

NONLINEAR OPTICAL PROPERTIES OF HYBRID NANOSTRUCTURES

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Annotation: Hybrid nanostructures, as nanomaterials created by integrating different materials and phase states, are of great interest in the field of science and technology. Due to their combinatorial nature, these materials have unique physical and optical properties, and are especially notable for their non-exciting optical properties. Non-exciting optical properties include complex processes that determine the spectral response of materials, their ability to emit and absorb light, and their interaction with electromagnetic waves.

Keywords: Hybrid nanostructures, non-polar optical properties, nanomaterials, optical properties, electromagnetic waves, spectral response, emission and reception, photonics, optoelectronics.

Abbreviations: TY - Saturable absorption, TTY - Reverse saturable absorption, 2FY - Two-photon absorption, 3FY - Three-photon absorption, NZ - Nanoparticle, KN - Quantum dot, TN - Thionine, IR - Infrared.

We will consider the nonlinear optical properties of some organic dye solutions and quantum dots. Organic dyes were among the first to be widely used in various fields of laser physics and technology, including changing the frequency of laser radiation in dye vapors, modulating its value, and synchronizing modes in various lasers. They have become the object of studying the effect of increasing the transparency of the medium (bleaching) under the influence of pulses of different durations and laser generation, etc. The high-frequency Kerr effect, TY, and TTY are the main nonlinear optical processes arising from the interaction of high-frequency laser pulses with dye molecules.

Nonlinear optical properties were first discovered in benzene vapor (C_6H_6), as well as in acetylene vapor (C_2H_2), where the third harmonic is formed in the UV range [9]. In 1967, a general overview of the spectroscopic properties of complex molecules was given, which showed that a simple two-level scheme was not sufficient to describe the optical decolorization of dye molecules [13]. Experimental data on the transfer of intense radiation from a ruby laser to several types of dyes were presented. Analysis of the balance equations made it possible to model photobleaching curves for the dyes under study. The optical decolorization process involves the transition of molecules from the ground state to other states with smaller absorption cross sections at the excitation frequency, and the decrease in absorption at this frequency is characterized by a complex nonradiative transition mechanism. Hoffmann R.C. and other dye examples demonstrated the ability of indanthrone and its derivatives to affect the nonlinear optical properties of dyes by changing their chemical structure [14]. These dyes exhibited TTY at wavelengths of 1064 and 532 nm in the nanosecond pulse range.

Due to the high similarity of their nonlinear sensitivities with the nonlinear sensitivities of atoms, conjugated double-bonded molecules have attracted the greatest interest. The above calculations showed that some organic dyes (tetracene, paraterphenyl, pentacene) have a third-order sensitivity. In this case, the irreversible changes detected in the dye molecules in the laser pulse range lead to a change in their nonlinear optical parameters, such as saturation intensity, nonlinear absorption coefficients, etc. [10]. To analyze the complex behavior of dyes, it is

necessary to know the nonlinear optical parameters such as 2FY, TY, TTY coefficients and, in some cases, the nonlinear refractive index using different laser sources. The high-frequency Kerr effect and induced nonlinear refraction rarely play a decisive role in the formation of optical nonlinearities in dyes. However, TY is often performed in many dyes. The dynamics of the singlet-singlet ($S_1 \rightarrow S_0$) transition of dye solutions is determined by the properties of the dye and the solvent. Accordingly, the high population of dye molecules in S_n ($n > 2$) opens the path of decomposition to the triplet state and photodissociation in the S_1 and S_0 states [11]. Photobleaching of dyes often occurs through intermediate states with the TY mechanism.

The initial process leading to the formation of a total nonlinear optical phenomenon in dye molecules is absorption. The process of absorption of light quanta leads to a change in the population of the ground and excited states and, as a result, to a change in the instantaneous absorption spectrum. Thus, important information about the change in the absorption of dye molecules can be obtained from the absorption spectra induced by the flash photolysis method. Since the objects of study in this work are high-performance dyes, and thiazine and xanthene dyes serve as model objects, let us consider the currently available experimental data on induced absorption for them.

