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Designed growth of WO_3/PEDOT core/shell hybrid nanorod arrays with modulated electrochromic properties

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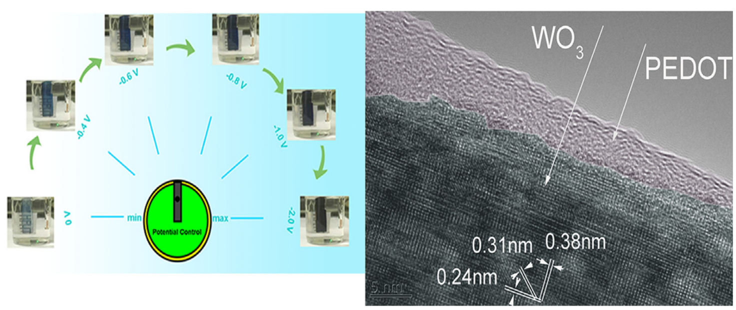
HIGHLIGHTS

- WO_3/PEDOT core-shell hybrid nanorod arrays are synthesized by wet chemical methods.
- The hybrid nanorods exhibit modulated electrochromic properties.
- Interfacial synergistic effect may play a vital role in the property enhancement.

GRAPHICAL ABSTRACT



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ABSTRACT

Designed growth of tungsten oxide (WO_3)/poly(3,4-ethylenedioxythiophene) (PEDOT) core/shell hybrid nanorod arrays has been obtained by combining solvothermal and in situ electropolymerization techniques. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Raman characterization results indicate that the hybrid nanorods are composed of single crystalline WO_3 nanocores wrapped by thin amorphous PEDOT nanoshells. The hybrid nanorods exhibit promising electrochromic performance of much shorter response time (3.8 s for coloring and 3.6 s for bleaching) than the bare WO_3 nanorods (12.4 s for coloring and 7.6 s for bleaching), while the optical contrast of the hybrid nanorods increases from 26% of PEDOT to 72% in 633 nm. And the coloring efficiency and stability of the core/shell hybrid nanorods are also enhanced compared to the individual components. Dynamic analysis suggests a synergistic effect between the WO_3 nanocore and the PEDOT nanoshell. In addition, color depth and optical contrast of the hybrid nanorods can be modulated by adjusting the applied voltage and the deposition of the PEDOT nanoshell. The hybrid nanorod films obtained by the cost-effective wet chemical methods may find promising applications in energy-saving windows, smart displays as well as other energy efficient technologies.

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1. Introduction

Electrochromic materials are of great interest owing to their switchable color and reversible modulation in optical performance (transmittance, absorbance or reflection) driven by a low operating potential, which renders them a promising candidate for smart displays, electronic papers, as well as energy efficient technologies [1–4]. Transition metal oxides (TMOS) feature changeable valence states, superior chemical and thermal stability, and their electrochromic performance has been extensively investigated over past decades [5–9]. Among the oxides, WO_3 is probably the most widely studied electrochromic material since it is built up from three dimensional network of WO_6 octahedrons arranged in corner-sharing or edge-sharing configuration, which provides abundant channels for transporting small ions that favor switchable color changes [10]. Nevertheless, response speed of WO_3 remains sluggish due to low ion diffusion coefficient and long diffusion path. An alternative solution is to synthesize nanostructured WO_3/conjugated conducting polymer hybrids [11–14], in which the hybrid architecture promises synergistic effect through the reinforcement or modification of each component and the nanostructure provides large surface area and facilitated charge transport pathway, thereby enhanced electrochromic properties are expected [15]. For example, Cai et al. prepared WO_3/polyaniline (PANI) core/shell nanowire arrays and observed remarkable improvement in optical modulation (59% at 633 nm), fast switching speed (2.2 and 4.8 s), high coloration efficiency (86.3 $cm^2\,C^{-1}$ at 633 nm) [16]. Ma et al. reported a nano hybridization of crystalline WO_3 and PANI showing enhanced electrochromic performance owing to interaction [17]. PEDOT is a conjugated conducting polymer featuring cathodically coloring from light blue to dark blue upon reduction with high coloration efficiency and short response time, however, low optical contrast [18–20]. By constructing WO_3/PEDOT hybrid nanostructures, electron donor–-acceptor pairs formed between WO_3/PEDOT through hybridization and similar cathodically coloring characteristics of the two components are both expected to afford reinforced electrochromic performance. To date, some techniques have been employed to prepare WO_3/PEDOT composite film such as spin coating or immersion methods [21–23]. Nevertheless, the obtained electrochromic properties still remained unsatisfactory due to simple physical contact and weak mechanical adhesion between the WO_3 and PEDOT as well as small interfacial areas

