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Self-Organized Formation of Embossed Nanopatterns on Various Metal Substrates: Application to Flexible Solar Cells

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ABSTRACT

We report metal substrate dependent formation of honeycomb-like nanopatterns via a versatile anodization method. During the anodization of metal foils, the well-known formation of well-aligned metal oxide nanotube arrays are observed, and honeycomb-like nano-hole patterns are successfully obtained after stripping the oxide nanotube array layers. Interestingly, the sizes of the nano-hole patterns are dependent upon the starting metal substrate for the anodization. By simple alternation of a metal substrate for anodization, it is possible to tune the radius and interpore distance of the resulting nanosized hole patterns. As one of applications for nanopatterned metal substrates, flexible dye-sensitized solar cells are fabricated, and the positive effects of the nanopatterned substrate on cell efficiency are investigated.

1. Introduction

Self-organized ordered 1D metal oxide nanotube array films prepared from anodizing of metal foil have been attracting increasing attention. First, 1D TiO_2 nanotube arrays have been applied for various applications such as sensors, solar cells, and photocatalysts and represented breakthroughs [1–4]. Second, in the case of self-organizing, porous alumina (Al_2O_3) films on aluminum (Al), they now attract increasing attention as templates for the synthesis of various 1D nanomaterials [5–7]. By carefully tailoring the electrolyte composition, temperature, anodization time, and anodization voltage, the dimensions of the 1D nanotube arrays can be controlled over a wide continuous range.

Recently, uniformly nanotextured clean films have been extensively investigated in the search for ideal nanometer-sized geometries for various applications such as surface-enhanced sensing and single molecule detection, catalysts, photovoltaics, light emitters, and metamaterials [8–14]. However, only limited applications have succeeded because of the lack of a robust and versatile template platform for the fast and simple fabrication of low-cost nanostructures with a reproducible morphology over large areas. Until now, many fabrication methods to create nanostructures on various substrates were reported. First, top-down fabrications such as electron beam lithography (EBL) and focused ion beam (FIB) are popular techniques that are capable of preparing the desired size, shape, and pattern of such nanostructures arbitrarily. However, the extensive processing time and high cost are the main drawbacks of EBL and FIB, especially for the fabrication of close-packed nanostructures over large areas. To solve these drawbacks of top-down processes, recently, colloidal crystal templates with 50 to 1000 nm in diameter or a nanoimprinting method have been used to make three-dimensional (3D) porous replicas, which have also been used to make a wide variety of structures with micrometer or sub-micrometer-sized pores, thin films, and freestanding membranes [15,16]. However, most bottom-up processes also still suffer due lack of well-defined, long-range ordered, and defect-free nanostructures.

Meanwhile, dye-sensitized solar cells (DSSCs) are a promising alternative to the conventional silicon solar cells due to their low-cost, non-vacuum, high conversion efficiency and eco-friendliness to nature [17–19]. Wide interest has been developing on flexible solar cells due to a wide range of applications such as power for wearable electronic devices [20,21]. Conventional DSSCs are brittle, hefty, and non-flexible due to the usage of transparent, conducting glass substrates (FTO) as an electrode to support either TiO_2 or Pt. Flexible and featherweight substrates are crucial in developing the roll-to-roll production of solar cells. So, plastics (PET/ITO) or metal foils (Ti, Zn, W, and stainless Steel)

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are used as conducting substrate to facilitate mass production and to broaden the application of DSSCs [20,21]. Applying plastic substrates in DSSCs has its own demerits, which can work only at low temperatures (150 °C) so that the particle connectivity between TiO_2 nanoparticles can act as a recombination sites and, thus, affects the photo conversion efficiency. As another concept to obtain highly efficient flexible DSSCs, our group proposed the use of metal sheets with low resistance as new flexible substrates [22]. Among them, Ti foil is a good alternative to the conventional FTO glass substrates due to their good flexibility, light-weight, low-sheet resistance, superior corrosion resistance, and high temperature tolerance [23–25]. Several research papers on Ti-based photo-electrodes in DSSCs have been reported [23–34]. Many research attempts tried to improve the efficiency of DSSCs. However, most of the researchers have mainly concentrated on electrode materials, novel dyes, and electrolytes [35–38]. However, few, if any, reports exist on the surface modification of Ti substrates for enhancing DSSCs performances by acid treatment, polishing, and adding of interfacial layer, which results in promising photovoltaic performance due to the enhanced electrical contact, reflectance, and suppressing the recombination. Though the above mentioned disordered nano-structure methods yielded positive effects in photovoltaic performance, there is still considerable room for improvement in these DSSCs [24,30–34].

