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Investigations of intensity dependant nonlinear optical properties of betanin/ZnO composites embedded in PVA

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ABSTRACT

In this report, we report the intensity dependant nonlinear absorption properties of bio-inspired hybrid materials (betanin-ZnO) embedded in polymeric matrices through the Z-scan technique using an Nd: YAG laser (532 nm, 7 ns, 10 Hz). We observed a change over in the sign of nonlinearity due to the interplay of exciton bleaching and optical limiting mechanisms. Light confinement effect and ship-in-a bottle effect play crucial roles. Theoretical analysis has been performed using a model based on nonlinear absorption coefficient and saturation intensity. The result of present study gives an additional mechanism for the gain enhancement in dye doped ZnO matrix.

1. Introduction

As we know, a great variety of low dimensional-related studies hold many researchers' interest and attention because of their amazing non-linear optical properties and their possible applications in many fields mainly in DSSC. The need for nonlinear optical materials for applications such as phase conjugation, image processing, optical switching, and optical limiting are increasingly becomes important. Recently, a large number of organic π-conjugated molecules have been investigated due to their large nonlinear optical susceptibility and the possibility of tailoring their properties, which allow these materials to be used to protect optical detection elements such as human eyes and optical sensors, by controlling the fluency on the image plane below the desired level. The outcome of such studies has helped to establish certain guidelines for molecular design of the third-order nonlinear optical materials with desired properties [1]. In general, an optimal nonlinear optical (NLO) material for optical limiting has a low loss, a high nonlinearity, high damage threshold, ease of processing and a broadband spectral response.

One approach to the design of technologically important class of oxide materials is the incorporation of the natural organic molecules to modify inorganic nano/microstructures. In this instance, the inorganic oxide contributes to the enlarged functionality by the structure-function relationship of hybrids and which exhibits an interface where there is a synergistic interaction between the organic and inorganic components. These organic–inorganic frameworks are particularly attractive from several perspectives such as they possess a remarkable chemical and structural diversity. It has influence on the bio-mineralization, hydrogen bonding, and hydrophilic-hydrophobic interactions. The ability to connect the functionalities to the material expands the scope of the science significantly. The chemistry of such nanocomposites depends mainly on their reactivity and structural relationship. Their development is especially trendy and has received a great deal of attention not only because of their potential in industrial applications but also from their fundamental point of view.

Such hybrid materials synthesized through green materials will generate increasing numbers of smart microelectronics, micro-optical and photonic components and systems and novel generations of photovoltaic. The term green materials generally stands for substances made from sustainable or recyclable items that do not exhaust the natural resources and are also non-toxic, eco-friendly and safer alternatives for human life. These hybrid materials also can provide promising applications in optics, electronics, ionics, mechanics, membranes, functional and protective coatings, catalysis, sensors and biology [2–4].

The organic–inorganic composites offer tremendous opportunities in material engineering to produce suitable materials with wonderful tailored physical properties. Sufficient attention has not been paid towards the proper utilization of their capabilities in photonic device applications. Thus, there exists a pressing need to develop novel optical materials, for which a deep insight into the optical processes is essential. By intercalating dye molecules which

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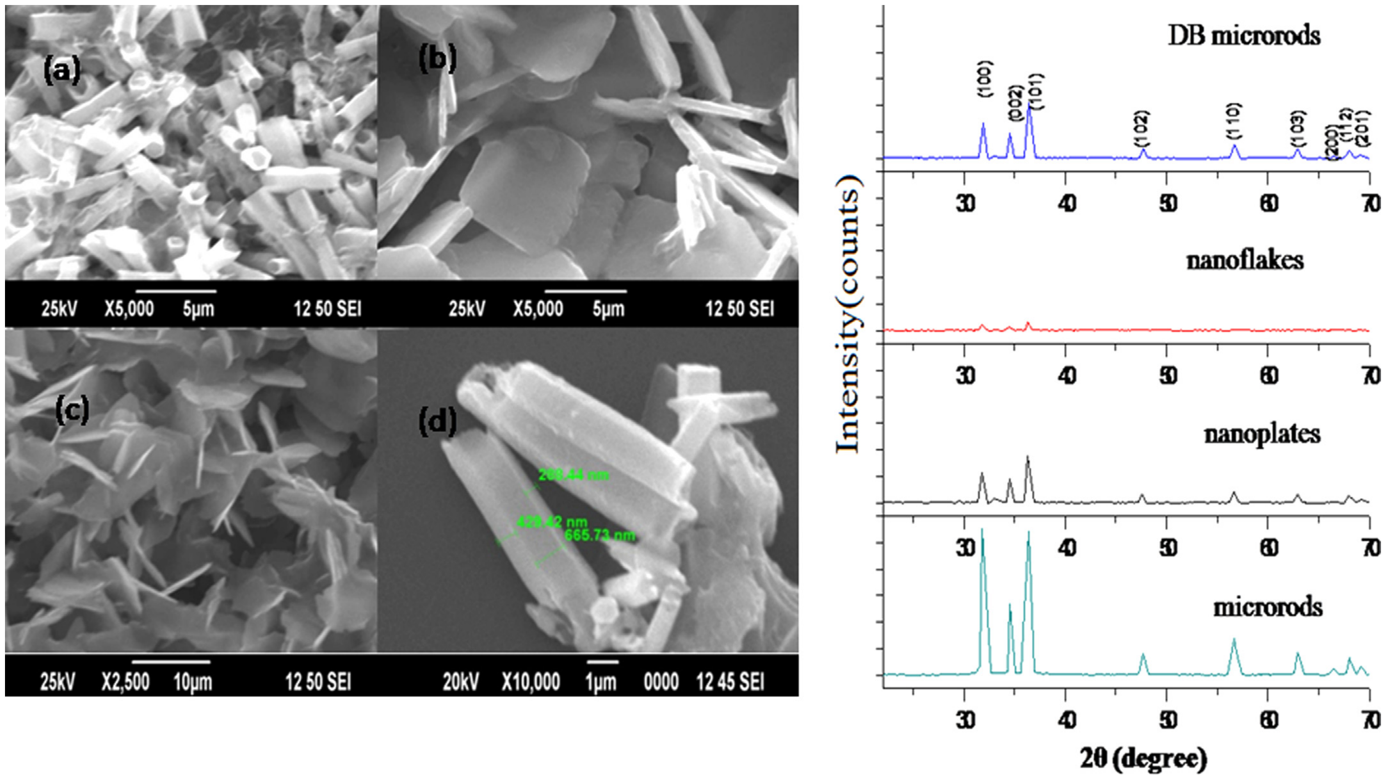