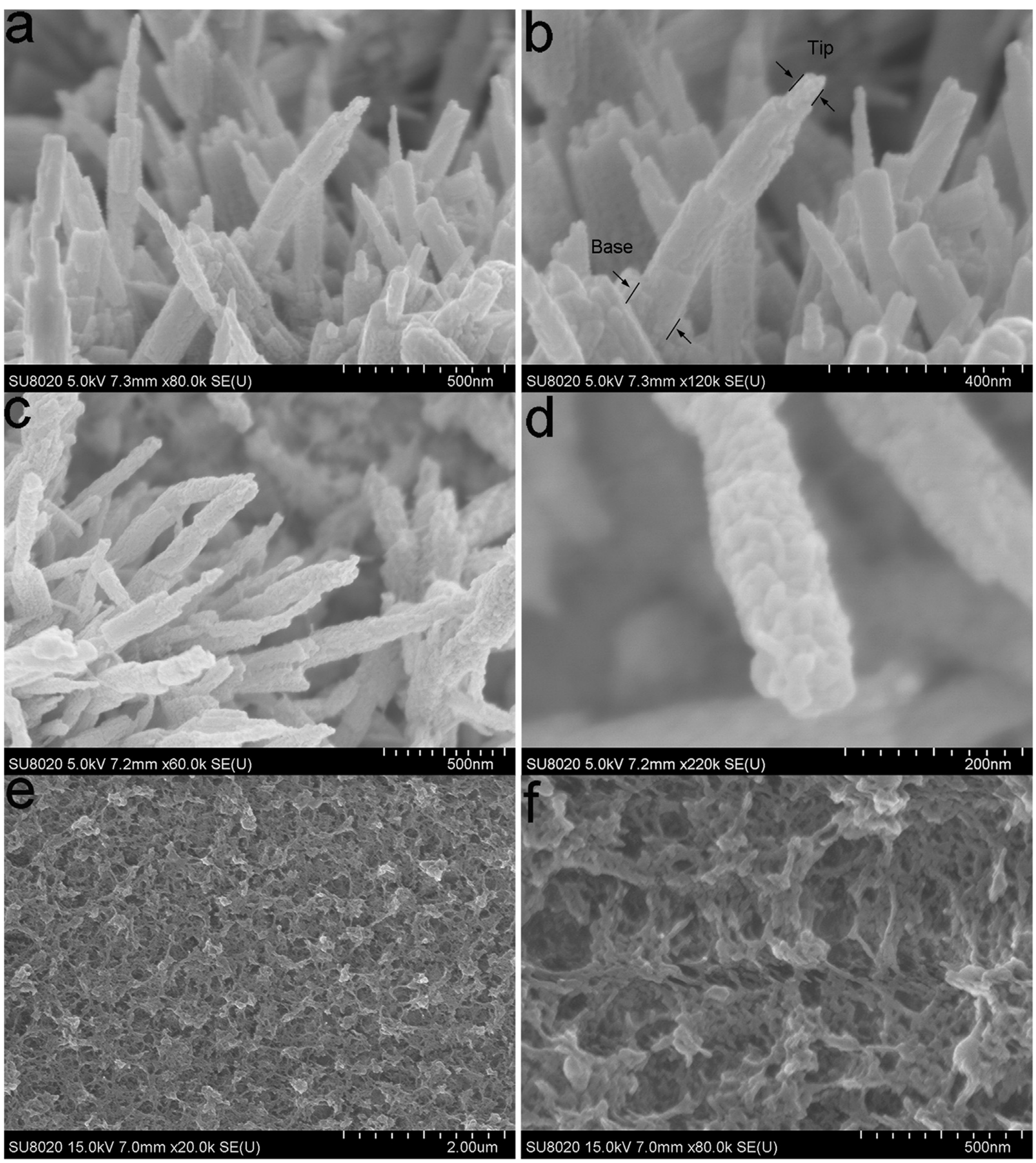

Fig. 1. SEM images of (a) and (b) WO_3 nanorod, (c) and (d) WO_3/PEDOT core/shell nanorod array, (e) and (f) PEDOT film.