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Dynamic orientational photorefractive gratings observed in CdSe/CdS nanorods imbedded in liquid crystal cells

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ABSTRACT

A novel type of orientational photorefractive device, which consists of liquid crystals and semiconductor nanorods synthesized in our lab with a new seeded type growth approach has been designed and fabricated. The device has a symmetric layered structure, formed by a glass substrate, an indium-tin-oxide electrode (ITO), an HTAB aligning layer, a CdSe/CdS nanorods photoconductive layer, a NLCs film. In order to study the photorefractive and the orientational responses of this device we employed asymmetric two-beam coupling (TBC) to measure two-beam coupling gain under the influence of an applied electric field.

A refractive index grating was written in the device in a holographic tilted configuration by two p-polarized laser beams at 514 nm. Self-diffraction of the writing beams and diffraction of a probe beam at 633 nm were measured. Our device revealed a very useful behavior in that the grating written in the sample is stable as opposed to the one without nanorods inclusion and it showed strong beam coupling effects. A very high TBC gain coefficient of over 350 cm^{-1} was achieved at a dc field applied of 3 V/μm. These results open up new possible applications for real-time image/signal-processing.

1. Introduction

Photorefractive (PR) effects have been observed in various inorganic and organic materials [1–26]. As they have been proven to be very useful for optical signal/image processing applications with power light extending from the visible to the near infrared, the search for more efficient materials continues rapidly. Nematic liquid crystals (NLCs) are a promising class of photorefractive materials because of their unique physical characteristics. Their fluid-like nature facilitates their integration in films, waveguides, fibers, etc., while their liquid crystalline characteristics allow their optical properties to be easily modified by low power lasers and/or other applied fields [6,27–29]. The grating generation mechanism is similar to the processes occurring in photorefractive crystals and the effects are named "orientational photorefractive effects" (OPR) of NLCs in the mesophase by Khoo et al. [4]. Since then, several LCs-based photorefractive (PR) materials have been reported [5–7,9–20,24–26]. Khoo et al. [12] also presented the basic mechanisms for photo-induced space-charge field formation, director axis reorientation, and refractive index change in fullerene C_{60} and dye doped NLCs. In PR materials (such as LCs doped with photo-charge producing agents) the reorientational effect is due to a photo-induced space-charge field, which occurs due to a charge separation (diffusion and drift) and conductivity and dielectric anisotropies in the bulk of LCs as reported in Fig. 1. Two interfering laser beams generate a light pattern which illuminates the NLC cell. The space-charge fields in NLCs are generated by spatially inhomogeneous photogenerated charge carriers which are diffused and drifted by a density gradient of charge carriers and applied electric field, respectively. The resulting optical torques which are caused by the combined effect of the applied electric field and the induced space-charge field, reorient the director axis of NLCs, yielding a photo-induced refractive index change and creating a phase grating inside the cell. Several experimental [7,9,10,15,16] and theoretical studies [12–14,17–19], however, have pointed out the important role played by the optically induced surface-charge modulation. These studies illustrate the importance of including surface-charge modulation as well as the bulk contributions in any quantitative study of photorefractive effects.

Furthermore, it has been discovered that the molecular director of NLCs can be much more effectively reoriented when small amounts of appropriate dyes are dissolved in NLCs, which is so-called "dye effect". In these contexts, various dopants have been investigated before, such as C_{60}, [5,7] C_{70}, methyl red [6], rhodamine 6G [3], carbon nanotubes [7], as well as, polymeric alignment layers [9,26]. Khoo et al. [12] reported on an enhanced photorefractive response in CdSe-doped NLC cells.

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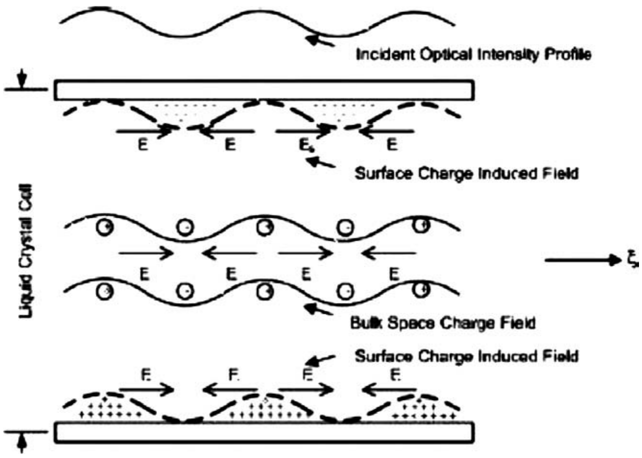

Fig. 1. Schematic diagram of bulk-space-charge field and surface-charge field in liquid crystal cell under combined action of applied dc field and sinusoidal optical intensity.

Indeed enhanced responses of the wave mixing efficiency by several orders of magnitudes can be achieved. Nevertheless, due to laser induced surface adsorption of these photo-excited dopants, the induced orientational gratings in the NLC tend to assume permanent and non-erasable nature upon prolonged illumination. This is an undesirable characteristic if the photorefractive effect is intended for real-time image/signal-processing application.

