Copper Oxide–Cobalt Oxide Nanoscale Heterostructures for Photocatalysis

Wenwu Shi,¹ Renu Pandit² and Nitin Chopra¹,*

¹Department of Metallurgical and Materials Engineering, Center for Materials for Information Technology (MINT), Box 870202, University of Alabama, Tuscaloosa, AL, USA. *nchopra@eng.ua.edu
²High School Intern, Northridge High School, Tuscaloosa, AL, USA

ABSTRACT

Hybrid nanoarchitectures composed of oxides have variety of applications due to their stability at high temperature, tunable band gap energies, and unique catalytic properties. Growth techniques can strongly influence their crystallinity, phase purity, and interfaces, which could alter their functionality. Herein we demonstrate a surfactant-free and dry method for fabrication of CuO-Co₃O₄ nanowires heterostructures by combining magnetron sputtering of cobalt and subsequent annealing. Thickness of cobalt layer on CuO nanowires was tuned by changing sputtering power and time. Heterostructures were thoroughly analyzed by multiple characterization techniques. Morphologies of these heterostructures could be tuned from nanoparticles on nanowires, core-shell nanowires, and baseball bat-like nanowires. Growth of Co₃O₄ branches on nanowires was also observed after air annealing of CuO nanowires coated with thick Co shells.

Keywords: nanowire heterostructures, sputtering, oxides, photocatalysis, magnetic property

1 INTRODUCTION

Due to their suitable band gap energies, chemical stability, and ability to be doped, nanostructured heterostructures based on oxides are attractive for solar energy conversion [1], environmental remediation [2], and energy storage [3-5]. Such heterostructures or hybrid nanomaterials have been synthesized/developed using photochemical and hydrothermal methods, atomic layer deposition, flame synthesis, and chemical vapor deposition [6-10]. However, the control over morphologies, chemical compositions, crystallinity, and interfaces as well as capability for large-scale production remains yet to be achieved [6,11]. Herein, we report the coating of CuO nanowires with cobalt by magnetron sputtering and their air annealing for the formation of CuO-Co₃O₄ nanowire heterostructures. This completely dry processing route allowed for control over the morphology and interfaces of the nanowire heterostructures by way of manipulating Co thickness and morphology at the stage of sputter coating process. The fabricated nanowire heterostructures were characterized using electron microscopy, elemental analysis, and diffraction methods. It was further proven that controlling the morphology will result in most optimized photodegradation abilities in visible as well as UV light illumination. In addition, the morphological control can further allow for eliminating the use of sacrificial agent, making the process of photocatalysis a completely clean and contaminant-free approach.

2 EXPERIMENTAL

A piece of copper foil (99.9 %, 0.254 mm thick) was cleaned in HNO₃ solution (HNO₃/H₂O v/v 1:2) for 15 s and washed with copious amounts of DI water. Dried copper foil was heated to 410 °C for 6 h. After air annealing, a black layer of aligned CuO nanowires was formed. The annealed foil was loaded inside the sputtering chamber. The sputtering system was pumped down until 2×10⁻⁷ Torr and sputtering was conducted at 50 W, 150 W, and 200 W for 5 min with 3 mTorr and 25 sccm Ar flow. In another experiment, prolonged sputtering (~4 h, with 1 µm thickness) was also conducted. The sputtered nanowires were annealed at 520 °C in air for 10 h. Nanowire heterostructures were thoroughly characterized using SEM, TEM, XRD, and Alternating gradient magnetometer (AGM). Magnetic property was measured for CuO-Co core-shell nanowires by attaching 3 × 3 mm² film to the probe with vacuum grease. Magnetic hysteresis with two orientations, parallel (perpendicular to nanowire) and perpendicular (along the nanowires) were measured. For the photodegradation of phenol, heterostructures was dispersed inside 3 mL phenol solution as concentration of 1 g/L with or without addition of 12 µL H₂O₂ as sacrificing agent. The mixture was illuminated with lights with different wavelength and concentration of phenol was determined by UV-vis spectroscopy [11].

3 RESULTS AND DISCUSSION

One of the major issues for fabrication of nanoscale heterostructures is the facile manipulation of chemical composition and morphologies. By tuning the thickness of cobalt with different sputtering power, these physical characteristics could be easily controlled. Figure 1 (A-C) shows CuO-Co₃O₄ nanowires heterostructures that were fabricated after annealing of CuO-Co nanowire heterostructures, where Co was sputtered at different
powers (50-200 W). Here all other sputtering conditions such as gas flow rate, pressure, and duration remained the same. A polycrystalline $\text{Co}_3\text{O}_4$ shells were formed after the annealing process. It is observed that the vertical alignment of CuO nanowires is well-maintained at lower sputtering power (50 W) but the nanowires are curved at higher power (200 W). This is because at higher sputtering power, the impinging Co species has greater momentum loss on the surface of CuO nanowires and results in nanowire bending, which remains even after the post deposition annealing process [11]. The increase of sputtering power can accelerate the sputtering speed, and effectively increase the loading amount of cobalt onto CuO. SEM images (Figure 1) clearly show that at low sputtering power, nanowire-nanoparticles heterostructures with bulb-shaped tips were formed. At higher powers, more Co was sputtered onto CuO nanowires, and the heterostructures are mainly in core-shell morphology. At 50 W sputtering powers, bulb-shaped tip morphology of nanowire heterostructures was observed and could be attributed to the migration of cobalt toward flat tip driven by chemical potential difference [11] between the curved nanowire surface and the flat nanowire tips. When sputtering power increased to 150 W, nanoparticles were found along the nanowires. Diameter of nanowires increased from ~67.3±12.6 nm at 50 W to ~96.9±16.4 nm at 200 W. More uniform shell formation is observed for thicker shells and at higher powers.

