Sculpting nanocavities via thermal stimulated Kirkendall effect oxidation

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Abstract

Controlling the shape, morphology, and porosity of hollow nanostructures is a pivotal issue for adjusting the characteristics of tailor-made nanomaterials to expand their application to more fields. Although many hollow metal oxides have been developed, studies on the construction of hollow bimetal oxide heterostructures with controllable nanocavities in different morphologies and high crystallinity through Kirkendall effect is still ascendant. Using this strategy, nickel nanotubes with smooth walls was acquired through continuous oxidation treatments on CuNi nanowires at 200 °C. Oxidation treatment at high temperature (300 °C) on CuNi nanowires produced nickel oxide nanotubes containing periodic copper nanoparticles, nickel oxide nanotubes with a bamboo-like structure and nanoforests. In addition, thin CuO nanowires with diameters of 5–10 nm grew on nanowires at 400 °C. Finally, the mechanisms of sculpting nanocavities at high and low temperatures were elucidated. An in-depth understanding of the thermally stimulated Kirkendall effect in bimetals has a significant influence on the design and fabrication of new hollow multifunctional hetero-nanostructures with potential applications in energy storage, catalysis, and gas sensing.

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1. Introduction

Hollow nanostructures have attracted increasing attention owing to their unique catalytic [1,2], sensing [3], electronic properties [4], which make them suitable for a variety of technological applications. Different methods have been applied for the fabrication of hollow nanostructures, such as the template-assisted method [5], Ostwald ripening [6], surface-protected etching [7], and galvanic replacement [8]; however, a more straightforward method to produce hollow nanostructures is to use the oxidation-mediated Kirkendall effect, which is preferred in practical applications because of the significantly reduced production cost, simplified synthesis procedures, and the ease of scaling up [9–11]. In brief, the Kirkendall effect refers to the boundary motion between two metals that occurs during thermal oxidation because of their disequilibrium ionic diffusion rates. When an oxide layer is initially formed on the metal surface, subsequent oxidation occurs by a combination of the out-diffusion of metal ions and in-diffusion of oxygen across the oxide layer. If metal ions diffuse faster than oxygen through the oxide layer, vacancy implantation will occur in the system. Accordingly, cavities are formed within the structure owing to the agglomeration of the vacancies [12,13]. Compared with that of mono-metals, the oxidation of bimetallic nanostructures is more complicated owing to the possible selective oxidation of one component [14–16]. For a wide range of bimetallic materials, controlling the shape, morphology and porosity of hollow nanostructures is a pivotal issue for tuning their structures and controlling their properties. For example, the magnetic performance of hollow nanostructures transformed from FeCo through cation exchange is improved [17]. Multi-shell CuO-NiO porous microspheres exhibit a larger-than-theoretical capacity of 1061 mAhg⁻¹ after 200 charge-discharge cycles, which is very prominent in various CuO or NiO electrode structures [18].

Notably, given the impending energy crisis and ever-increasing negative effects on the environment, transition metal oxides are outstanding materials for energy-related applications including fuel cells, lithium-ion batteries, and supercapacitors with satisfactory cycling performance [19,20]. Among these oxides, CuO has fascinating characteristics such as abundant availability, non-toxicity,
low cost, and easy fabrication of various shapes with nanometer size [21]. Owing to its high specific capacitance and electrical conductivity, NiO has also been considered as a promising electrode material for supercapacitors, lithium-ion batteries, and solar cells [22]. More recently, promising multi-component combinations or gentle methods have been used to enhance the specific capacitance, which can not only integrate the properties of different components, but also exert a synergistic effect on various properties. Nevertheless, the cycling performance of all transition metal oxides remains unsatisfactory, mainly because of the large volume expansion/contraction associated with the ion insertion and extraction processes. An efficient approach to address this issue is to fabricate porous electrode nanostructures [18,23]. When used as an energy storage material, hollow structure metal oxide always mixed with conductive material and binder in proportion as electrodes. The conductivity of the electrode can be effectively improved through using conductive polymers as a binder or adding conductive components into the binder [18,24]. Moreover, the mechanical strength of the polymer binder plays a critical role in maintaining the integrity of the electrode structure [25]. Although some transitional metal oxide hollow nanostructures have been acquired using the oxidation-mediated Kirkendall effect, such as CuO [26], NiO [14,27], FeO$_2$ [28], CoO [29], Al$_2$O$_3$ [30,31] and ZnO [32], studies on the construction of hollow bimetal oxide hetero-nanostructures with controllable nanocavities in different morphologies and high crystallinity on account of the nanoscale Kirkendall effect is still ascendant.