Thiotinine molecules are characterized by a clearing in the range of 510-630 nm (Fig. 1). Experimental data on the study of nonlinear optical properties, as well as induced absorption spectra for other thiazine dyes (azure A, azure B, azure C, etc.) were not found in the literature. The paper presents the results of the study of induced absorption of Ery aqueous solution. With zero time delay between the source pulse and the test pulse, a strong illumination of the absorption band occurs, associated with the $S_0 \rightarrow S_1$ transitions. The observed decrease in optical density is interpreted as a superposition of two processes: saturated absorption $S_0 \rightarrow S_1$ and forced emission in the S_1 state.

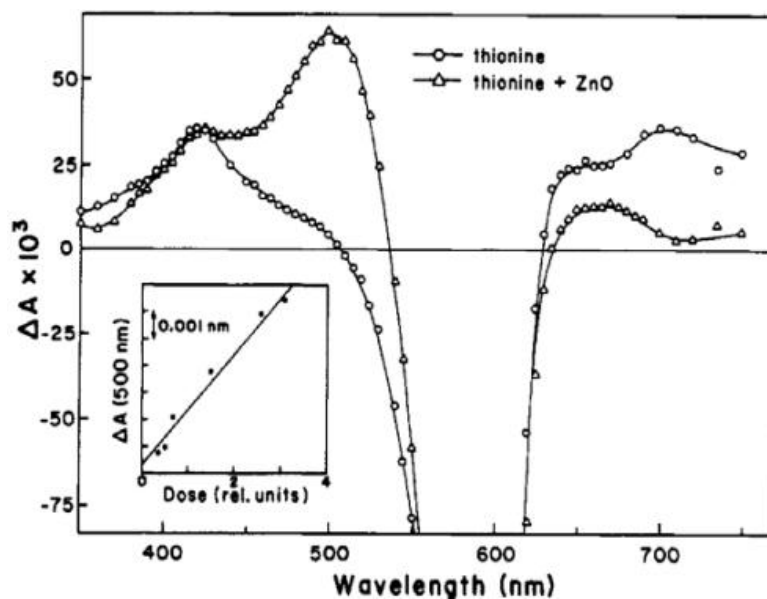


Figure 1-
absorption

shows the induced spectra (pulse duration 6 ns) of a TN (2.5×10^{-5} M) ethanol solution recorded after excitation with a pulsed laser at a wavelength of 532 nm [1]. As can be seen from Figure 2, a broad spectrum of induced absorption appears for wavelengths greater than 550 nm. The maximum optical density of the induced absorption is 0.05. This absorption does not decrease significantly until a delay time of 1.5 ns.

It was concluded that the observed absorption is due to triplet-triplet transitions. The rapid occurrence of triplet-triplet absorption indicates efficient interspin conversion. At shorter wavelengths around 460 nm, the additional absorption band rapidly disappears simultaneously with the stimulated emission at longer delay times, due to singlet-singlet transitions from the S1 excited state. Thus, the characteristic optical nonlinearity expected at the wavelength of the second harmonic of the neodymium laser (532 nm) for Er is TY.

