Structural and morphological evolution of free-standing Co₃O₄ nanowires via water vapor-assisted thermal oxidation of Co foil

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Abstract

Nanostructured cobalt oxide (Co_3O_4) has been regarded to be of great interest for catalysis, gas sensors, and energy conversion/storage. In this paper, we reported a water vapor-assisted thermal oxidation approach for the scalable synthesis of free-standing Co_3O_4 nanowires with controlled size, crystallization, and spatial density. Thermodynamic calculation was carried out to understand the fundamental mechanism of the water vapor-assisted nanowire formation process. For the first time, we found the incorporation of water vapor in the growth system modified the nanowires formation pathway. Cobalt hydroxide ($\text{Co}(\text{OH})_2$) was recognized to take a critical intermediate role during the growth. The proposed mechanism was further verified by understanding the influence of various growth parameters on the thermal oxidation process and product morphology. It was observed that the feeding rate of water vapor and type of oxygen source have a critical influence on the spatial density of Co_3O_4 nanowires while the temperature shows a dominant effect on the product morphology. Finally, the representative Co_3O_4 products were characterized for their composition, optical and magnetic properties. This study accumulates deeper understanding on the fundamentals of water vapor-assisted thermal growth of metal oxide nanostructures and successfully provides a facile approach for the scale production of Co_3O_4 nanowires for future applications.

Keywords: Co_3O_4 nanowires, water vapor-assisted thermal oxidation, thermodynamics, optical and magnetic properties

1. Introduction

Recently, great attention has been paid to the development of nanostructured cobalt oxide (Co_3O_4) materials due to their excellent (electro-) catalytic performance, attractive theoretical specific capacitance (3560 F g^{-1}) and high corrosion stability [1-3]. Moreover, Co_3O_4 itself is an earth-abundance, low-cost, and environment-friendly material, which makes it of more promise as a substitute for many noble and rare materials (Au, RuO_2 , IrO_2 , for instance). The broad application areas evolve heterogeneous catalysis, gas sensors, lithium-ion batteries and supercapacitors [4-8]. However, at current the main challenge for the utilization of Co_3O_4 materials lies in their high electric resistance, poor structural stability and low heterostructuring possibility. The performance of Co_3O_4 materials was found to have a great dependence on their specific surface area and electron state [9,10]. Thus, the development of novel synthetic strategies to realize the fabrication of a variety of Co_3O_4 nanostructures with controlled morphology and improved crystalline state will be of great worth and importance. With this regard, one dimensional nanowire structure of Co_3O_4 provides increased specific surface area, optimized pathway for electron and mass transport, and increased electrochemical reactivity [11-14], which might be of great favor for its application as electrode materials, catalytic substrates and sensors.

Various approaches have been proposed for the preparation or growth of Co_3O_4 nanowires however most of these are associated with the precursor-based wet-chemical or hydrothermal process [15-17]. These methods lead to difficulty in the control of product morphology and chemical purity, meanwhile, the obtained Co_3O_4 nanowires have large size (200 nm to 300 nm in diameter) and polycrystalline structure [18,19], which are not preferred for the transfer of (photo-

excited) electrons or holes in photocatalytic and electrochemical processes. Another widely-used method for the growth of similar metal oxide (e.g., CuO, ZnO and Fe₂O₃) nanowires is associated with the direct oxidation of their metal foils [20-22]. The nanowires obtained by this approach show uniform and well-controlled size as well as good monocrystalline [22,23]. However, this method was found to be difficult for the growth of Co₃O₄ nanowires. Several studies have reported the direct oxidation of a cobalt foil [24-26], however, the obtained Co₃O₄ nanowires were either distributed in the edge area only [24] or have very low yield on the main surface [26]. Recently, a water vapor-assisted thermal oxidation approach was widely proposed for the growth of similar metal oxide nanowires [27-29]. It is believed that the presence of water vapor accelerated the thermal oxidation by promoting nucleation and nanostructure growth. Meanwhile the water vapor generated in-situ are also expected to catalyze the decomposition of oxygen gas required for the oxidation of metal species on substrate [30,31]. However, to the best of our knowledge, there has been no systematic study focused on large scale production of Co₃O₄ nanowires using such water vapor-assisted thermal oxidation method.

To sum up, achieving the facile growth of monocrystalline Co₃O₄ nanowires with large yield is of great worth and meaning. In this paper, we report the water-vapor assisted thermal oxidation method for the single-step growth of free-standing Co₃O₄ nanowires with controlled size, good crystallization, and high spatial density. Fundamental thermodynamic calculation was conducted to understand the basic principle of the water-vapor assisted thermal growth and the function of water vapor during the formation of Co₃O₄ nanowires. Systematic parameter study was carried out to optimize the growth process and further verify the proposed thermal oxidation mechanism. It's worth mentioning that besides the winning of high-yield Co₃O₄ nanowires, several other interesting cobalt oxide nanostructures were also obtained. Thus, this study not only provides

deeper knowledge on the water vapor-assisted thermal growth of Co_3O_4 nanowires but also opens new insights for future structural development of novel metal oxide nanostructures.

