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Electro-optic properties of liquid crystal devices doped with cucurbit(6)uril-protected zirconia nanowires

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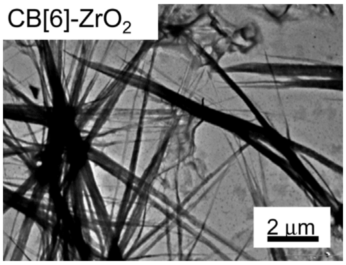
HIGHLIGHTS

- Cucurbit(6)uril-protected ZrO_2 nanocolloids were prepared in a tetraethylene glycol solution of zirconium (IV) in the presence of cucurbit(6)uril.
- Cucurbit(6)uril-protected ZrO_2 nanoparticles had an average diameter of 7.4 nm.
- The average width and length of cucurbit(6)uril-protected ZrO_2 nanowires were 240 nm and 13.7 μm, respectively.
- ZrO_2 nanowires show superior electro-optic properties of liquid crystal devices.
- We report a electro-optic properties of liquid crystal devices doped with cucurbit(6)uril-protected ZrO_2 nanowires.

GRAPHICAL ABSTRACT



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ABSTRACT

Zirconia protected by cucurbit(6)uril nanoparticles were prepared by using a microwave reactor equipped with ultrasonic nozzle mixing at 240 °C for 30 min in a tetraethylene glycol solution of zirconium (IV) ethoxide in the presence of cucurbit(6)uril. Particles in cucurbit(6)uril-protected ZrO_2 nanoparticles had an average diameter of 7.4 nm and mainly distribute within the range of about 4–11 nm. Cucurbit(6)uril-protected ZrO_2 nanowires were prepared by refluxing method at 240 °C for 5–20 min. The average width and length of cucurbit(6)uril-protected ZrO_2 nanowires were 240 nm and 13.7 μm, respectively. Cucurbit(6)uril-protected ZrO_2 nanowires were mixed with 4′-pentylbiphenyl-4-carbonitrile at room temperature resulting in a liquid crystal sol of 4′-pentylbiphenyl-4-carbonitrile containing 0.075 wt% of total metal. The response time of this twisted nematic liquid crystal devices in the presence of cucurbit(6)uril-protected ZrO_2 nanowires was faster than that in the absence.

1. Introduction

Liquid crystal devices (LCDs) are common electronic devices and are widely used any place and at any time. The display is an interface for information between man and machine. From this

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viewpoint, LCDs are useful for information technology at present. The modification of physical properties of liquid crystals by doping nanocolloids has received much attention from the view point of the enhancement of the performance of LCDs. Reflecting these trends several research groups reported on heterogeneous liquid crystal suspensions using; ferromagnetic particles [1], ferroelectric nanocolloids [2,3], fullerene [4], carbon nanotubes [5,6], diamond powders [7], MgO or SiO_2 nanocolloids [8], noble metal nanocolloids [9–11], semiconductor nanocolloids [12], and Au nanorods [13,14]. For example, Müller et al. demonstrated an electrically controlled light scattering by gold nanocolloids in a nematic liquid crystal mixture [15]. Kossyrev et al. showed a dynamic, continuous and reversible voltage-controlled color tuning promoted by gold nanodot arrays formed on the glass substrate of a sandwiched nematic liquid crystal cell [16]. Apart from influencing the optical and electro-optical properties of liquid crystals, nanocolloids were also found to induce and affect their alignment of liquid crystals [17,18], a critical prerequisite for the application of these materials in many devices. Hegmann et al. reported the hexanethiol-, dodecanethiol-, and naproxen-functionalized Au nanocolloids in a nematic liquid crystal mixture [19,20].

Nanocolloids (e.g. nanoparticles and nanowires) protected by organic molecules are now creating a new class of materials different from either conventional bulk materials or atoms, giving one of the smallest building blocks of matter [21,22]. Metal nanocolloids are stabilized by citrate ion [23], surfactants [24], polymers [25], and organic ligands [26]. For example, palladium nanoparticles, obtained by UV irradiation of a tetrahydrofuran solution of palladium(II) acetate in the presence of 4-cyano-4′-pentylbiphenyl, were protected by 4-cyano-4′-pentylbiphenyl and used as a dopant for a guest-host LCD [27]. Poly(cyclodextrin)-protected Rh nanoparticles were prepared by refluxing of rhodium (III) chloride in the mixture of water/ethanol in the presence of poly(cyclodextrin) and worked as a dopant for twisted nematic LCD with high speed response [28]. Thus, stabilizers play important roles for not only protecting nanoparticles but also controlling properties. Cucurbiturils, a series of cyclic oligomers of glycoluril doubly bridged by methylene linkers, have a pumpkin-like shape with all the ureido oxygen atoms being situated on both portals. The cavity is hydrophobic while the portals are hydrophilic. Premkumar et al. prepared Au nanoparticles by 1-pot synthesis of potassium tetrachloroaurate(III) and cucurbit(7)uril at room temperature [29]. Au nanoparticles protected cucurbit(5)uril were prepared by reduction of the aqueous solution of tetrachloroauric(III) acid in the presence of cucurbit(5)uril by addition of sodium borohydride [30]. However, to the best of our knowledge, there is no report on synthesis of metal oxide nanowires by using cucurbituril as a protective agent. Since liquid crystals have many special properties like liquidity, self-assembly, crystallinity, and optical anisotropy, the nanowires having anisotropy can be at the same time expected to have many functions arising from such properties.