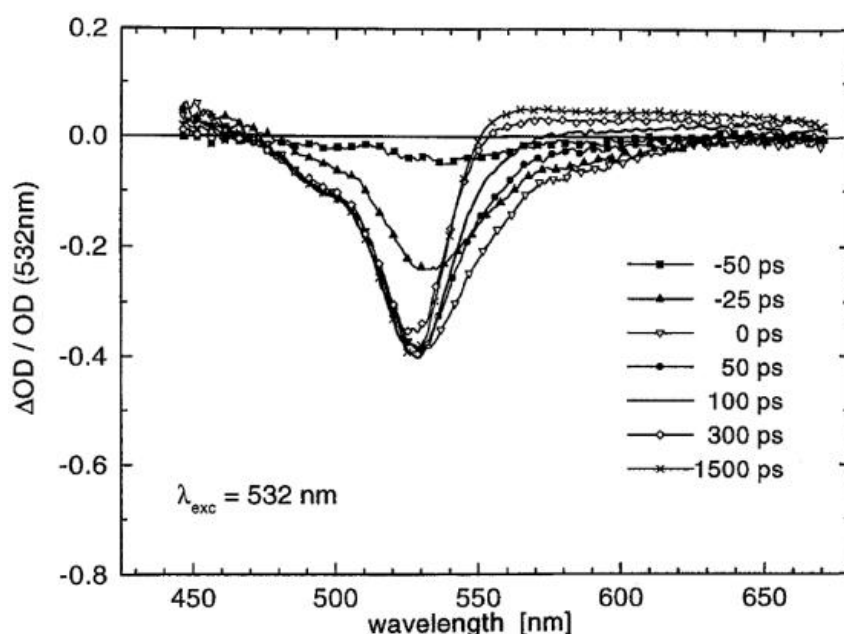


Figure 2 - Induced absorption spectra of an aqueous solution of Ery.

Previously, nonlinear optical effects of absorption in Ery were analyzed using pulsed laser thermal lens spectrometry of this solution [12]. It should be noted that photothermal spectroscopy is an indirect method for measuring nonlinear absorption. In this work, the laser source was a He-Ne laser, which did not allow us to analyze short-term nonlinear optical absorption processes.

The Z-scanning technique is widely used to determine the nonlinear optical parameters of some dyes. Such studies are not available for Ery molecules. However, they have been performed for other dyes. This method was used to find nonlinear absorption, refraction, and optical power limitation for a neutral red organic dye in the field of 532 nm nanosecond laser pulses [2].

Modeling the mechanisms of nonlinear optical response can be done by taking into account certain literature data on the absorption cross sections of singlet and triplet transitions, as well as the lifetimes of excited states. Similar studies have been conducted for dyes of the phthalocyanine series. The authors have shown the possibility of controlling the degree of induced absorption by modifying dyes with metal-coordinated complexes of phthalocyanines using molecular engineering methods.

The next important objects of great interest in nonlinear optical properties are hybrid organic-inorganic nanostructures. The components of such structures can be organic dyes, semiconductor nanocrystals, plasmonic nanocrystals (nanoparticles), etc. The new properties of such compounds are most clearly manifested in the vicinity of optical resonances of plasmonic

nanocrystals, dye luminescence edges and semiconductor nanocrystals [5]. The laws that show the manifestation of the interaction of the components of hybrid associations in the nonlinear optical properties are of great interest due to various practical applications.

The authors of the literature observed a change in the nonlinear optical result in hybrid associations of attenuated graphene oxide and Au nanocrystals grown on its surface (Fig. 3). Thus, in these structures, upon pulsed laser irradiation (5 ns) at a wavelength of 532 nm, the nonlinear optical response of cTY to TTY components changes upon coupling. According to the authors, the nonlinear optical effect is due to charge transfer from the nanoparticles to the reduced graphene oxide film.