2. Experimental section

2.1. Materials and methods

Cobalt foil was purchased from Alfa Aesar (Ward Hill, MA), Cobalt powders were purchased from ACROS (Geel, Belgium). Cobalt targets (99.999%) were supplied by AJA International, Inc. Nitric acid was purchased from VWR (Atlanta, GA). DI-water ($18.1 \text{ M}\Omega\text{-cm}$) was obtained using a Barnstead International DI water system (E-pure D4641). All chemicals were used without further purification. Branson 2510 Sonicator (Danbury, CT) was used to assist the surface clean of Co foil/powders in acetone and DI-water. Thermal oxidation experiments were carried out in a MTI GSL-1100X CVD furnace.

2.2. Synthesis of Co_3O_4 nanostructures by thermal oxidation of Co foil

The as-purchased Co foil was first sonicated in acetone and DI-water for 5 min in sequence. This was followed by further treating the Co foil in 10% HNO_3 solution for 15 s to remove the native surface oxide. Various surface-treating methods were used to improve the Co_3O_4 nanowire growth: surface polishing of Co foil was done using BASI PK-4 polishing kit; the bended Co foil was obtained by manually bending the sample for ~20 times; the scratching of Co foil was conducted using an X-ACTO blade; Sand-blasting of the Co foil was conducted using the ALC Plastic Benchtop Sandblaster (ALC-40390); Co film with various thickness were sputtered on oxidized Si substrate using the ATC ORION sputtering system (AJA international, Inc.); the as-

purchased Co powders were treated with acetone, DI-water and 10% HNO₃ as described above. For the growth of Co₃O₄ nanowires, the prepared substrate was put in the center of the quartz tube furnace. Possible growth installations were schematically shown in Fig. S1 (Supplementary Information). The furnace was then heated up to the target temperature and further kept for certain time.

2.3. Characterization methods

JEOL-7000 Scanning Electron Microscopy (SEM) equipped with energy dispersed X-ray spectroscopy (EDS) were used for morphology observation, dimensional measurement and composition analysis. Tecnai F-20 Transmission Electron Microscopy (TEM) were used for the morphology and structure analysis. TEM samples were prepared by dispersing the as-prepared samples on lacey carbon TEM grids (Ted Pella Inc. Redding, CA). Raman spectra were collected using Bruker Senterra system (Bruker Optics Inc. Woodlands, TX) equipped with 785 nm laser source. XRD patterns were obtained in the Philips X'Pert-MPD X-ray Diffraction (XRD) System. Magnetic properties were characterized using a Princeton PMC Micromag 2900 alternating gradient force magnetometer (AGM). Uv-vis reflectance spectra were collected with DH-2000 UV-VIS-NIR light source and the optical transition energies of Co₃O₄ nanostructures were further determined using equation (1):

$$ah\nu = A(h\nu - E_g) \quad (1)$$

where a is the absorption coefficient, A is a constant, $h\nu$ is the energy of light and n is a constant depending on the nature of the electron transition (n assumes the values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions,

respectively.). Since the absorption coefficient a is proportional to Kubelka-Munk function ($F(R)$):

$$F(R) = \frac{(1-R)^2}{2R} = \frac{a}{s} \quad (2)$$

(where R is the reflectance, k is the absorption coefficient and s is the scattering coefficient), the band gap energy can be obtained from the plots of $[F(R)hv]^{1/2}$ vs. hv as the intercept at $[F(R)hv]^{1/2} = 0$ of the extrapolated linear part of the plot.

3. Results and Discussion

3.1. Water vapor-assisted thermal growth and mechanism

The Schematic in Fig. S1 (see Supplementary Information) shows two basic experimental setups for the growth of cobalt oxide nanostructures *via* the water-vapor assisted thermal oxidation of Co foil. We proposed two designs for the feeding of water vapor. As shown in Fig. S1A, water vapor was generated by evaporating DI-water on a hot plate. The water vapor was then mixed with air and fed into the furnace for the growth. The flow rate can be modulated by controlling the temperature of the hot plate. In the second design (Fig. S1B), air and water vapor was fed into the furnace separately. DI-water was constantly fed into the quartz tube with an accurate syringe pump (Fisher Scientific). As the DI-water reached the high-temperature region, it was evaporated and flowed into the furnace. The first design (Fig. S1A) allowed a good mixing of water vapor and air however the feeding rate could not be controlled accurately and large water vapor fluctuation was also observed, as a result the second design (Fig. S1B) was preferably used afterwards.