The goal of this work was to realize a device exhibiting photorefractive effects with strong beam coupling effects and induced orientational gratings transient in nature. Our idea was to use photoconductive nanorods layers in order to both enhance the charge generation thus improving the nonlinear response and to induce transient orientational gratings. The last feature is due to the organic capping on the nanorods which inhibits adsorption of the optically excited nanorods layers on the device windows.

In this paper, we presented a novel type of orientational photorefractive device consisting of a symmetric layered structure formed by glass substrate, indium-tin-oxide electrode (ITO), HTAB aligning layer, CdSe/CdS nanorods photoconductive layer and NLCs film. We observed in such a novel nanocomposite enhanced photorefractive effects for dynamic holographic application with a high two-beam coupling gain coefficient of over 350 cm^{-1}, with a nonlinear index coefficient n_2 which is 8 times bigger than that of a pure K15 liquid crystal homeotropic cell without any CdSe/CdS nanorods photoconductive layer and is comparable to that of C_{60}-doped K15 sample [4].

2. Experimental

2.1. Nanocrystal preparation and characterization

The dot/rod core/shell CdSe/CdS nanocrystals were synthesized by a "seeded growth" approach (Fig. 2a) [29], which yields highly uniform nanocrystals in terms of distribution of rod lengths and diameters, that additionally emit wavelength-tunable, linearly-polarized light with high quantum efficiency. In particular, the synthetic procedure relied on the rapid co-injection of preformed spherical CdSe nanocrystal seeds and elemental sulphur dissolved in trioctylphosphine, in a reaction flask that contains a solution of cadmium oxide in a mixture of trioctylphosphine oxide, hexylphosphonic acid and octadecylphosphonic acid at high temperature (350 °C) [29].

A morphological analysis of the stock solution of CdSe/CdS nanorods dissolved in toluene was carried out by means of Transmission Electron Microscopy (TEM) and is reported in Fig. 2b.

Optical absorption and photoluminescence (PL) spectra of CdSe/CdS nanorods in solution are reported in Fig. 3. These CdSe/CdS rods present the appealing characteristics of strong and tunable light emission from green to red according to the different aspect ratios considered (rod length/rod diameter).

2.2. Device preparation

In order to study the orientational photorefractive effect, we designed and fabricated the structure schematically shown in Fig. 4. Our device was prepared according to the following procedure: two flat glass substrates coated with transparent conductive indium-tin-oxide (ITO) layer were spun with a stock solution of CdSe/CdS nanorods dissolved in toluene (v = 2500 rpm, t = 20 s, a = 100 rpm/s). The molar concentration of nanorods in this solution was in the 10^{-6} M range (see a recent work from us on how the concentration of nanoparticles is estimated in solution [30]). Then, they were spaced from each other by placing Mylar spacers between them. Homeotropic alignment of the NLC molecules was achieved by treatment of the ITO-coated cell windows with the surfactant hexadecyl trimethyl ammonium bromide (HTAB) [31]. The cell had an internal thickness of 35 μm and was filled by capillarity with the nematic liquid crystal 4-pentyl-4′-cyanobiphenyl, also known as K15 [4,12,27], (molecular formula $C_{18}H_{19}N$, molecular mass 249.35 g/mol, density ρ 1.0220 g/cm^3 at 24 °C).

2.3. Optical retardation technique

In order to measure the degree of orientation of the NLC, both polarized microscopy and optical retardation measurements were

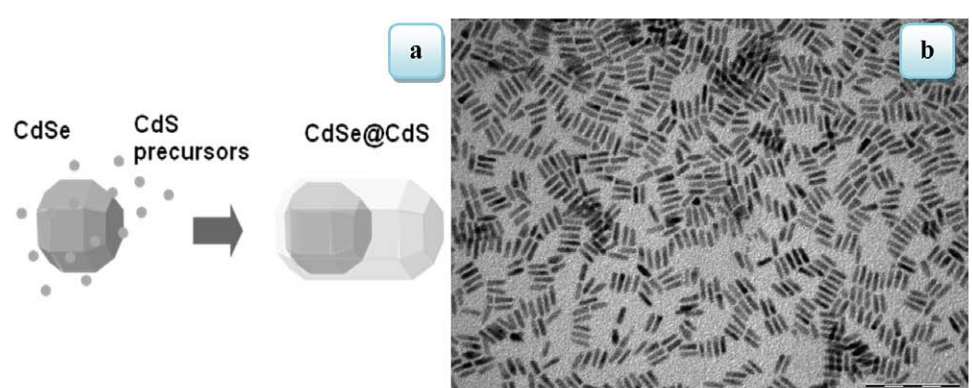

Fig. 2. (a) Sketch of the seeded growth approach. (b) A transmission electron micrographs of CdSe/CdS nanorods dissolved in toluene. The average rod diameter and length, as determined by TEM were 4 nm and 20 nm, respectively.