In this study, a thermal oxidation reaction under ambient air was used to synthesize a diverse set of hollow copper oxide-nickel oxide hetero-nanostructures by controlling the temperature and reaction time. These hetero-nanostructures included nickel nanotubes with uniform wall thickness, nickel oxide nanotubes containing periodic copper nanoparons, and nickel oxide nanotubes seamlessly integrated with copper oxide branches (NiO-CuO 3D nanowire architecture, namely nanoforests). Furthermore, the different oxidation behaviors of CuNi core-shell nanowires were divided into low- and high-temperature mechanism. An in-depth understanding of the Kirkendall effect in bimetals provides new avenues for engineering multifunctional hollow hetero-nanostructures with potential applications in energy storage, catalysis and electronics.

2. Experimental methods

2.1. Preparation of CuNi nanowires

Copper-nickel core-shell nanostructures were synthesized according to a previous study [33]. First, cetrimonium bromide (CTAB) and hexadecyl amine (HAD) were mixed and melted. Next, copper acetylacetone was added to the solvent, reaction vessel was incubated at 130–200 °C for 6 h, and precipitate was acquired from the bottom of the vessel. After the synthesis of Cu nanoparticles, nickel acetate was added to the reaction solution to obtain the Cu core-Ni shell nanowires. Finally, the precipitate was collected and re-dispersed in toluene for further experiments.

2.2. Thermal heating and structural characterization

Structural evolution of CuNi nanowires was performed using two thermal stimulation approaches. In the first approach, pristine CuNi nanostructures were dissolved in toluene to obtain a homogenous nanowire solution; then, a drop of the solution was dispersed onto the frame of a Mo transmission electron microscopy (TEM) grid. Ex situ oxidation was performed by utilizing a tube furnace in air at 200 °C, 300 °C, and 400 °C, and then the nanostructures were analyzed by TEM imaging (Fig. 1a). In the second approach, an in situ thermal heating experiment was carried out using TEM and a heating stage (Protochips Aduro™) with an electrical heating chip that served as both the specimen support grid and the heating element, and the configurations are showed in Fig. 1b. Energy dispersive X-ray spectroscopy (EDS) images and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images were obtained utilizing a probe-side aberration corrected FEI Titan 80–300 S/TEM “ChemiSTEM™” instrument operated at 300 kV. In situ structural evolution was acquired using a Tecnai 20 TEM instrument (FEI).

3. Results and Discussion

CuNi nanowires were synthesized by a modified synthesis process according to previously published research [33]. The HAADF-STEM and TEM images of the CuNi nanowires (Fig. S1a and S1b) indicated that the as-synthesized nanowires had excellent dispersibility and an overall average size of 50 nm. The corresponding line scan intensity of the synthesized CuNi nanowire in Fig. S1c demonstrated that Cu was concentrated in the core region, whereas Ni was distributed in the shell. The oxidation behavior with structural evolution of CuNi nanowires was investigated by utilizing a tube furnace in air, and the schematic diagram is shown in Fig. 1a. Dispersed CuNi nanowires were chosen for analysis to guarantee that the vapor transmission of oxygen to the nanowires was not hindered by the adjacent nanowires. Moreover, to investigate the influence of oxygen on the structural evolution, in situ thermal treatment experiments were carried out using the previously mentioned Titan 80–300 TEM instrument operated at 300 kV under a vacuum of 1.8 × 10$^{-5}$ Pa. The configurations of the electrical heating chip and heating holder are shown in Fig. 1b, and the details are described in a previous study [34].

