

Indium Tin Oxide@Carbon Core–Shell Nanowire and Jagged Indium Tin Oxide Nanowire

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Abstract This paper reports two new indium tin oxide (ITO)-based nanostructures, namely ITO@carbon core–shell nanowire and jagged ITO nanowire. The ITO@carbon core–shell nanowires (~ 50 nm in diameter, 1–5 μm in length,) were prepared by a chemical vapor deposition process from commercial ITO nanoparticles. A carbon overlayer (~ 5 – 10 nm in thickness) was observed around ITO nanowire core, which was in situ formed by the catalytic decomposition of acetylene gas. This carbon overlayer could be easily removed after calcination in air at an elevated temperature of 700°C , thus forming jagged ITO nanowires (~ 40 – 45 nm in diameter). The growth mechanisms of ITO@carbon core–shell nanowire and jagged ITO nanowire were also suggested.

Keywords Chemical vapor deposition · Core–shell · Indium tin oxide · Nanowire

Introduction

Indium tin oxide (ITO), a wide band-gap semiconducting material, has been widely used in various fields including liquid crystal display, solar cell, gas sensor, and optoelectronic devices [1–14]. Therefore, extensive efforts have been reported to the synthesis and application of ITO materials with various morphologies including nanopowders, films, and nanorods/nanowires [1–3, 8–19]. ITO nanorods and nanowires have been prepared by carbon-

assisted synthesis [9], Au-catalyzed vapor–liquid–solid growth [10, 11], direct thermal heating [12, 13], and solvothermal method [14]. These nanorods or nanowires displayed some interesting properties that were ascribed to the unique one-dimensional shape. It is anticipated that some unusual but interesting properties may be generated by further varying morphologies of ITO materials. However, there is few report about complex ITO-based one-dimensional (1D) nanomaterials. Recently, Wang et al. reported ITO-TiO₂ core–shell nanostructure with enhanced properties when used as electrode for solar cells [15].

Chemical vapor deposition (CVD) technique is an effective route to grow one-dimensional carbonaceous materials such as carbon nanotubes or carbon nanofibers [20–22]. Catalysts, such as Co, Fe, are usually required to facilitate the decomposition of carbon source gas. Carbon nanotubes-encapsulated Sn-Sb nanorods have been fabricated in a CVD process in our previous efforts [21]. In this study, we demonstrated that a CVD process could be applied to the fabrication of ITO@carbon core–shell nanowires directly by commercial ITO nanoparticles. The ITO nanoparticles were used as self-catalysts to decompose acetylene gas, thus forming a new ITO-based complex 1D structure, namely ITO@Carbon core–shell nanowires. Furthermore, this core–shell structure could be converted to jagged ITO nanowires by removing carbon overlayer.

Experimental Details

In a typical synthesis, commercial indium tin oxide (ITO) nanopowders suspension (Aldrich, In₂O₃: 90 wt%, SnO₂: 10 wt%, particle size: <50 nm, surface area: $27\text{ m}^2/\text{g}$) were purified by repetitive filtration and washing with deionized water. After drying, 0.1-g indium tin oxide nanopowders

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were uniformly distributed in an alumina crucible. This crucible was then put in the center of a tubular furnace and heated at 650°C for 4 h under flowing 200 sccm mixed gas (10% C₂H₂ and 90% N₂). Then, the crucible was cooled naturally in the same gas mixture to room temperature. The black product obtained was ITO@C core-shell nanowire. The ITO@C structure was calcined in air at 700°C for 3 h to prepare jagged ITO nanowires.

The obtained products were characterized by X-ray diffraction (XRD, Rigaku D/max-2,550 V, Cu K α radiation), laser Raman spectrometer (Renishaw inVia, 785 nm laser), field-emission scanning electron microscopy (FE-SEM, JSM-6700F), and transmission electron microscopy/selected area electron diffraction/energy dispersive X-ray spectrum (TEM, JEOL JEM-200CX and JEOL JEM-2010F/SAED/EDX) in the Instrumental Analysis and Research Center, Shanghai University.

