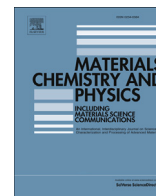




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Synthesis of freestanding water-soluble indium oxide nanocrystals capped by alanine nitric acid via ligand exchange for thin film transistors and effects of ligands on the electrical properties

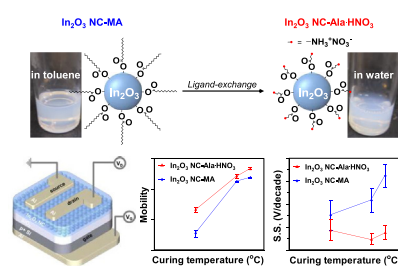
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HIGHLIGHTS

- Freestanding water-soluble In_2O_3 nanocrystals (NCs) were synthesized by ligand exchange.
- Thin film transistors (TFTs) of colloidal NCs were fabricated by spin-coating method.
- Water-soluble In_2O_3 NC TFTs showed higher mobilities due to shorter ligand length.
- Surface defects of NCs were notably reduced by surface etching during ligand exchange.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate synthesis of freestanding water-soluble indium oxide nanocrystals (In_2O_3 NCs) by ligand exchange to β -alanine nitric acid ($\text{Ala}\cdot\text{HNO}_3$) and its application for active channel layer in thin film transistors (TFTs), with investigation of the effect of curing temperatures on the TFT properties in terms of thermal behaviour of the ligand molecules at 150, 300, and 350 °C. After ligand exchange from long alkyl ligand (myristic acid, MA) to short $\text{Ala}\cdot\text{HNO}_3$, the mobility of NC TFTs cured at 150 °C increased by over 1 order of magnitude, from $1.3 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $4.5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, due to enhanced tunnelling rate (Γ) between adjacent NCs. Higher curing temperatures such as 300 and 350 °C, inducing thermal decomposition of the organic ligands, led to further enhancement of the mobility, particularly up to $2.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the In_2O_3 NC- $\text{Ala}\cdot\text{HNO}_3$ TFT cured at 350 °C. It is also found that the ligand exchange of In_2O_3 NC in acidic condition (e.g. HNO_3) would be simple and effective to reduce the surface defects by surface etching, which may lead to better device performances.

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1. Introduction

For the last decade, metal oxide semiconductors have been explosively investigated for applications in electronics, such as for thin film transistors (TFTs), due to achieving the apparently

contradictory properties of optical transparency and outstanding electrical performances, including high carrier mobility [1]. In addition, the metal oxide semiconductors have also drawn tremendous research attention due to high environmental stability as well as low-temperature and solution processibilities [2–4]. Such low-temperature and solution processes are favoured for next-generation electronics by, respectively, enabling the use of flexible substrates and adoption of printing techniques such as

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spin-coating, dip-coating, ink-jet, and so on. These are all directing to ultimately roll-to-roll processes which are cost-effective because of high throughput and coverage of a large area [2,3].

In general, the fabrication methods of solution-processed metal oxide semiconductor TFTs can be widely classified into two approaches, those that are (1) precursor-based and (2) colloidal nanoparticle (NP)- or nanocrystal (NC)-based [2]. Though the precursor-approach, which usually utilizes coating solutions of metal salts in organic solvents, has been well investigated and was demonstrated to exhibit good electrical performances [3], it has the critical drawback of requiring annealing process at high temperatures, usually over 400 °C, to fully convert the metal salts into metal oxide networks, activating electrical properties [3,5]. On the other hand, the NP- or NC-approach can skip the post-annealing process at high temperatures because well-defined metal oxide NPs or NCs are used as the building blocks.

Among the many metal oxide semiconductors, indium oxide (In_2O_3) has been considered as a promising material for TFT applications due to its wide band gap (3.6–3.75 eV) and excellent single crystal mobility (160 $\text{cm}^2/\text{V s}$) [6,7]. While the fabrication of In_2O_3 TFTs using the precursor-approach [5,8–10] and NC TFTs of zinc oxide (ZnO)-based have been well investigated [11–17], fabrication of In_2O_3 TFTs via the NC-approach (In_2O_3 NC TFTs) has of yet been rarely investigated, despite the fact that synthesis of mono-disperse and high-crystalline In_2O_3 NC has been well developed to date [18–22]. Recently, we demonstrated the first solution-processed In_2O_3 NC TFTs from freestanding NCs, and discussed the effect of the NC size on the TFT performances [23]. The In_2O_3 NC TFTs are considered promising for device configuration to realize the high-performance of TFTs due not only to the low-temperature processability as mentioned above but also to the reasons as following: (1) the carrier transport in a single NC may occur by band transport mechanism, allowing high mobility and (2) the carrier transport throughout the NC solid could be controlled by the NC size and interdistance between the NCs, which can be understood on the concept of artificial solids [24,25]. Moreover, it was found in some cases that In_2O_3 TFTs are not functional as transistors when the carrier concentration is too high, which can be altered by deposition conditions, losing off state (all conducting), although very high carrier mobility is achieved due to the high carrier concentration [3,26]. However, by using the NC-approach to fabricating In_2O_3 NC TFTs, it might be possible to control the switching property by suppressing carrier transport modulated by NC interdot distance, even while maintaining the high carrier concentration for high mobility.

