PEDOT inverse nanotube arrays: synthesis in TiO2 nanotubes

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Intrinsically conducting polymers such as polypyrrole (PPy), polyaniline (PANI), poly-3,4-ethylene-dioxythiophene (PEDOT), poly-3hexylthiophene (P3HT) have been of wide interest since the first demonstration of electric conductivity in doped polyacetylene by Shirakawa *et al.*[1, 2] Presently, the polymers find applications in plastic solar cells, fuel cells, self-healing materials, light-emitting diodes, actuators, electro catalytic materials, battery systems, *etc.* The polymers have different band-gap structures and light absorption properties that determine their applications. For instance PEDOT is often used as a charge collector in plastic solar cells and is considered as transparent electrode in touchscreens and electronic paper due to its transparency for visible light. To improve the performance of the devices the nanoscale arrangement of the polymers is often necessary. This is typically achieved by synthesis of nanofibers, nanotubes, nanowires, and micro/nano-spheres by using hard alumina templates, micelle soft templates, mesoporous silica spheres, interfacial polymerization and dispersion polymerization.

Recently, 1-D TiO_2 nanotubes became of high interest due to a very high degree of control over its geometry and functional properties arising from semiconductive nature of titania.[3] Combining the anodization process (TiO_2 nanotubes) and electrodeposition (polymers) it is possible to construct organic/inorganic composites or use TiO_2 nanotubes as a template for formation of polymers with unique geometrical architectures.[4-6]

Herein we demonstrate an approach which allows deposition of PEDOT in titania nanotubes. Figure 1 shows the PEDOT nanostructures formed in TiO_2 nanotubes by pulsed deposition. By adjusting the current pulse protocol parameters two distinctly different selective deposition patterns can be established. Either the conducting polymer can be deposited in space between titania nanotubes or on both sides of titania nanotube, *i.e.* in and out of tube. Specific geometries between p-type organic polymer and n-type inorganic semiconductor (Fig. 1) are synthesized. Further dissolution of titania leads to formation of polymer nanostructures in the form of polymeric nanopore-array or polymeric inverse-nanoutube-array.

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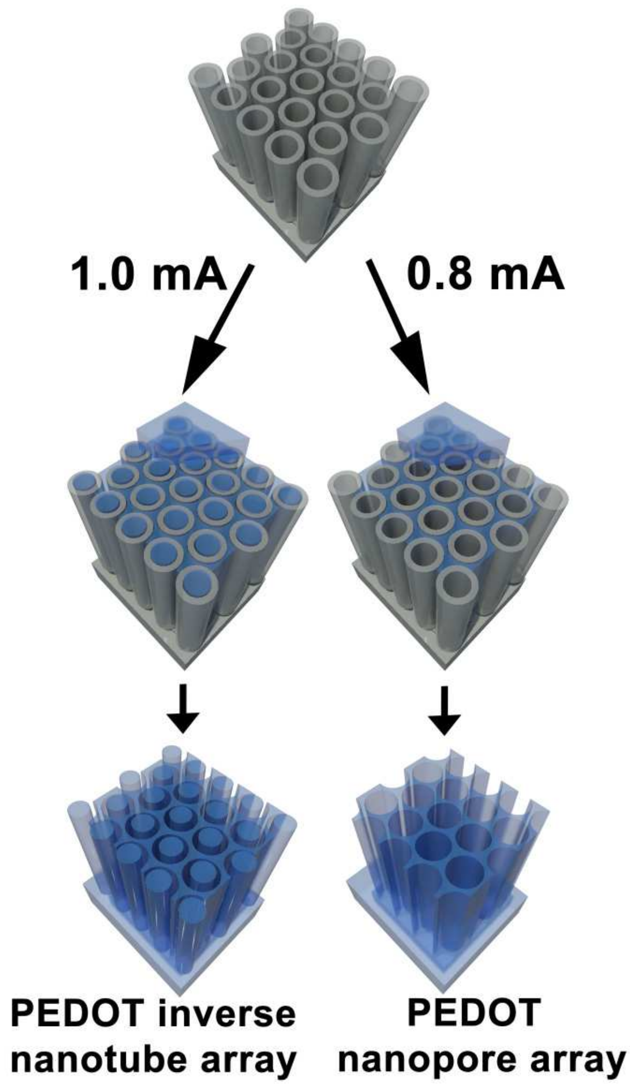

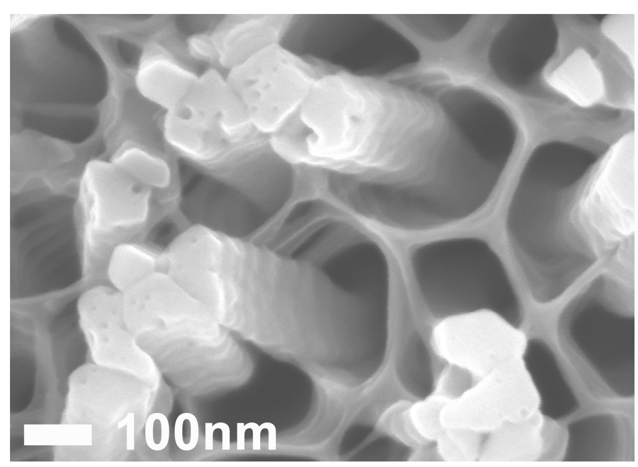

Figure 1. a) Synthesis of PEDOT inverse-nanotube-array and nanopore-array by selective electrodeposition with pulse current at 1.0 and 0.8 mA, respectively. The upper image represents titania nanotube electrode, the middle ones composites of titania and PEDOT, the lower images represent nanostructures of PEDOT obtained after dissolution of the template; b) SEM image of PEDOT inverse nanotube array.