Results and Discussion

Figure 1 is the XRD pattern of ITO@C and ITO products. A few characteristic peaks such as (222), (400), (440), (622) of indium oxide could be identified for ITO@C nanowires, which agrees well with previous report of indium tin oxide nanorods [2]. The Sn was incorporated into the indium oxide lattice. The absence of carbon peaks in ITO@carbon revealed that amorphous carbon was obtained by C₂H₂ decomposition at 650°C, which is in accordance with previous study [21]. There was a trace of indium metal in this product, which is because some indium tin oxides were reduced to indium by the reductive C₂H₂ gas. After further heat treatment of ITO@carbon at 700°C in air to oxidize indium and remove carbon overlayer, all peaks of the product could be perfectly indexed to cubic indium tin oxide (PDF 06-0416) [12].

The FE-SEM image (Fig. 2a) shows the commercial ITO nanoparticles (In₂O₃: 90 wt%, SnO₂: 10 wt%, particle size: <50 nm), which were used as the starting material for

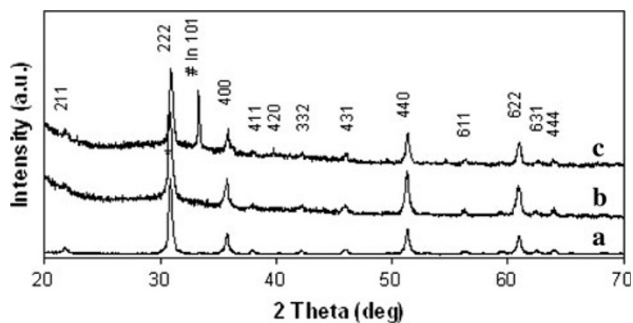


Fig. 1 Powder X-ray diffraction patterns of ITO-based samples: **a** commercial ITO nanopowders, **b** ITO nanowires (700°C in air), and **c** ITO@carbon nanowires (650°C in acetylene)

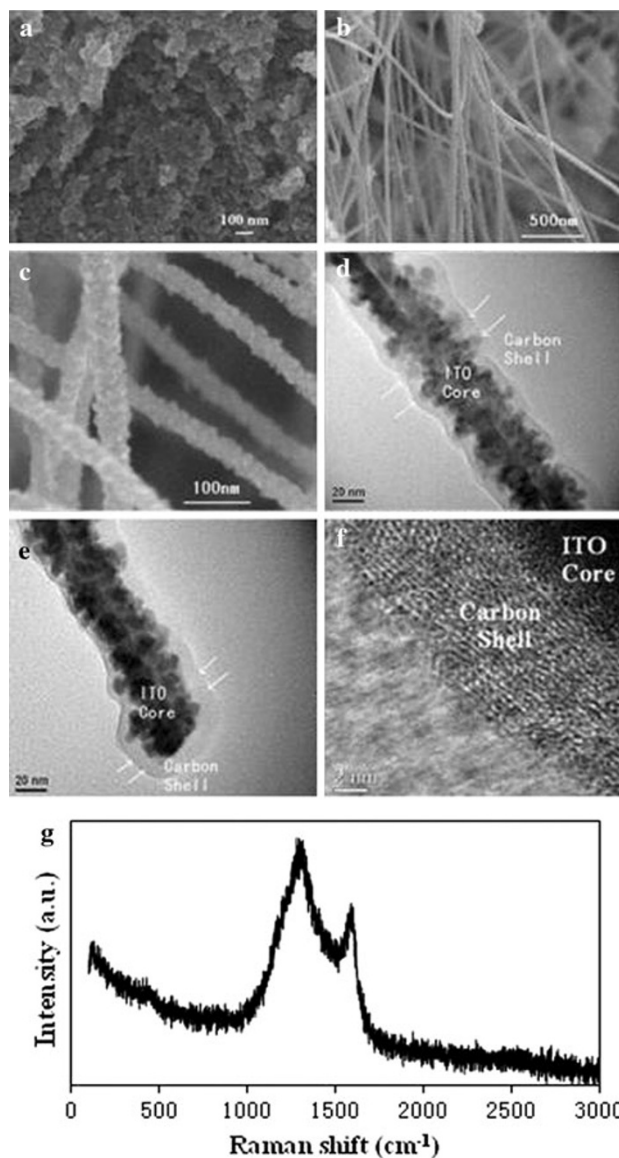


Fig. 2 **a** SEM image of commercial ITO nanopowders, ITO@carbon nanowires: **b** low-magnification FE-SEM image, **c** high-magnification FE-SEM image, **d** TEM image, body section, **e** TEM image, tip section, **f** HRTEM image, **g** Raman spectra