The thermal oxidation process was performed at different temperatures and reaction times, and the TEM images and corresponding schematic diagrams of the four different morphologies are shown in Fig. 2. At lower temperatures (200 °C), as indicated in the TEM image shown in Fig. 2b, CuNi nanowires were transformed into nanotubes by thermal oxidation. Under these conditions, a nanowire with a relatively short length was transformed into a hollow structure with a comparatively smooth surface as indicated by red arrows in Fig. S2, whereas the middle section of a nanowire with a relatively long length was still solid (Fig. S2), which might be related to the formation mechanism of the hollow nanotube. As shown in Fig. S3, there is some material flowing out from both ends of the nanowire as pointed by red dotted circles. EDS spectra from Fig. S3a marked by 1, 2, 3 were shown in Figs. S3e-3g, indicating this material was Cu.
element (Mo signal is from Mo frame). Whereas the nickel shell of the core–shell nanowire did not change, resulting in the formation of relatively smooth nanotubes. Thin amorphous nickel oxide shells were observed on the shell (Fig. S4), which was consistent with a previous study [35]. The prolonged oxidation time did not increase the thickness of the shell at 200 °C, demonstrating that nickel oxide shells of 2–3 nm thickness were passivating layers that hindered further oxidation. The distribution of Ni, Cu, and O in the nanotubes was determined by EDS analysis in the HAADF-STEM mode. As shown in Fig. S5b, the elemental map of a representative nanotube demonstrated that Cu and Ni were uniformly distributed throughout the shell, indicating the formation of the nanotube. Additional evidence for nanotube formation was provided by line scanning analyses in the HAADF-STEM mode. As shown in Fig. S5c, Ni was more prevalent than Cu and O in the elemental composition of the shell. In addition, the high-resolution TEM (HRTEM) (Fig. S5e) images of the nanotubes also indicated well-developed crystallinity and clear lattice fringes with spacing corresponding to Ni ((111)−2.0 Å and (200)−1.7 Å). After structural evolution, the average size of the nanotubes was 53 nm, which was larger than their core-shell parents.

When these bimetallic nanowires were exposed to air at 300 °C for 10 min of oxidation, nickel oxide nanotubes containing periodic copper nanoparticles were obtained (Fig. 2c). In contrast to Cu nanowires, which form completely hollow oxide nanotubes after 5 min of oxidation [36], discontinuous copper cores remained within the nanotubes in the case of CuNi nanowires. Noticeably, there is still some materials flowed out at the end of the CuNi nanowire as indicated by the red dotted circle (Fig. S6). Larger lattice spacings were observed after oxidation-induced shell growth, and the lattice spacings of approximately 0.24 nm and 0.20 nm corresponded to the values of the (111) and (200) planes of NiO (Fig. S7b), respectively, further demonstrating that the formed shell was made of nickel oxide. The HRTEM and EDS spectra further suggested that the out-of-shell effluent was mostly amorphous copper oxide (Fig. S7c). Interestingly, for oxidation durations exceeding 30 min at 300 °C, the nickel oxide nanotubes containing periodic metallic particles were converted into bamboo-like nickel oxide nanotubes (Fig. 2d). At the same temperature, as the heating time increased, Cu will gradually diffused outward and finally formed a fully empty nickel oxide nanotube with copper oxide branches (nanoforests), as shown in Fig. 2e.

However, unlike the structural evolution that occurred at low temperatures, copper oxide (CuOx) nanowires grew perpendicular to the surface of the CuNi nanowires when the oxidation temperature was raised to 400 °C [37], as demonstrated by the TEM image and EDS spectrum in Fig. S8. The HRTEM image of the newly grown nanowire showed in Fig. S8c clearly had lattice spacings of 0.34 nm that did not match the known proportion of copper oxides, thus this mixture was composed of CuOx. The formation of CuOx oxide nanowires was driven by the stress originates from the molar volume mismatch at the CuOx/CuNi interface. The CuOx layer adjacent to the interface was subject to the compression imposed by the CuNi nanowire owing to its smaller molar volume, while the outer surface of the CuOx layer was stress-free. Hence, a stress gradient existed throughout the CuOx layer and prompted the outdiffusion of Cu ions from the high-stress regions of the CuOx/CuNi interface via grain boundaries in the CuOx layer to the low-stress region of the outer surface, where Cu ions were deposited and then reacted with impinging oxygen molecules to form CuOx. Subsequently, to investigate whether a higher oxidation temperature was a necessary condition for such a phenomenon, a comparable method was used to achieve complete oxidation at an oxidation temperature of 200 °C for 10 h. The HAADF-STEM image and corresponding line scan intensity of the nanotube shown in Fig. S9 revealed that a multiwalled CuOx-NiO nanotube was generated due to the Kirkendall effect instead of the newly formed nanowires.