One of the additional advantages of utilizing colloidal NCs as a building block for the NC TFTs (NC-approach) is that the physical and chemical properties of the NCs can be easily modulated by making surface modifications to the NCs [25]. Since the colloidal semiconductor NCs are usually stabilized by capping the surface with organic ligands via coordinate bonds from the synthesis, the surface modification can be achieved by exchanging the original ligand to a desired ligand that is specially designed for the purpose, which is normally called the ligand exchange process [25]. Particularly, by adopting bi-functional ligands in which one terminal is coordinated to the surface stabilizing the NCs and the other is placed outside to interact with solvent molecules, freestanding water-soluble semiconductor NCs have been obtained [27–31]. These freestanding water-soluble NCs are stable under ambient conditions, due to proper surface-functionalization with ligand molecules, so that they can be readily utilized for many optical and electrical applications through eco-friendly and simple solution processes [27–31]. However, the fabrication of freestanding water-soluble In_2O_3 NC and investigation of its application for the active channel layer in TFTs have rarely been attempted, to the best of our

knowledge, in spite of that dispersion of In_2O_3 NC with organic stabilizer in water and its TFT application was demonstrated in recent [32].

In this study we demonstrate synthesis of freestanding water-soluble In_2O_3 NCs, being environmental-friendly, by ligand exchange to the simplest short amino acid molecule, β -alanine (Fig. 1), and examine its application for channel material in TFTs (Figs. 5–7).

2. Materials and methods

2.1. Materials

Indium acetate ($\text{In}(\text{Ac})_3$, 99.99%), myristic acid (MA, $\geq 99\%$), 1-octadecene (ODE, 90%), oleylamine (OLA, 70%), β -alanine (Ala, $\geq 99\%$), toluene (anhydrous, 99.8%), and deionized water ($\leq 4.3 \mu\text{S}/\text{cm}$) were obtained from Sigma–Aldrich and used without further purification. Chloroform ($\geq 99.5\%$), acetone ($\geq 99.5\%$), methanol ($\geq 99.5\%$), and nitric acid (HNO_3 , 60%) were purchased from Daejung chemicals (Siheung-city, South Korea) and used as received.

2.2. Synthesis of myristic acid-capped In_2O_3 nanocrystals (In_2O_3 NC–MA)

Myristic acid-capped In_2O_3 nanocrystals (In_2O_3 NC–MA) were synthesized following the published procedure with a few modifications [33]. All the synthesis procedures were carried out in inert Ar atmosphere using a conventional Schlenk line technique. 2.92 g of $\text{In}(\text{Ac})_3$ and 6.85 g of MA were loaded in a 500 mL three-neck flask equipped with a magnetic stir bar. 200 mL of ODE was added to the flask. The solution was purged with Ar several times and then degassed under vacuum at 110 °C for 2 h. In a separate 100 mL three-neck flask, 8.1 g of OLA and 10 mL of ODE were prepared and the same procedure was performed. After degassing of the both solutions under vacuum at 110 °C for 2 h, they were refilled with Ar. The former solution was heated to 295 °C and then the OLA solution was rapidly injected to it. The solution temperature was then dropped to 280 °C and maintained for 1 h. The temperature was further reduced to 240 °C for an additional 1 h. After the solution was cooled to room temperature, the In_2O_3 NC–MA was collected by dissolution/precipitation technique using chloroform and acetone solvents. To the solution, 100 mL of chloroform was added and 200 mL of acetone was poured to precipitate the product down. The product was collected by centrifugation at 15,000 rpm for 10 min and then washed using chloroform and acetone three times more. After drying the solvents using a rotary evaporator, around 1.5 g of In_2O_3 NC–MA in yellowish green colour was obtained.

2.3. Ligand exchange of myristic acid (MA) in MA-capped In_2O_3 nanocrystals (In_2O_3 NC–MA) to β -alanine nitric acid (Ala- HNO_3) to produce water-soluble Ala- HNO_3 -capped In_2O_3 nanocrystals (In_2O_3 NC–Ala- HNO_3)

Water-soluble β -alanine nitric acid-capped In_2O_3 nanocrystals (In_2O_3 NC–Ala- HNO_3) were prepared by exchange the MA ligand in the as-synthesized In_2O_3 NC–MA to Ala- HNO_3 . The ligand exchange reaction was performed in homogeneous mixture of three solvents: chloroform, methanol, and water. First, Ala- HNO_3 target ligand solution was prepared by following procedures; 0.5 mL of 1 M Ala in H_2O solution was mixed with methanol 4.5 mL. To this solution, approximately 0.053 g of HNO_3 (60%) was added and stirred for over 30 min to yield 0.1 M Ala- HNO_3 in H_2O /methanol solvents, in which the volume ratio between H_2O and methanol was intended to be around 1 to 9. In a 100 mL round flask, 500 mg of as-synthesized In_2O_3 NC–MA was loaded and dissolved in 50 mL of

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