the growth of ITO@C and ITO nanowires. These ITO nanoparticles were spherical and ~5–50 nm in particle size. Fig. 2b, c show the SEM images of ITO@C composite after CVD growth. A large number of wire-like products are clearly shown in the Fig. 2b with the diameter of ~50 nm and length up to a few micrometers. The high-magnification FE-SEM image (Fig. 2c) reveals the surface of ITO@C was pretty rough due to the deposited carbon on ITO materials.

The TEM (Fig. 2d, e) were further used to characterize the product in both body and tip sections. It was found that the product actually had an ITO nanowire-carbon core-shell structure. The ITO nanowire core consisted of many

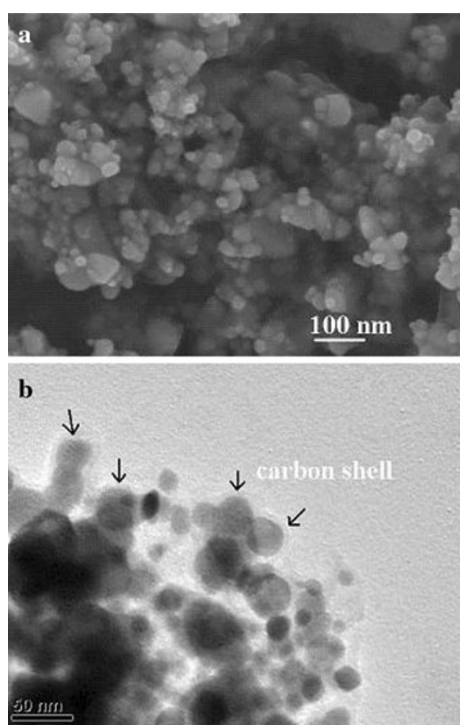


Fig. 3 ITO@carbon core-shell nanoparticles prepared by benzene: **a** SEM image and **b** TEM image

small ITO nanoparticles (~ 5 – 20 nm in size) that were self-assembled along the axis. The carbon shell of ~ 5 – 10 nm in thickness was clearly indicated by arrows in the Fig. 2d. The HRTEM image in Fig. 2f shows the ~ 7 -nm carbon overlayer consisting of staggered, shortened graphene sheets, which was confirmed by the observation of stronger disordered D band than the ordered G band in the Raman spectra of the composite (Fig. 2g). It is suggested that the ITO nanopowders were rearranged and self-assembled into 1D structure at high temperatures, which may be catalyzed by indium liquid (melting point 157°C). Metal droplets have been suggested to be essential in the growth process of one-dimensional nanostructure based on vapor-liquid-solid mechanism [23, 24]. Indium droplet was formed by the C_2H_2 reduction of In_2O_3 at 650°C . The carbon overlayer was in situ formed around ITO nanowire by the decomposition of C_2H_2 gas [21–24]. C_2H_2 appeared to be an important factor in the growth process because if the benzene vapor was used instead of C_2H_2 gas (the benzene vapor was carried into the tube furnace in the 30 sccm flow of nitrogen gas, and the reaction was performed at 950°C), only ITO nanoparticle-carbon core-shell nanoparticles were obtained as indicated by SEM image (Fig. 3a) and TEM image (Fig. 3b). There was no trace of indium element in the final product prepared by benzene, which was indicated by XRD patterns (data not shown). It is believed that C_2H_2 gas is a stronger reductive source

