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Application of patterned growth of aligned zinc oxide nanoarrays by mirocontact printing in quantum dots-sensitized solar cells

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HIGHLIGHTS

- To prepare patterned ZnO films by microcontact printing.
- Patterned ZnO NWs as light scattering layer.
- To prepare patterned ZnO NWs by hydrothermal method.

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ABSTRACT

This paper describes a simple method for patterned growth of ZnO nanoarrays (NAs) that is based on a combination of the microcontact printing process for patterning ZnO seed films and the low-temperature hydrothermal approach for depositing ZnO NAs. The patterned ZnO seed films were achieved via printing patterned TiO_2 sol on ZnO seed films. It is found that the pattern quality is mainly affected by the viscosity of TiO_2 ink and the pressure including value and direction. To assess the possibility of patterned ZnO NAs applied to devices, the patterned ZnO NAs were used as light scattering layer in CdSe-sensitized solar cells. The diffuse-reflection, absorption and transmission spectra show that the patterned ZnO NAs greatly enhance the light scattering and absorbance in the visible range. The enhancement of cell performance is attributed to the patterned ZnO NAs: 1) multiple-light scattering improves the light absorbance, and 2) NAs with high electron mobility facilitate the electron collection.

1. Introduction

One-dimensional (1D) nanostructures such as wires, belts, and tubes have been a particular area of intense research because of their potential applications in physical and chemical nanodevices. ZnO nanoarrays (NAs) are the most promising material for the realization of useful nanodevices, such as light-emitting diodes [1], UV photodetector [2], chemical sensors [3], field emission [4] and nanolasers [5], due to their unique properties such as a direct wide band gap (3.37 eV), piezoelectric characteristics, high sensitivity and selectivity for chemical and optical species, and the specific electrical and optical properties of a semiconductor with a large exciton binding energy (60 meV).

Some methods have been developed for preparing ZnO NAs, which can be classified into two categories: vapor-phase and hydrothermal methods [6,7]. Vapor-phase method requires the high growth temperature and the noble metal as catalyst, which is generally used to prepare the high quality of NAs. Hydrothermal method is carried out at low temperature (80–100 °C). In particular, it has also been widely innovated recently, such as laser heating inducing local growth [8]. The hydrothermal method is low cost, large-scale production and catalyst-free, but controlling the topography of ZnO NAs is difficult.

In recent years, the controlled growth of orientation, position and morphology of ZnO NAs has been reported widely. In order to achieve the microstructure device, ZnO NAs should be patterned, and a major challenge for researchers is to find the way to control NAs arrangement. Up to now, lots of reports have been given the successful realization of well-patterned 1D ZnO nanomaterials using various methods. The patterning process includes a combination of photolithography [9] or electron-beam lithography [10] and subsequent deposition of zinc metal by sputtering [11] followed by selective etching, or deposition via metal organic

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chemical vapor deposition (MOCVD) [12,13]. Hydrophobic/hydrophilic interactions for self-assembled monolayer [14], microsphere self-assembled monolayer formation [15] and atomic force microscope (AFM) manipulation [16] have been employed to pattern the seed particles. Nanostructure ZnO NAs were then grown from the patterned seed layers by various synthetic methods, these techniques usually require highly sophisticated equipment and time consuming processes, severe fabrication conditions (high pressure and temperature) and the aid of catalytic metal, such as Au, Ag, and Pt.

Soft lithography has recently become a very promising technique for micro or nanostructure in a wide range of materials. Compared with the standard photolithographic or electron beam lithographic patterning strategies, soft lithography appears more suitable for patterning large areas in a one-step process. Microcontact printing (μCP) as one of soft lithographic techniques relies on the use of a poly(dimethylsiloxane) (PDMS) elastomer as a stamp, mold or mask, which ensures the conformal contact between PDMS and substrates of interest and the easy release without destroying the formed microstructure.

There are a few reports on preparing well-aligned ZnO NAs by μCP. Currently, two methods (μCP) were adopted to achieve the patterned ZnO seeds, one is to self-assemble monolayers (SAMs) of OTS ($CH_3(CH_2)_{17}$–$SiCl_3$) on the surface of ZnO seed films, the other is to directly print ZnO nanoparticals on the substrate [17,18]. But the drawback is that the former requires a dry conditions or a protection of inert gas and the latter causes a big tilt angle of ZnO NAs due to the nonuniform ZnO nanopartical seeds. With this background in mind, we first utilize TiO_2 sol to prepare the pattern on ZnO seed films by μCP, and then patterned ZnO seeds films is exposed to the growth of ZnO NAs by a hydrothermal method.

Photonic crystals (PCs) have recently been studied extensively because of interesting optical properties, such as multiple scattering, and slow photon (SP) effect, which has been widely used in the field of sensors [19], solar cells [20] and photocatalysis [21]. For photonic crystals solar cell, one of the most intriguing properties for periodic structures is the high light scattering, which facilitates light harvesting. In this paper, patterned ZnO NAs were first used as light scattering layer in CdSe-sensitized TiO_2 NPs solar cell. By light scattering, visible light was effectively confined within the photoanodes and absorbed by the photosensitizer, and the Jsc was greatly improved. The efficiency of cells with patterned ZnO NAs is higher than that of cells without ones.

