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Enhanced optical limiting performance in phthalocyanine-quantum dot nanocomposites by free-carrier absorption mechanism

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ABSTRACT

Enhanced nonlinear optical properties (in dimethyl sulphoxide) is observed for 2(3),9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium(III) chloride (InPc) when covalently linked to CdSe/ZnS or CdSe quantum dots (QDs). The experimental nonlinear optical parameters were obtained from Z-Scan measurements. Contributions from two-photon absorption (2PA) due to the InPc, and free-carrier absorption (FCA) by QDS have been identified as the main factors responsible for the enhanced optical limiting. The effective nonlinear absorption coefficient for InPc-CdSe/ZnS was found to be 700.0 cm/GW. The FCA cross-sections for InPc-CdSe/ZnS and InPc-CdSe composites were found to be 1.52×10^{-19} and 6.00×10^{-20} cm^2 respectively. A much lower limiting threshold of 92 mJ cm^{-2} was observed for InPc-CdSe/ZnS nanocomposite, hence, making it suitable for use as optical limiting material. Density Functional Theory (DFT) calculations on similar phthalocyanine-quantum dots system was modeled in order to explain the enhancement in the observed nonlinear optical properties of the Pc in the presence of the QDs. The experimentally determined nonlinear optical properties are well within the range of the DFT calculated properties.

1. Introduction

An ideal optical limiter is a device that exhibits a linear transmittance below a threshold, and clamps the output to a constant above it; thus providing protection to sensors and the eyes [1]. A wide range of materials with strong nonlinear optical (NLO) properties contributing to optical limiting (OL) have been investigated [2,3]. Most of the materials reported were shown to perform their OL functions via a two-photon (2PA) or multiphoton (*n*PA) reverse saturable absorption (RSA), excited state absorption (ESA), nonlinear light scattering (NLS), nonlinear refraction (NLR) or free-carrier absorption (FCA) mechanisms [2–5]. Usually, the investigated materials have displayed more than one of these NLO processes [2,5]. Researchers over the years have devised means of blending two or more materials with the intent of developing an efficient optical limiter. However, previous attempts in this regard, have focused mostly on the functionalization of carbon nanostructures with either porphyrins, phthalocyanines (Pcs) or other highly aromatic organic chromophores [6–8].

In recent years, the optical limiting behavior of various types of semiconductor quantum dots (QDs) has become a subject of interest [9]. Phthalocyanines on the other hand are known to exhibit good OL behavior with large nonlinear absorption coefficients (β_{eff}) [10–13]. In spite of the advantages abound in these two materials, it is surprising to know that research on the use of phthalocyanine-quantum dot nanocomposites for OL applications is still relatively scarce. Britton et al. reported on the OL behavior of some selected metallophthalocyanines (MPcs) in the presence of CdTe QDs without covalent linkage [14]. It should be mentioned that Pc-QDs composites obtained via a covalent interaction are known [15]. However to the best of our knowledge, such nanocomposite materials have not been studied before for OL applications. It is thus expected that the combination of these two materials: Pcs and QDs, will yield materials with enhanced NLO properties.

Among the underlining mechanisms for NLO processes, 2PA, FCA and NLS have been particularly identified as the major processes contributing to the OL behavior of semiconductor nanoparticles [1,16,17]. Since QDs fluoresce upon excitation by one-photon absorption in the visible spectral range, and two-photon absorption in the IR spectral range [17], it is expected that at 532 nm, the contribution of QDs to OL via a 2PA would be negligible. However for Pcs, the wavelengths for 2PA include 532 nm, the region with negligible linear absorption and reasonably strong triplet–triplet absorption [18,19]. FCA on the other hand is usually produced when excitation takes place at the wavelengths where there is linear absorption [16]. FCA may be attributed to the excited-state absorption of electrons in the conduction band, and holes in the

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