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Enhanced electrochromic porous cobalt oxides nanowall electrodes: A new way for fast modulation of yellow-brown light

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ABSTRACT

Construction of high-efficiency electrochromic electrodes with large and fast optical modulation is important for development of advanced smart windows. In this work, we report highly porous metal oxide (Co_3O_4) nanowall arrays via solvothermal method. Noticeable porous structure and cross-linked network are realized in the interconnected Co_3O_4 nanowalls. Improved porosity and faster ion/electrons transportation are combined in this unique nanowall architecture. The electrochromic properties of Co_3O_4 nanowall arrays are characterized via optical-electrochemical measurements. Cyclic voltammetry and transmittance tests demonstrate that the interconnected Co_3O_4 nanowall arrays show larger (52% at 632 nm) and faster (0.8–0.9 s) modulation of yellow-brown light, and higher electrochemical reactivity and smaller polarization as compared to the common Co_3O_4 nanowall arrays (31% at 632 nm with 1.3–1.5 s). The enhanced optical modulation is owing to the porous cross-linked nanowall structure with more active sites and shorter diffusion paths for ions/electrons.

1. Introduction

Electrochromic phenomenon has bee widely explored over the past decades due to interesting characteristics of reversible color/optical change under an external low voltage [1–6]. To date, lots of electrochromic color systems are constructed including transparent, black, blue, green, purple [7–10]. Nevertheless, the electrochromic yellow-brown system is rarely studied due to lack of suitable materials [11,12]. Fortunately, cobalt oxides can present reversible change between yellow and brown system [13,14]. But cobalt oxides are p-type semiconductors with low electrical conductivity resulting in slow color/optical change. Moreover, the dense structure of cobalt oxide films is not beneficial for ions penetration/transfer leading to insufficient active sites and low optical modulation [15–19]. Hence, it is critical to design or reconstruct electrode structure of cobalt oxides to boost the electrochromic performance.

Currently, there are several important indicators (such as large optical modulation, fast switching speed, long cycle life) proposed for advanced electrochromic electrodes [8,12,20,21]. All these indicators are highly associated with the electrochromic reactions. It is well accepted that the electrochromic reaction is an electrochemical process, which involves redox reactions with phase change accompanying color and optical modulation [22,23]. Hence, the electrochromic process is restrained by electrochemical rules, namely, the transfer characteristics of ions/electrons in the electrochromic electrode [24,25]. It is demonstrated that optical modulation is related to surface area. Generally, large surface area corresponds to more active sites leading to high optical modulation [11,26]. In addition, switching speed is associated with the reaction kinetics, which needs fast ions/electron transfer path. Moreover, long cycle life is built on the strong mechanical stability of electrode, which can withstand harsh long-term working environment [27]. In this context, high performance of electrochromic cobalt oxide films largely relies on nanostructure engineering accelerating reaction kinetics with the aid of large porosity and high surface area.

Up to now, numerus Co_3O_4 nanostructures have been prepared by different methods [13,28,29]. Unfortunately, power form material is not suitable for electrochromic application. As for the film products, several free-standing Co_3O_4 nanostructure arrays (e.g., nanoflakes [29], nanowires [30]) have been reported with enhanced performance. But there are no reports on highly porous Co_3O_4 nanowall arrays (NWAS) and their application for electrochromics. In the present work, we develop a high-efficiency solvothermal method for controllable synthesis of hierarchical

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porous Co_3O_4 NWAS. Interconnected porous nanowall structure with fast ion/electron transportation is realized. The electrochromic properties of porous Co_3O_4 NWAS are studied in detail. Our research shows another way for construction of advanced electrodes for yellow-brown light modulation

2. Experimental

The porous Co_3O_4 NWAS were fabricated by a facile solvothermal method as follows. The solvothermal aqueous solution was prepared by mixing 0.3 g $Co(NO_3)_2$ and 0.3 g hexamethylenetetramine in 75 ml ethanol. Then the above solution was put into Teflon-lined autoclave liners and maintained at 150 °C for 2 h. Clean ITO glass was used as the substrate. Finally, the samples were rinsed and annealed at 350 °C for 2 h in argon to form porous Co_3O_4 NWAS. For comparison, the normal Co_3O_4 NWAS (their walls were not porous) was prepared by another solvothermal method. The reaction solution was prepared by mixing 0.3 g $Co(NO_3)_2$ and 0.3 g urea in 75 ml ethanol. The other fabrication parameters were as the same as those of porous Co_3O_4 NWAS. The pore formation was mainly due to the release of H_2O