Figure 1. SEM and TEM images of CuO-$\text{Co}_3\text{O}_4$ core shell nanowires with different sputtering power. (A-C) 50 W, (D-F) 150 W, (G-I) 200 W. Lattice spacing of 0.467 nm in (C, F, I) corresponds to $\text{Co}_3\text{O}_4$ (111).

Prolonged Co sputtering deposition duration to 4 h led to very thick Co shells with a baseball bat-like morphology (Figure 2A). The authors believe that the competition between Co surface migration and chemical potential differences on the nanowire surface for this prolonged duration was dominated by line-of-sight deposition process and resulted in the observed morphology. In addition, nanowire tips directly facing the incident depositing species acquired thicker Co as compared to the nanowire base. The role of shadowing effect cannot be ruled out here. Average diameter of tip was calculated to be ~1.3 µm while the root was ~200 nm (Figure 2B). XRD (Figure 2E) showed well-crystallized Co with hcp structures. Annealing of thick CuO-Co nanowires in air could convert Co into $\text{Co}_3\text{O}_4$ as showing in Figure 2(C and D) and Figure 3. Before annealing, Co:O ratio from EDX is ~ 8.44. This is mainly due to large content of sputtered cobalt. After annealing, atomic percentage of oxygen increased to 48.25% owing to oxidation of cobalt. SEM image at high magnification (Figure 2D, dotted cycle) shows growth of $\text{Co}_3\text{O}_4$ nanowires. This is also observed for cobalt foil annealed at high temperature with water vapor [12]. The magnetic property was also measured by AGM (Figure 2F). Compared with non-magnetic CuO nanowires, CuO-Co nanowire heterostructures showed $1.42\times10^{-4}$ emu for perpendicular and $9.95\times10^{-5}$ emu for parallel. This difference between two orientations indicates the existence of magnetic anisotropy in CuO-Co nanowire heterostructures [13].

Figure 2. (A) SEM and (B) TEM image of CuO nanowires coated with thick Co layers showing baseball bat-like morphology. (C and D) SEM images of CuO-$\text{Co}_3\text{O}_4$ nanowire heterostructures after annealing. Dotted circle in (D) shows the growth of nanowires on thick Co layer. (E) XRD pattern and (F) magnetic hysteresis loops for CuO-Co CuO-Co nanowire heterostructures.
Effects of Co$_3$O$_4$ shell thickness on final phenol photodegradation efficiency were also studied (Figure 4) [11]. The dotted box in the figure 4 indicates the highest photodegradation efficiency for different conditions. It clearly shows that both UV light and H$_2$O$_2$ could significantly improve the efficiency. However, photodegradation under visible light illumination and without sacrificing agent is the most desired for photodegradation. Thus, figure 4 shows that ~6 nm Co$_3$O$_4$ on CuO nanowires showed the highest efficiency for phenol photodegradation in visible light illumination and without sacrificial agent [11]. This could be attributed to the thin Co$_3$O$_4$ shell on CuO nanowires, which allows for retaining the photoactivity of the core CuO nanowires and increases the charged transfer at the interfaces with high suppression of charge recombination processes. The analysis of band gap energies for such nanowire heterostructures as well as their band diagrams have been recently reported [11].

4 CONCLUSIONS

Co layer with different thicknesses were coated onto CuO nanowires by sputtering at different sputtering power and duration. Subsequent annealing of CuO-Co nanowire heterostructures resulted in CuO-Co$_3$O$_4$ nanowire heterostructures with different morphologies including nanowire-nanoparticles, core-shell nanowire, and baseball bat like nanowires. The baseball bat-like morphology could be attributed to line-of-sight sputter deposition dominating surface migration and chemical potential differences for Co species onto the CuO nanowires. Effects of shell thickness on photodegradation efficiency at different conditions were also studied. Approximately 6 nm Co$_3$O$_4$ on CuO nanowires resulted in highest efficiency under visible light illumination without sacrificing agent due to improved charge carrier lifetime assisted by charge transfer at the interface.

ACKNOWLEDGEMENTS

This work was funded by National Science Foundation (Award No. 0925445), the associated NSF-REU supplemental award, 2012 NSF-EPSCoR RII award, and Research Grant Committee awards to Dr. Chopra. The authors thank the Central Analytical Facility (CAF) for characterization and UA microfabrication facility for clean room. The authors thank Dr. S. Kapoor for proof reading the manuscript.

REFERENCES

[7] X. Luan, D. Guan, Y. Wang. “Enhancing High-Rate and Elevated-Temperature Performances of Nano-Sized...


