TiO$_2$ Nanotubes- Applications in Nanotemplates and Photovoltaics

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Introduction

TiO$_2$ nanotube (TiO$_2$ NT) arrays obtained by anodization provides a large specific surface area as well as a direct pathway for charge transport, thus rendering superior capabilities in light harvesting[1], environmental sensing[2], energy storage[3], *etc*. Constructing 3D core-shell structures by employing TiO$_2$ NT template has been demonstrated on various guest materials via electrodeposition [4]. However, high efficiency filling the entire pore network still remains a challenge because of the small pore size and conformably conductive nature of the host material.

In this paper, a reductive doping process is employed to form a more conductive layer at the NT bottom. Following electrodeposition leads to high yield nanowires and nanotubes with tunable morphologies embedded in TiO$_2$ tubes. Subsequently, the reductive doping is further applied in constructing dye-sensitized solar cells (DSSCs). The increased conductivity of NT bottom offers a reduction of series resistance (R_s) in the DSSCs, leading to an enhanced performance.

Experimental

Self-organized TiO$_2$ NT films are prepared by a two-step anodization method on Ti foil (0.3 mm thickness, 99.5% purity) in ethylene glycol solution containing 0.3 wt% NH$_4$F and 2 wt% H$_2$O. The as-anodized TiO$_2$ NTs are re-crystallized in air ambient under 580 ^{o}C for 6 hours. TiO$_2$ NT films are reductively doped in a conventional three-electrode electrochemical system. The doping process is achieved by applying cyclic voltammetry in 1 M NH$_4$Cl aqueous solution at a scan rate of 100 mV/s. One-dimensional (1-D) matal (Cu, Ni) and semiconductor (Cu$_2$O) materials are then filled into TiO$_2$ NTs by electrodeposition. The doped TiO$_2$ films (~20 μm thickness) are

also adopted in the DSSC assembly. Dye loading is performed by dipping the film into a 0.3 mM N719 dye (Solaronix) in *t*-butanol/acetonitrile solution (1:1 volume ratio). The electrolyte containing 0.5 M LiI, 0.05 M I$_2$, 0.5 M *tert*-butylpyridine in acetonitrile and valeronitrile (1:1 volume ratio) is injected into the assembled DSSCs. The photovoltaic performances are tested under simulated AM 1.5 illumination (100 mW/cm^2).

Results and Discussion

Fig. 1a shows the oblique view of self-organized NTs after two-step anodization. The film thickness obtained in fresh electrolyte represents linear growth rate (thickness with respect to anodization time is ~167 nm/min) (data not shown).
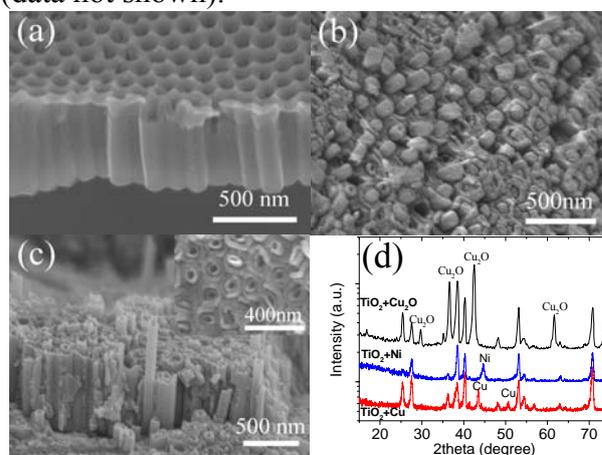

Fig. 1 (c) Oblique view of TiO$_2$ NTs after second-step anodization. (b) Cu and (c) Cu$_2$O embedded in TiO$_2$ NT arrays. (d) XRD patterns of Cu, Ni and Cu$_2$O embedded in TiO$_2$ NTs.

The SEM images in Figs. 1b and c indicate that the Cu$_2$O and Cu are well embedded in the TiO$_2$ NT channels. Interestingly, the as-deposited Cu shows tubular structure with the outer diameter in consistency with the TiO$_2$ tubes' inner diameter (Fig. 1c). A nearly 100% filling rate is observed from the top view as shown in the inset of Fig. 1c. The formation of tubular structure arises from the conducting

nature of crystallized TiO_2, which provides a continuous pathway for the metal electroplating onto the tubes' inner sidewalls. In addition, the nanoscale channels with high aspect ratio inhibit the ionic diffusion and promote the formation of the tube-in-tube structure[5].