Herein, we report the formation of hexagonally-ordered hemisphere (honeycomb) nanopatterns on various metal substrates. Interestingly, the sizes of nano-hole patterns were dependent upon the starting metal substrate for the anodization. By simple alternation of a metal substrate for anodization, it is possible to tune the radius and interpore distance of the resulting nanosized hole patterns. In particular, the nanopatterns from the anodization of Al foil as starting material exhibits very small pore sizes of around 30-40 nm with excellent uniformity. As one of applications of nanopatterned metal substrate, flexible DSSCs with Ti foil were fabricated. The honeycomb patterning had fruitful effects in several aspects for the efficiency improvement such as light-scattering effect, improved electrical contact between the TiO_2/Ti substrate interface, and reducction in recombination.

2. Experimental section

2.1. Fabrication of honeycomb shaped metal substrates

The Ti, Zr, and Al foils were cleaned in an ultrasonication bath using acetone, ethanol, and DI (deionized) water sequentially for 10 min each and dried using a nitrogen gas blow. The cleaned substrates were cut into the required size (6×6 cm^2) for the anodizing process. Highly ordered TiO_2, ZrO_2, and Al_2O_3 nanotube (TNT) arrays were prepared on the Ti substrate after the anodization process in a two-electrode electrochemical bath. In detail, square-shaped metal foils were used as a working electrode with platinum foil as the counter electrode. 20 V of voltage, ethylene glycol electrolyte with 0.3 M NH_4F and 4 vol% H_2O, and 3 h of anodizing time were used for anodizing all metal substrates. To prepare irregular shaped porous metal substrates, we used 80 V of voltage with same electrolyte composition. To strip the nanotube arrays from the metal substrates, the nanotube arrays on metal substrates were sonicated for several minutes in a DI water bath. Then, it was removed from the water bath and cleaned using a nitrogen gas blow, and thus, it provided the uniform porous 2D honeycomb-like, nanopatterned metal foil substrates (Fig. 1).

2.2. Fabrication of photoanodes for DSSC

Pre-cleaned bare and honeycomb-patterned Ti substrates were dipped at 70 °C for 30 min in a 40 mM aqueous titanium tetrachloride ($TiCl_4$, Aldrich) solution and then rinsed with ethanol. Subsequently, the nanocrystalline, transparent TiO_2 electrodes (TiO_2 paste-20 nm EnB Korea) were doctor-bladed on the previously prepared bare and honeycomb-patterned Ti substrates and sintered at 550 °C for 30 min. In order to further improve the connectivity between TiO_2 nanoparticles, a 40 mM aqueous $TiCl_4$ treatment was done at 70 °C for 30 min and sintered at 550 °C for 30 min. Once cooled to 80 °C, the sintered electrodes were immediately immersed in a 0.3 mM solution of N719 dye in ethanol for 24 h. A Pt counter electrode (CE) was prepared simultaneously by spin coating the Pt precursor solution (H_2PtCl_6 in isopropyl alcohol) on a FTO glass substrate and subsequently sintered at 450 °C for 30 min. The photoanodes and CE were

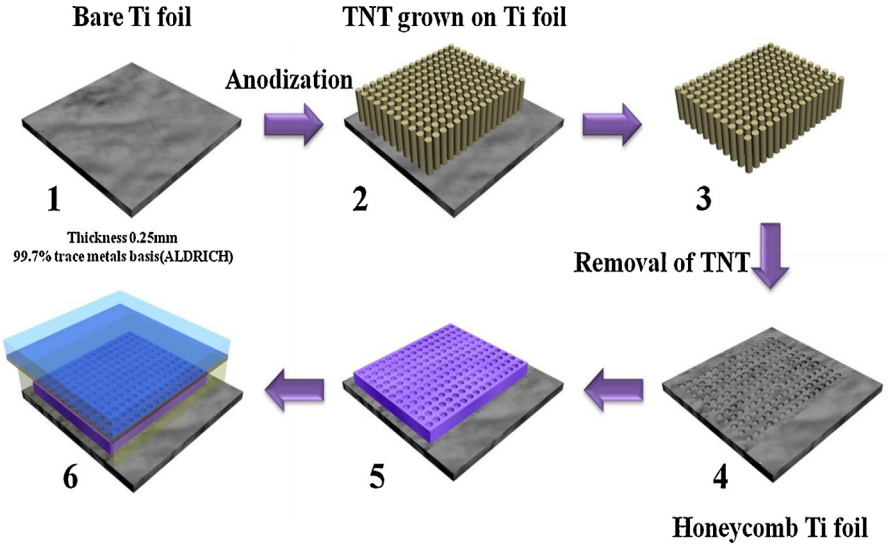

Fig. 1. Schematic diagram of the honeycomb-patterned Ti photo-electrode synthesis route and device assembly. Step 1) Bare Ti was cleaned and cut into the required size; Step 2) TiO_2 nanotube (TNT) was grown on the Ti substrate using anodization; Step 3) As grown TNT was removed from the Ti substrate by dipping in water and sonication; Step 4) After TNT removal the honeycomb Ti substrate was obtained; Step 5) 20-nm nanocrystalline TiO_2 was deposited onto the honeycomb Ti substrate; and Step 6) Pt-deposited FTO substrate was sandwiched onto the already prepared photo electrode.