Fig. 1. SEM images of ZnO crystals (a) DB microrods (b) nanoflakes (c) nanoplates and (d) microrods; and their corresponding XRD pattern.

exhibit strong nonlinear absorption, Canva et al. have also demonstrated the usefulness of these films towards true 3D displays [5]. However, most of the synthesized materials require elaborate preparation procedures and safety measures, use or generation of hazardous materials, costly materials. Therefore, we suggest natural dye extracts as environment friendly, safe, and inexpensive materials, as well as having high chemical stability during optical excitations with coherent light sources.

The present work is an attempt to design and characterize efficient optical materials embedded in a PVA matrix and the effect of betanin natural dye on their non-linear optical properties of ZnO crystals will be discussed using open aperture (OA) Z-scan technique. Also, we are presenting some of our findings and suggestions. It is well known that ZnO is a promising material for these applications because of its large room temperature band gap of 3.37 eV and also the fact that the exciton binding energy of 60 meV should ensure excitonic survival well above room temperature [6]. Therefore it is a suitable candidate for ultraviolet optoelectronic applications.

However, most of the synthesized materials require elaborate preparation procedures and safety measures, use or generation of hazardous materials, costly materials, as well as fragile or chemically unstable structures beyond certain threshold irradiance. Therefore, we suggest natural dye extracts as environment friendly, safe, and inexpensive materials, as well as having high chemical stability during optical excitations with coherent light sources. The betalain pigments are water soluble and nitrogen containing pigments is relatively stable over the broad pH range from 3 to 7 [7] have several applications in foods such as deserts, dry mixes and dairy, comprise the red–purple betacyanin, betanin (I) and betanidin (II), with maximum absorptivity at λ_{max} about 535 nm, and the yellow betaxanthins with λ_{max} near 480 nm[8].

The basic absorption processes in dyes can be divided into linear and nonlinear absorption. Nonlinear absorption is a phenomenon defined as a nonlinear change (increase or decrease) in absorption with increasing intensity. This can be of either two types: saturable absorption (SA) and reverse saturable absorption (RSA). These properties are commonly defined in terms of intensity dependant non-linear absorption coefficient α (I), which can be written in terms of linear absorption coefficient α and two photon absorption coefficient β as

$$\propto(I)= \propto +\beta I \quad (1)$$

With increasing intensity, if the excited states show saturation owing to their long lifetimes, the transmission will show SA characteristics. If, however, the excited state has strong absorption compared with that of the ground state, the transmission will show RSA characteristics.

2. Experimental method

All chemicals were purchased from Merck Ltd. used as received without further purification. The nutrient solution was prepared from an aqueous solution of zinc nitrate hexahydrate [Zn $(NO3)_2 6\,H_2O$] and hexamethylenetetramine (HMTA) [$(CH_2)_6N_4$] heated at 80 °C. Different morphologies are obtained from different growth duration [9]. The ZnO dumb bell microrods: PVA (ZnO 1), ZnO nanoflakes: PVA (ZnO 2), ZnO microrods: PVA (ZnO 3) were prepared for the z scan measurements; using aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 6H_2O$) and hexamethylenetetramine (HMTA)($(CH_2)_6N_4$) [9]. The extracts of the red beets were obtained from fresh biological materials, pigments can be water extracted and slight acidification of the extraction medium enhances the betacyanin stability and avoids oxidation. The pigment extracts must be protected from direct light exposure should be kept in cool place. Dye extracts have been optically characterized by measuring maximum absorptivity at about 535 nm is attributable to betanin [10].

To determine third order nonlinear optical characteristics of samples such as nonlinear absorption, the single beam z scan