One of the pivotal issues in the oxidation of bimetals is whether the oxidation of all elements occurs uniformly, or whether one element oxidizes in preference to other elements [38,39]. STEM was utilized to perform HAADF imaging coupled with spatially resolved EDS to detect the distribution of Cu, Ni, and O in the obtained morphologically complicated heterogeneous nanostructures, as shown in Fig. 3. Fig. 3a clearly shows that the newly prepared CuNi
nanowire had a core-shell structure with a smooth surface. First, we focused on sample oxidation at 200 °C for 30 min. Based on the line scan intensities in Fig. S5c, the shell was dominated by Ni, but also contained Cu and O. To further investigate the composition of the nanotube, corresponding HRTEM images were obtained, as shown in Fig. S5e. This nanotube most likely was composed of Ni. Consequently, Ni exhibited a certain degree of selective oxidation during the oxidation process. For the nanowires oxidized at 300 °C for 10 min, the STEM-EDS mapping indicated that the cores of the newly formed structures exhibited periodic Cu particles, whereas the shell was composed of Ni and O elements (Fig. 3b). In this case, when periodic copper nanoparticles were formed in the nanotube, the axial diffusion of copper through the ions in the core was hindered because the particles were no longer connected [40]. The out-diffusion rate of copper atoms perpendicular to the nickel oxide shell is greater than the diffusion rate along the axial direction. At this stage, the copper ions diffused arbitrarily out of the tube through the oxide shell (Fig. 3c).

In addition, we annealed CuNi nanowires at 450 °C (even as high as 650 °C) in an ultra-high vacuum environment. The chamber pressure was maintained below approximately 10⁻⁸ Torr during annealing. In this case, only phase segregation occurred in the nanowires, and no oxidation occurred (Fig. 510). According to the EDX spectra, the dark color is Cu phase, and the light color is Ni phase. Hence, the result that oxygen has a great influence in controlling the formation of nanocavities is raised, although the formation of heterojunctions is partially driven by temperature.

The significant morphological changes observed in these figures have been suggested to be characteristic of the Kirkendall effect at the nanoscale [41,42]. According to the experimental data, the distinct behaviors pertaining to the formation of nanocavities via thermal oxidation of CuNi nanowires can be explained utilizing low (200 °C) and high (300 °C) temperature regimes (Fig. 4). In all situations, a thin nickel oxide shell would come into being encircling CuNi nanowires during the early stages of oxidation. At low temperatures, the thin nickel oxide shell becomes a passivating layer that prevents void formation caused by the Kirkendall effect [35,43,44]. Nickel shells require higher temperatures for significant conversion to nickel oxide [35]. In this case, for the copper cores at both ends, since there is no isolation of the nickel shell (as pointed by red arrows in Fig. S5f), the copper element is in direct contact with the external environment. When an oxide layer is initially formed on the Cu surface, subsequent oxidation occurs by a combination of the out-diffusion of Cu ions and in-diffusion of oxygen across the oxide layer. Since the coefficient of the out-diffusion of copper ions through the oxide shell is higher than that of the in-diffusion of the oxygen ions [26], vacancy implantation will occur at the ends of nanowires, as shown in Fig. 4a. Therefore, nickel nanotubes with smooth walls were obtained.

