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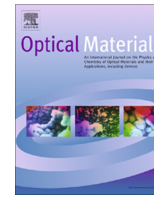

Indium phthalocyanine–CdSe/ZnS quantum dots nanocomposites showing size dependent and near ideal optical limiting behaviour

Kayode Sanusi, Tebello Nyokong *

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

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Indium phthalocyanine–CdSe/ZnS quantum dots (QDs) nanocomposites (InPc–CdSe/ZnS) of three sizes (5.57, 8.12 and 8.75 nm) were synthesized according to known procedures. The particle size of the CdSe/ZnS QDs alone are 3.95, 6.02, and 6.66 nm, and are denoted as QD1, QD2 and QD3 respectively. The nonlinear absorption (NLA) properties of the nanoconjugates (InPc–CdSe/ZnS) were investigated with nanosecond laser radiation at 532 nm wavelength. Enhanced NLA properties compared to the InPc alone were observed in the conjugates. The NLA was found to increase with the size of the CdSe/ZnS particles attached to the phthalocyanine. The observed increase was due to the availability of more free-carrier ions in the larger QDs, thus giving rise to the enhanced free-carrier absorption. The measured free-carrier absorption cross-sections (σ_{FCA}) are 1.10, 1.65 and 1.95 ($\times 10^{-19}$ cm^2) for InPc-QD1, InPc-QD2 and InPc-QD3 respectively. The nanoconjugates (InPc–CdSe/ZnS) showed a much lower threshold for optical limiting together with a much lower transmission at high fluences, than the previously reported nanocomposite limiters.

1. Introduction

Hazards associated with indiscriminate use of laser devices have been shown to be preventable by employing passive optical power limiting materials developed from basic organic and/or inorganic molecules [1–5]. Among the many materials that have been screened purposely for optical limiting (OL) applications, phthalocyanine (Pc) derivatives appear to be the most attractive due to their characteristic large third-order nonlinear susceptibility values ($I_m[\chi^{(3)}]$), ease of preparation and purification and ease of molecular structure modification [6–8]. On the other hand, research on semiconductor quantum dots (QDs) for possible applications in OL has over the last two decades been a subject of extensive investigation [9–11]. It is worthy of note that the covalent combination of these two materials, Pcs and QDs, for optical limiting application has received very little attention.

We have reported on enhanced nonlinear optical behaviour of phthalocyanines when mixed (not chemically linked) with quantum dots [12] and the effect of sizes was not explored. Also the QDs employed in Ref. [12] were core rather than core shell. Surface defects have been shown to reduce fluorescence emission of QDs [13–15], and have been minimized by coating the core with an extra layer of semiconductor nanoparticle such as ZnS to form a shell [16], or in some cases several layers to form multiple shells around the core [17]. In the current work, three different sizes of CdSe/ZnS QDs have been synthesized, and linked covalently to InPc (Scheme 1). The QDs are referred to here as QD1 (3.95 nm), QD2 (6.02 nm) and QD3 (6.66 nm), according to their particle sizes. The absorbance of different sizes of QDs at 532 nm will differ; hence their contribution to free-carrier absorption (FCA) will differ. An ideal optical limiter should show a transmitted versus input intensity curve that starts to deviate from the linear transmission at low intensities and becomes completely flat at some input intensity as will be shown in this work. The OL properties of the synthesized nanocomposites were studied using the Z-scan technique.

Most of the materials reported in literature were shown to perform their OL functions via two-photon absorption (2PA), multi-photon absorption (nPA), reverse saturable absorption (RSA), excited state absorption (ESA), nonlinear light scattering (NLS), nonlinear refraction (NLR) or FCA mechanisms [18]. Since QDs fluoresce upon excitation by one-photon absorption in the visible spectral range, and two-photon absorption in the IR spectral range [19], 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 [20,21]. FCA on

* Corresponding author. Tel.: +27 46 603 8801; fax: +27 46 622 5109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

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