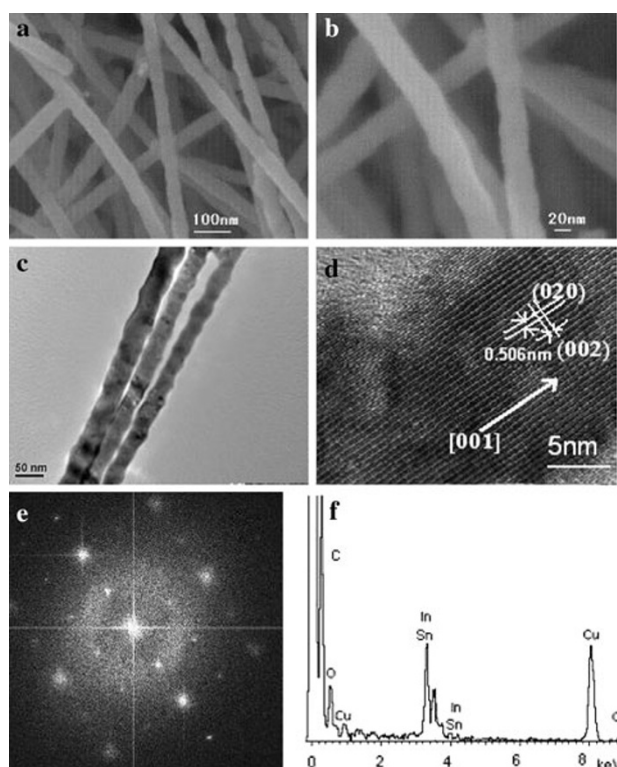


Fig. 4 The jagged ITO nanowires: **a** FE-SEM images, scale bar = 100 nm, **b** FE-SEM image, scale bar = 20 nm, **c** TEM image, **d** HRTEM image, **e** the corresponding fast Fourier transform, and **f** EDX

than benzene, and the formed indium could be the effective liquid catalyst for the growth of ITO nanowires based on vapor-liquid-solid growth mechanism [23, 24].

The ITO@carbon core-shell structure could be easily converted to pure ITO nanowires by calcination in air to remove carbon overlayer. The SEM and TEM images in Fig. 4a, c show that the diameters of ITO nanowires were reduced to be ~ 40 – 45 nm compared to previous ITO@C core-shell product (~ 50 nm). It was also noticed that ITO nanowires exhibited a jagged surface, which is because its precursor (ITO@C nanowire) consisted of a rough core of nanoparticle nanowire. The high-temperature calcination increased nanowire crystallinity and facilitated the surface uniformity of ITO nanoparticle nanowire. A nearly single crystalline structure in the final product (ITO nanowires) could be determined by the HRTEM image and corresponding fast Fourier transform in Fig. 4d, e. The (002) and (020) planes could be identified by measured interplanar distance of 0.506 nm, and the nanowire growth was along [001] direction. The energy dispersive X-ray spectrum (EDX) in Fig. 4f confirmed the presence of In and Sn. The molar ratio of In to Sn was around 10:1, which agrees well with the starting commercial ITO particles. A schematic representation of growth process for ITO@carbon

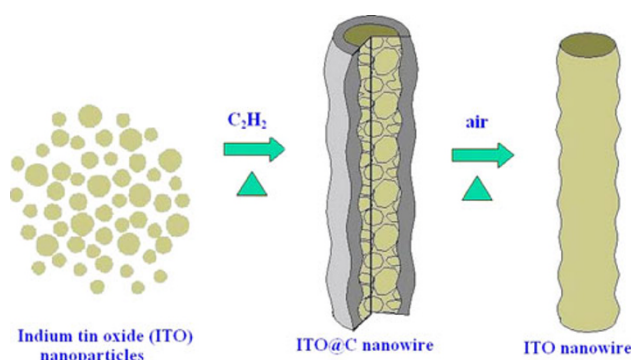


Fig. 5 Schematic representation of the growth of ITO@C nanowires and jagged ITO nanowires

core–shell nanowire and jagged ITO nanowire is illustrated in Fig. 5. The reductive C₂H₂ gas was employed not only to produce indium catalyst to promote the vapor–liquid–solid growth of ITO nanowires, but also to form in situ a compact carbon shell on the ITO nanowire core.

Conclusion

In summary, a few new ITO-based nanostructures, namely ITO@carbon core–shell nanowires (~ 50 nm in diameter and ~ 5 – 10 nm in carbon thickness) and jagged ITO nanowires (~ 40 – 45 nm in diameter), were reported in this study. ITO nanowires were formed by self-assembly of ITO nanoparticles in a chemical vapor deposition process. A thin layer of carbon was also in situ uniformly coated around ITO nanowire core. To the best of our knowledge, these morphologies were not presented previously and may find potential applications due to their special morphology tuning.

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