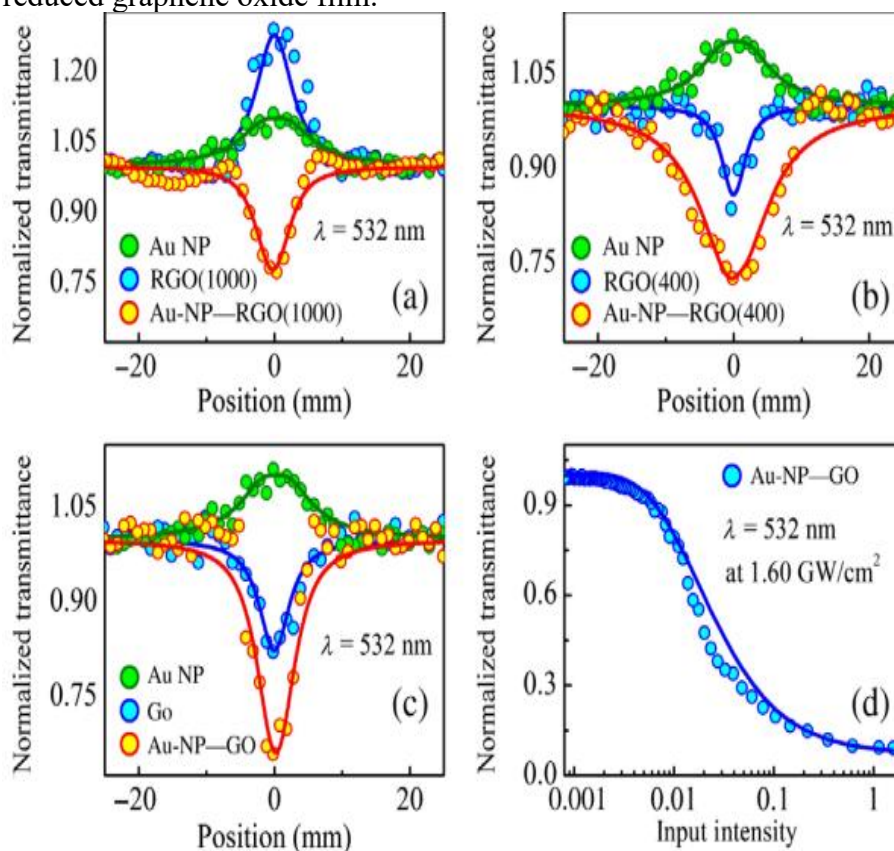


Figure 3 - The change of the nonlinear optical response of RGO and Au NZ from TY to TTY during hybrid association in the field of nanosecond pulses at a wavelength of 532 nm [3].

The most discussed situation is related to the analysis of the nonlinear optical effect in the associations of silver and gold NZ with dyes. The associations of metal NZ with molecules of Phenothiazine, Methylene Blue, Uranium, Radomin 6J, betacyanin, etc. are considered.

For molecules with gold NZ, a decrease in the threshold for the onset of TTY and an increase in nonlinear refractive indices were found for methylene blue molecules under the influence of continuous radiation from a diode solid-state laser with a wavelength of 532 nm and a power of 50 mW. In this work, a self-focusing of a thermal nature was observed using the Z-scanning technique. The observed nonlinear absorption was associated with TTY in MV molecules.

The asymmetric decrease in the Z-scan characteristic of Au NZ was associated with TTY, which raises some doubts, especially since the contribution of the nonlinear optical response of dynamic light scattering to the observed picture was not taken into account. In addition, in the

discussion of the results of the work, the possible influence of the process of exchange of electronic excitations between the components of the assemblies is indicated. Thus, despite the significant changes in the nonlinear optical response accompanying the formation of hybrid associations, the observed nonlinear mechanisms remain largely speculative.

An increase in the power threshold of nanosecond (7 ns) laser pulses with a wavelength of 532 nm was obtained by mixing phenothiazine with plasmonic gold nanoparticles (Fig. 4) [6]. A photophysical method was used to synthesize hybrid nanostructures from Au NZ and phenothiazine molecules with an average size of 28 nm. The resulting composite showed a significant decrease in photoluminescence intensity, which the authors attributed to electron/energy phototransfer between the components. The increase in depth in the Z-scan of the composite compared to the original components is explained by the field effect and the exchange of electronic excitations.

