The CdSe-ZnS nanoparticle with slight aggregation could be clearly seen in the (chitosan/CdSe-ZnS QDs)₆ film with QDs on the top layer. It should be mentioned that, for such small nanoparticles, it is difficult to determine the actual size and surface coverage because of the convolution with the tip shape.²⁹ The average height was around 5 nm, comparable to the diameter of QDs determined by TEM. Figure 2B showed the AFM image of the chitosan layer surface of (chitosan/CdSe-ZnS QDs)₁ film. The surface was smooth and the polymer grains were close packed with an average diameter of about 200 nm and height variation of about 3 nm.

B. Linear Absorption and Fluorescence Spectra. The UV-vis spectrum of CdSe-ZnS core-shell QDs in water solution is shown in Figure 3a, and the first absorbance peak at 590 nm (2.1 eV) blue-shifted with bulk CdSe ($\lambda = 678$ nm, 1.8 eV) materials is an indication of quantum confinement effect. The

fluorescence spectral band around 610 nm with 25 nm fwhm indicates a narrow size distribution.

Chitosan is transparent in the range of 350–800 nm, thus the band edge absorption of CdSe-ZnS QDs at 590 nm was a monitor of the efficiency for the LBL bilayer growth. Figure 3b shows the build-up of multilayers for chitosan LBL films alternated with CdSe-ZnS QDs, where the absorbance at 590 nm is plotted against the number of bilayers. The absorption spectra of (chitosan/CdSe-ZnS QDs) films were in agreement with that of CdSe-ZnS QDs solution, illustrating a successful incorporating of QDs into the films. The linear increase with the adsorption of bilayers suggests that equal amounts of CdSe/ZnS QDs were adsorbed after each deposition cycle, resulting in a buildup of a homogeneous film. It can be estimated that the absorbance at 590 nm increases by ca. 0.053 for each bilayer.

C. Third-Order Optical Nonlinearity. The imaginary and real parts of the third-order optical susceptibility $\chi^{(3)}$ are related to the nonlinear absorption and nonlinear refraction, which were measured by closed- and open-aperture Z-scan, respectively. The femtosecond laser pulses with low peak irradiance $I_0 = 5.5$ GW/cm² were employed in the measurements to minimize the thermal effect. The intense radiation of laser pulses can induce considerable changes of absorption and refraction in the nonlinear material. Nonlinear adsorption refers to the change in the transmittance of a material as a function of intensity or fluence. At sufficiently high intensities, the probability of a material absorbing more than one photon, before relaxing to ground state, can be greatly enhanced,⁷ which was measured by using open-aperture Z-scans. The measurement results for (chitosan/CdSe-ZnS core-shell QDs)₉ films are shown in Figure 4a, in which open circles are the experimental data and the solid lines are the fitting curve from the formula for TPA absorption:³⁰

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(1 + z^2/z_0^2)^m (1 + m)^{3/2}} \quad (1)$$

where, $q_0 = \beta I_0 L_{\text{eff}}$, β is the two-photon absorption coefficient, L_{eff} is the effective thickness of the sample, z_0 is the Rayleigh range and the peak irradiance at the waist of the Gaussian laser beam, respectively. Thus, the nonlinear absorp-

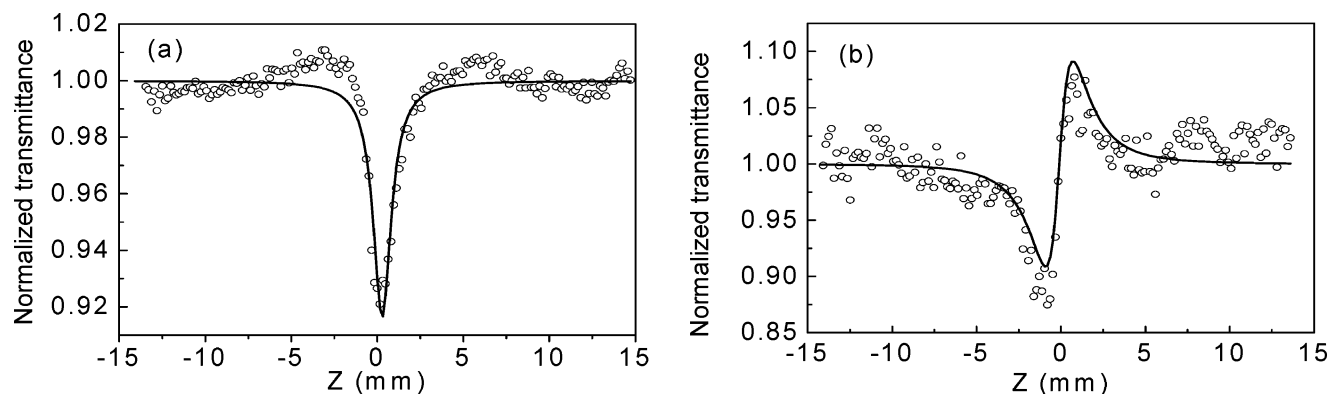


Figure 4. (a) Open aperture Z-scan in chitosan/CdSe–ZnS QDs multilayer films. (b) Closed-aperture Z-scan in chitosan/CdSe–ZnS QDs multilayer films. The open circles are measured data and the solid curves are the theoretical fits described in the text.