X-ray diffraction (XRD) patterns of as-synthesized materials are presented in Fig. 1d, which can be indexed to Cu, Ni, and Cu_2O respectively. The unlabeled peaks arise from anatase, rutile TiO_2, and Ti substrate.

A prototype solar cell is constructed based on core–shell Cu_2O/TiO_2 radial p–n junctions as illustrated in Fig. 2a. The generated electron–hole pairs are separated at the Cu_2O/TiO_2 core–shell interface. Fig. 2b demonstrates the J-V characteristics after annealing at 200 ^{o}C with active area of 0.057 cm^2. An efficiency of ~0.01 % is estimated with open-circuit voltage (V_{oc}) = 0.1V, short-circuit current density (J_{sc}) = 0.33 mA/cm^2, and a fill factor (FF) 0.27. Optimizing the Cu_2O electrodeposition parameters and replacing Au top electrode by transparent conductive oxide (TCO) could further improve the devices' performance.
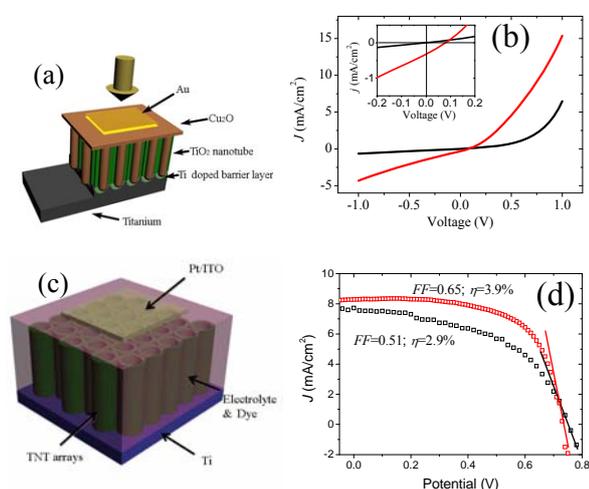

Fig. 2 (a) Schematic illustration of Cu_2O/TiO_2 solar cell, and (b) the corresponding J–V characteristics. (c) Schematic illustration of TiO_2 NT based DSSC, and (d) the corresponding J–V characteristics with (red) and without (black) reductive doping treatment.

Besides serving as a nanotemplate for constructing 3-D core-shell structures, TiO_2 NTs can also be used to optimize the performances of TiO_2 based DSSCs (Fig. 2c). It is expected that the high resistance in the tubes bottom renders a higher series resistance (R_s), which leads to the suppressed fill factor (FF) and short-circuit current (I_{SC}).

To improve the conductance of TiO_2 NT matrix, the doping method mentioned above is applied. For comparison, DSSCs without bottom treatment are also fabricated. The J–V characteristics of DSSCs with and without bottom doping treatment are plotted in Fig. 2d. By employing the reductive doped TiO_2 NT, the DSSC shows an enhanced photo conversion efficiency (η~3.9 % with an increased Jsc (8.28 mA/cm^2) and FF (0.65). The open circuit voltage remains the same, V_{oc} = 0.74 V, given by the energy level difference between the Fermi level of TiO_2 and the redox potential of the electrolyte. The shunt resistance approximated from the slope of reverse J-V sweep at J_{sc} is on the order of 1×10^3 $\Omega \cdot cm^2$ for both devices. While the R_s shows a significant improvement from 20.5 to 10.2 $\Omega \cdot cm^2$, that can be estimated from the slopes of the J-V curves at V_{oc}.

Conclusions

Highly ordered TiO_2 NT with enhanced bottom conductivity are achieved by reductive doping in electrochemical cells. 3-D core–shell structures are achieved by simple electrodeposition, which holds far reaching potential applications in photovoltaics, catalyst, battery, supercapacitor, etc. Moreover, the bottom treated nanotubes, serving as photoanode, are assembled into dye-sensitized solar cells. Benefited from the reduction of series resistance, the as-fabricated solar cells demonstrate improved performance with enhanced FF and J_{SC}.

References

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