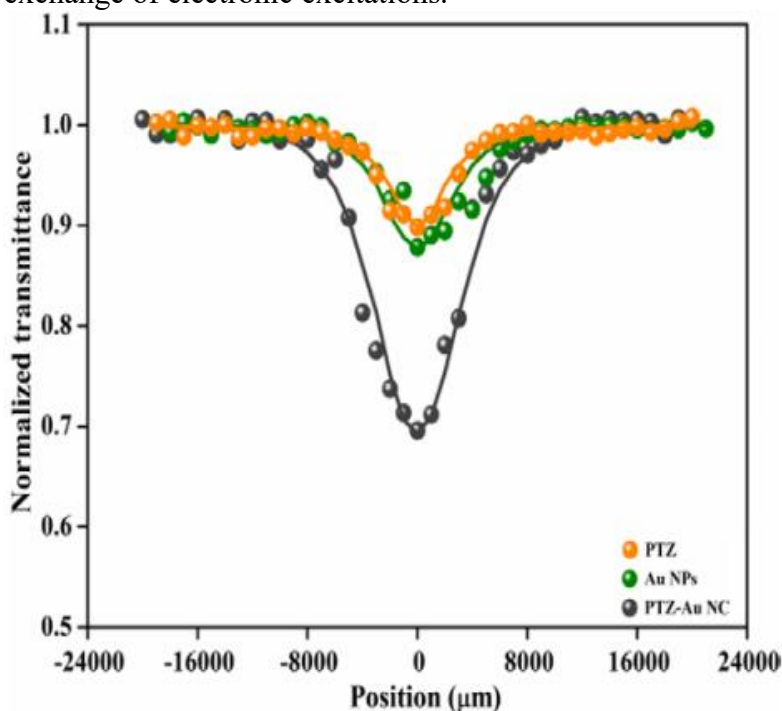


Figure 4 - Nonlinear absorption enhancement during the association of phenothiazine and gold nanoparticles in the region of nanosecond pulses at a wavelength of 532 nm.

The work [7] demonstrates the Rabi splitting and Fano effect in the absorption spectrum of the IR-806 laser dye associated with gold nanocylinders. The authors attribute these effects to the manifestation of plexitonic coupling. For such a hybrid association, an increase in nonlinear absorption at a wavelength of 532 nm was found.

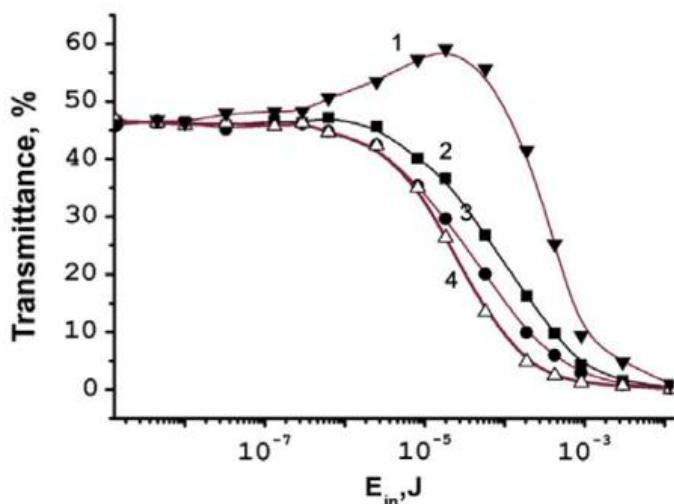


Figure 5 - Dependence of solution transmittance on radiation energy at $\lambda= 532$ nm. 1: KN CdSe/ZnS; 2: 0.75C60+0.25CT; 3: C60; 4: 0.75C60+0.25KN+perylene. According to [4].

Non-stationary absorption spectroscopy was used to study the nonlinear optical process of resonance-coupled systems of Ag NZ organic dyes (Uranine, Rhodamine 6Zh). It was found that silver nanoparticles coated with dye molecules exhibit the Fano effect in the extinction spectra, and at the same time, the nonlinear absorption coefficient and nonlinear changes increase compared to the original Ag NZ [8]. The scope of studies for KN-based associations is very small. Of interest is the work discussing the observed decrease in the optical power limiting threshold of laser radiation at a wavelength of 532 nm in the hybrid association of CdSe/ZnS QDs (average size 3.4 nm) with C60 fullerene and perylene molecules [4]. The association of these materials leads to photoinduced electron transfer and charge separation in the QD, which in turn contributes to the optical power limiting (Fig. 5).

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