tion coefficient β of the multilayer film is measured to be about 6.5×10^{-8} m/W. The imaginary third-order susceptibility is calculated from the formula $\text{Im}\chi^{(3)} = n_0^2 \epsilon_0 c \lambda \beta / 2\pi$,³⁰ where n_0 is the linear refractive coefficient, ϵ_0 is the dielectric index in a vacuum, c is the speed of light in a vacuum, and λ is the wavelength of the input laser, which gives $\text{Im}\chi^{(3)} = 2.6 \times 10^{-9}$ esu for the nine-bilayer (chitosan/CdSe–ZnS core–shell QDs) sample.

By the same way, the nonlinear absorption coefficient of the nine-bilayer CdSe QDs sample was measured to be about 9.8×10^{-8} m/W, $\text{Im}\chi^{(3)} = 3.9 \times 10^{-9}$ esu. Although the nonlinear absorption coefficient is proportional to the filling factor of the QDs in the film,³¹ and the filling factor (ξ) of the CdSe–ZnS core–shell QDs is 11.8% and that of CdSe QDs is 9%, derived from linear absorption measurements, the nonlinear absorption of each CdSe–ZnS core–shell QD film is a little less than that of the CdSe QDs film. It indicates that the core–shell structure can in some degree decrease the nonlinear absorption. Notice that the nonlinear absorption of both CdSe–ZnS core–shell QDs and CdSe QDs are greatly enhanced compared to that of bulk CdSe (6.4×10^{-11} m/W).³² Reasons for the high nonlinear absorption coefficient of QDs were considered to be quantum confinement effects.

The nonlinear refraction index n_2 of the self-assembled biopolymer/QDs multilayer films were measured by closed-aperture Z-scan technique. The normalized transmittance of (chitosan/CdSe–ZnS core–shell QDs)₉ film through a closed aperture at wavelength $\lambda = 790$ nm is shown in Figure 4b. The prefocal minimum followed by a postfocal maximum indicates a positive nonlinear index of refraction. The phase shift on the optical axis ($\Delta\phi_0$) can be obtained from:³⁰

$$T = 1 + \frac{4\Delta\phi_0 Z/Z_0}{((Z/Z_0)^2 + 9)((Z/Z_0)^2 + 1)} \quad (2)$$

where $\Delta\phi_0$ relates to third-order nonlinear refractive index n_2 through the expression $\Delta\phi_0 = n_2 k I_0 L_{\text{eff}}$ and n_2 for CdSe–ZnS sample is measured to be 1.6×10^{-14} m²/W. The real third-order susceptibility $\chi^{(3)}$ is calculated from the formula $\text{Re}\chi^{(3)} = 2n_0^2 \epsilon_0 c n_2$,³⁰ and it gives $\text{Re}\chi^{(3)} = 1.0 \times 10^{-8}$ esu, thus the value of $\chi^{(3)}$ is 1.1×10^{-8} esu.

In general, both electronic (Kerr effect) and thermal effects could contribute to the n_2 in closed-aperture Z-scan method. In this experiment, the thermal effect is highly depressed by employing femtosecond laser pulses with very low irradiance ($I_0 = 5.5$ GW/cm²) and working at the transparent region of the sample. The n_2 contributed from the thermal effect is calculated to be about 1.2×10^{-19} m²/W by using J. N. Hayes's

formula,³³ which is many orders of magnitude smaller than the measured results. In addition, the nonlinear refractive index of the composite film at 790 nm was of minor changes under different input irradiation. Thus, we concluded the dominating response of nonlinear refraction of the QDs sample is the electron Kerr effect.

By using the same method, the nonlinear refractive index for the CdSe QDs film is measured to be about 5.8×10^{-15} m²/W. It should be noticed that the CdSe–ZnS core–shell QDs sample has a much larger nonlinear refractive index than that of the CdSe QDs sample. Previous study shows that the surface chemistry strongly affects the optical nonlinearity.³⁴ Overcoating the CdSe core with a wider band gap semiconducting material ZnS permits passivation of surface states and reduces the leakage of exciton outside the core. The CdSe–ZnS core–shell QDs film has a stronger controlled structure. The large third-order nonlinear susceptibility of core–shell structure maybe attributed to the localized electric field effects.

4. Conclusion

In conclusion, we fabricate a novel self-assembled chitosan/CdSe–ZnS core–shell QDs multilayer film by using LBL technology. UV–Vis and AFM images indicated that the film possesses a well-ordered nanoscopic structure. Good control over the architecture and composition of the multilayer films leads to large third-order nonlinearity. The third-order nonlinear susceptibility of nine-bilayer chitosan/CdSe–ZnS core–shell QDs film was 1.1×10^{-8} esu. The mechanism of the third-order nonlinearity of the composite film was considered to be of an electronic nature. The strategy described in this work opens a new avenue to further development of suitable materials for production of highly efficient third-order nonlinear devices that can be used in optical communication and optical information processing for, e.g., all-optical switching and optical data storage.

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