In this paper, we report the results of preparation of cucurbit(6)uril-protected ZrO_2 nanowires, which can improve the compatibility of ZrO_2 nanowires with 4′-pentylbiphenyl-4-carbonitrile (5CB: a liquid crystal molecule). LCDs fabricated by 5CB doped with the cucurbit(6)uril-protected ZrO_2 nanowires show an obvious fast electro-optic switching.

2. Experimental

2.1. Materials and experimental procedure

Cucurbit(6)uril, zirconium (IV) ethoxide and tetraethylene glycol from Wako Pure Chemical Industries, Ltd. were used without further purification. Other reagents employed here were of a commercial G.R. grade and used as received.

Cucurbit(6)uril-protected ZrO_2 nanocolloids were prepared by using a microwave reactor equipped with ultrasonic nozzle. Cucurbit(6)uril (0.014 mmol in monomeric units, 0.1 times the total amount of zirconium (IV) ethoxide) and zirconium (IV) ethoxide (0.14 mmol) were mixed in tetraethylene glycol to form a 200 cm^3 solution. Mixed solutions filled with pure nitrogen and then exposed to the microwave (2450 MHz) and ultrasonic waves (150 W, 20 kHz). Contaminants like ions in the dispersions were removed by washing the dispersions three times with ethanol by using an ultrafiltration. Complete removal of the solvent and volatile byproducts by vacuum evaporation gave cucurbit(6)uril-protected ZrO_2 nanocolloids.

2.2. Characterization

UV–vis (ultraviolet and visible light) absorption spectra were measured with a Shimadzu UV-2500PC recording spectrophotometer using a quartz cell with 10 mm of optical path length. Transmission electron microscopy (TEM) images were observed with a JEOL TEM 1230 at accelerated voltage of 80 kV. An average diameter and standard deviation were calculated by counting the diameters of 200 particles on the enlarged TEM photographs.

2.3. Fabrication and electro-optic properties of LCDs containing cucurbit(6)uril-protected ZrO_2 nanowires

Cucurbit(6)uril-protected ZrO_2 nanocolloids were mixed with 5CB at room temperature resulting in a liquid crystal sol of 5CB containing 0.075 wt% of total metal (sum of Zr). The sols were injected into an empty cell for a twisted nematic mode with a cell gap of 5 μm, supplied by Sun Trading Co., Ltd. The electro-optic properties, especially applied voltage versus optical transmittance (*V*–*T*) curves of twisted nematic liquid crystal devices (TN-LCDs) were measured by applying the 100 Hz square wave alternating current at 25 °C with a LCD evaluation system (Photal Ohtsuka Electronics, Ltd., model LCD-5200).

3. Results and discussion

3.1. Characterization of ZrO_2 nanocolloids

Cucurbit(6)uril-protected ZrO_2 nanocolloids were prepared by using a microwave reactor equipped with ultrasonic nozzle mixing at 240 °C for 30 min in a tetraethylene glycol solution of zirconium (IV) ethoxide in the presence of cucurbit(6)uril. Fig. 1 shows UV–vis absorption spectra of dispersions of cucurbit(6)uril-protected ZrO_2 nanocolloids. The dispersions of cucurbit(6)uril-protected ZrO_2 nanocolloids obtained after ultrasonic and microwave reaction show broad absorption spectra. Chen et al. gave for zirconia an absorption peak at 230 nm, which is assigned to Zr–O–Zr linkage [31]. For bulk phase ZrO_2, a band maximum in the UV–vis spectrum was also signaled between 230 and 240 nm, by Zaitseva [32]. It can be concluded the absorption peak between 230 and 250 nm show the formation of ZrO_2 nanocolloids.

Fig. 2 exhibits TEM photographs and size distribution histogram of the obtained nanoparticles. The most cucurbit(6)uril-protected ZrO_2 nanoparticles at mole ratio of cucurbit(6)uril to zirconium of 0.1 were distributed in the range of 4–11 nm, suggesting that the size of ZrO_2 nanoparticles is homogeneous. The results reveal that cucurbit(6)uril-protected ZrO_2 nanoparticles examined here have the average diameter of 7.4 nm and relatively small standard deviation. The average diameters of cucurbit(6)uril-protected ZrO_2 nanoparticles are in good agreement with that of poly (γ-cyclodextrin)-protected ZrO_2 nanoparticles (7.2 nm) by

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