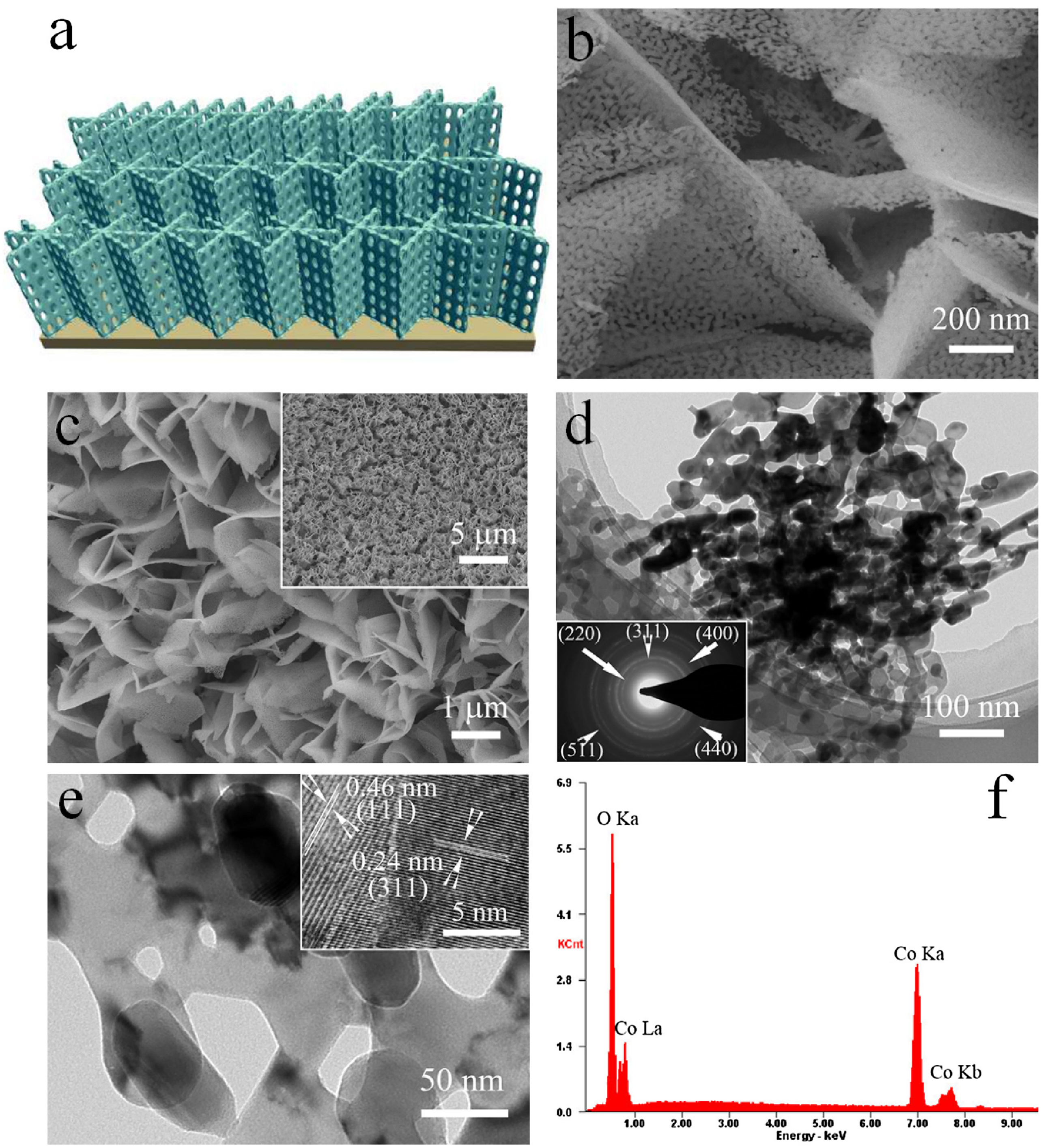

Fig. 1. Schematics of porous Co_3O_4 NWAs. Microstructure characterization of porous Co_3O_4 NWAs: (b-c) SEM images (low magnification SEM image in inset); (d–e) TEM images (SAED pattern and HRTEM image in inset); (f) EDS spectrum.