2. Experimental section

Fig. 1 outlines the strategy we employed to fabricate patterned ZnO NAs. It includes three main stages: (1) elastomeric stamp (PDMS) fabrication (Fig. 1(a_1,a_2), (2) patterning of ZnO seed films (Fig. 1(b_1–b_6), and (3) selective hydrothermal growth of ZnO NAs and preparation of hybrid photoanodes (Fig. 1(b_7,b_8)).

2.1. PDMS stamp production

The well-shaped master was produced on Si substrates by conventional photolithography and dry etching process [22,23]. PDMS stamps were prepared by mixing PDMS precursor (obtained from Dow Corning as Sylgard 184) with a curing agent (10:1), followed by degassing in a desiccator and pouring the bubble-free mixture onto the master (Fig. 1a_1). After the precursor was hardened at 70 °C for 10 h, the stamps was peeled off the master (Fig. 1a_2) and cut into the desired size (0.25 ± 0.05 cm^2). Before carrying out the μCP, the stamps were cleaned in ethanol by ultrasonic.

2.2. Patterned ZnO seeds

Glass and indium-tin-oxide (ITO) substrates were cleaned by ultrasonic in acetone and DI water. ZnO seeds were deposited on ITO substrates by sol–gel method (Fig. 1b_4) [24]. Often, the μCP process includes the inking and printing step. Firstly, TiO_2 sol using as ink was spin-coated (3000 rpm, 30 s) on the glass (Fig. 1b_1), the stamp was lightly placed in contact with the glass substrate and peeled away after 30 s (Fig. 1(b_2,b_3)); then the stamp with ink was brought into conformal contact with the ZnO seed films for 30–60 s then peeled away (Fig. 1(b_5, b_6)); last the wet patterned seed films were annealed at 400 °C for 30 min. In the process, when the retention time is too short or long, TiO_2 sol can not be transferred well between the stamp and substrates, the results confirmed that the most appropriate time is 30–60 s. In addition, in order to obtain clear and regular pattern, a vertical pressure added on stamps make PDMS stamp sufficiently contact with substrates.

2.3. Quantum dot-sensitized solar cell

After the selective growth of ZnO NAs was carried out by a low temperature hydrothermal method (Fig. 1b_7) [24], TiO_2 paste

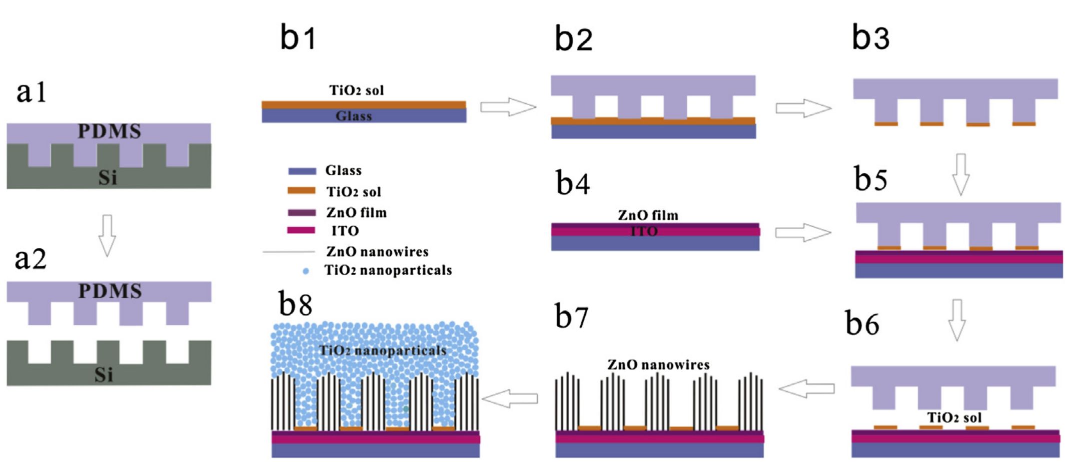

Fig. 1. The process flow of PDMS stamp and patterned ZnO NAs–TiO_2 nanoparticals hybrid photoanode preparation. (a_1, a_2) PDMS stamp production. (b_1) A thin layer of TiO_2 sol was deposited by spin-coating (3000 rpm, 30 s). (b_2, b_3) TiO_2 sol was transfer to PDMS by inking. (b_4) Prior to patterning ZnO seed films, ZnO seeds were deposited by sol–gel method. (b_5, b_6) TiO_2 sol on PDMS was transfered to ZnO seed films to generate a patterned mask. (b_7) Patterned ZnO NAs were grown by a low temperature hydrothermal method (at 80 °C) (b_8) TiO_2 nanoparticals paste was filled by larger centrifugal force (5000 r/min, 10 min).