On the other hand, when oxidation occurred at 300 °C, the diffusion coefficients increased progressively which are very low at low temperature [45]. At the metal/oxide interface, nickel and oxygen ions diffused outward and inward through the formed oxide shell, respectively, as shown in Fig. 4b. Because the outward diffusion of nickel ions (i.e., outside the nanotube) through the thin nickel oxide shell is much faster than the inward diffusion of oxygen ions (i.e., towards the metal core), vacancies coalesce to form voids [46]. The saturation and aggregation locations of these vacancies are determined by the vacancy generation rate and the vacancy diffusion rate, which are important parameters to consider when comprehending the Kirkendall effect [47]. For many metals, the diffusion rate of metal ions across the oxide (vacancy implantation rate) is much higher than the vacancy diffusion rate during the oxidation process [27,48]. This indicates that the creation of vacancies at the metal/oxide interface is quicker than the diffusion of vacancies away from the interface. The low mobility rate of these created vacancies can cause rapid generation of vacancies in their vicinity, enhancing the probability of aggregation along the interface. Therefore, under this situation, a large number of small voids appear along the metal/oxide interface [49]. Nevertheless, Ni is a distinctive material owing to its high vacancy diffusion rate. The vacancy diffusion rate and injection rate are very close [27]. Because of this, during nickel nanostructure oxidation, the implanted vacancies at the metal/oxide interface have an adequate mobility rate to diffuse over long distances towards the metal core before they coalesce. This makes the construction of larger voids in the core possible. During this process, Cu ions will also diffuse outward, and oxygen will also enter Cu core, but at this time, the oxidation of Ni element is dominant. With the increase of the nanowire volume and the appearance of large voids in the nanowire, the Cu core will be separated causing the formation

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**Fig. 3.** Scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF) images and energy dispersive X-ray spectroscopy (EDS) elemental mapping images of the CuNi nanowires before and after thermal oxidation under ambient air. (a) 0 min, (b) At 300 °C for 10 min, and (c) At 300 °C for 30 min. Rose red represents Ni, green represents Cu, and red represents O in the images.
As the reaction proceeds, the oxygen outside the nanowire will enter the Cu core through the nickel oxide shell, and the oxygen in the hollow hole formed by the oxidation of the nickel shell in the nanowire will also enter the copper core along the axial direction. Meanwhile, driven by the stress and vapor pressure in the void structure, the Cu ions would outdiffuse. However, since the periodic copper nanoparticles shaped in the nanotube are no longer attached, the outdiffusion rate of copper atoms perpendicular to the nickel oxide shell is greater than the diffusion rate along the axial direction [40]. At this moment, the copper ions diffuse arbitrarily towards the outside of the nanotube through the oxide shell. Noticeably, as the annealing time is prolonged, the oxide shell broke (Fig. S11). These cracks offered diffusion channels for oxygen ions through the oxide shell to react with the copper ions, causing the expansion of the shell [50]. As the oxidation process progressed, the atoms that escaped from the hollow tube crystallized in the outer layer of the oxide shell, causing the bamboo-shaped hollow nanotube to transform into a hollow dendritic structure.

4. Conclusion

In summary, through controlling the oxidation time and temperature of copper-nickel nanowires, many different hollow nanostructures were obtained, such as nanotubes, bamboo-like structures and nanoforests. The mechanisms of sculpting nanocavities via thermal oxidation of CuNi nanowires can be divided into low- and high-temperature regimes. For low-temperature oxidation (200 °C), the fabrication of hollow nickel tubes was mainly due to the diffusion of the copper core from the two ends of the nanowire, since the oxidation of the nickel shell required a higher temperature. The high-temperature (300 °C) regime was dominated by the Kirkendall effect on account of the thermal-enhanced diffusion rate of nickel and copper ions via the oxide layer. An in-depth understanding of
declaring competing interests

Luping Tang, Yiwie Liu, Xiaof Wang: Do the experiments, Analyze the data, Edit the manuscript.
Lanran Wang, Jing Sun, Kuibo Yin, Tao Xu: Help to analysis and Calculate the data.
Longbing He: Revise the manuscript.

Applying Appendix: Supporting information

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References