Fig. 1 demonstrates the influence of water vapor on the morphology and structure of Co_3O_4 products. Direct thermal oxidation of Co foil in air environment led to the growth of Co_3O_4 nanowires on the vertical edge area (Fig. 1A), however, very less nanowires were observed on the top surface of the substrate. This is consistent with the observation reported by Z. Dong et al. [17] We estimated the spatial density of Co_3O_4 nanowires on the top surface appearing to be $10^3\sim 10^4$ counts per cm^2 . TEM images of these Co_3O_4 nanowires were shown in Fig. 1B and C. One can observe that the diameter of the nanowires distributes in a wide range from ~ 100 nm to ~ 150 nm and the estimated nanowire length is $3\sim 5$ μm . High resolution TEM image (Fig. 1C) confirms the excellent single crystalline of the Co_3O_4 nanowires with (111) lattice plane, which is also indicated by the inset Fast Fourier Transform (FFT) image.

To evaluate the influence of water vapor on the morphology and structure of the Co_3O_4 products, water vapor was singly fed into the system. In this case, air in the tube was eliminated by water vapor and thus we observed the formation of Co_3O_4 nanorods (Fig. 1D and E). High resolution TEM image in Fig. 1F indicates that these Co_3O_4 nanorods also show single crystalline with a lattice orientation of (111). Towards this end, the co-feeding of air and water vapor (see inset in Fig. 1F) led to the growth of free-standing Co_3O_4 nanowires with highly increased spatial density (Fig. 1F). The nanowire is much more uniform (Fig. 1G), with an average diameter of ~ 96 nm and length of $4\sim 6$ μm . The lattice structure in Fig. 1H shows a lattice orientation of (220) for these Co_3O_4 nanowires.

To better understand the basic principle of cobalt oxide nanostructure formation with absence or presence of water vapor, thermodynamic calculations were carried out for various possible chemical reactions at a temperature range of 200 K to 1400K. As shown in Fig. 2A, formation of

CoO and Co₃O₄ *via* the direct reaction of Co with O₂ shows negative Gibbs free energy (ΔG) and thus is thermodynamically possible. However, this oxidation approach is prone to form cobalt oxide film on the substrate [32,33], leading to less formation of nanowire structure. With the feeding of water vapor in the growth system, ΔG for the formation cobalt oxide becomes positive (Fig. 2A), indicating the direct formation of oxide will be inhibited. This also explains the formation of very less Co₃O₄ nanorods in Fig. 1D. With the co-feeding of water vapor and air, ΔG for the oxidation reaction decrease but is still positive in a wide temperature range (Fig. 2A). Thus, it is reasonable to predict that the formation of Co₃O₄ nanowires is probably completed in several substeps. Several studies have proved the critical role of Co(OH)₂ on the formation of Co₃O₄ nanostructures [34-36]. As inspired, we proposed the following mechanism for the formation of Co₃O₄ nanowires. As shown in Fig. 2B, the system forms a galvanic cell with the co-presence of water vapor and oxygen. One half reaction leads to the decomposition of H₂O to OH⁻ while the other half reaction oxidizes the cobalt substrate to Co²⁺. The reaction of Co²⁺ and OH⁻ resulted in the formation of Co(OH)₂. Since Co(OH)₂ is not stable at high temperature, it is prone to convert into CoO. Finally, the oxidation of CoO to Co₃O₄ has a much negative ΔG and becomes thermodynamically feasible, leading to the formation of Co₃O₄ nanowires. The (electro-) chemical reactions of each step were further summarized in the following:

(1) Reduction of O₂:

(2) Oxidation of Co:

(3) Acid-base reaction:

(4) Dehydration and further oxidation:

This thermodynamic results indicate that the absorption of water vapor on the substrate would inhibit the formation of cobalt oxide film (also referred as cobalt oxide underlayer afterwards) and thus leads to the growth of large amount of free-standing Co_3O_4 nanowires. SEM images were collected to confirm the formation of cobalt oxide underlayers. As shown in Fig. S2A and B (Supplementary Information), we observed such oxide layer was composed of two sublayers. The overall layer thickness obtained with co-feeding of air and water vapor as well as its bottom layer were significantly decreased as compared with that obtained in air environment. EDS analysis were further conducted to evaluate the composition (Fig. S2C-F, Supplementary Information). Even through such EDS analysis in general is not accurate for oxygen element, one can also observe the oxygen content in the top layer is higher than that in the bottom layer (Fig. S2G and H, Supplementary Information). Based on previous reports of similar metal oxide system [22,23, 37], it is reasonable to predict that the bottom layer and top layer are corresponding to CoO and Co_3O_4 , respectively. These literatures also indicate that the formation of such oxide layer is of importance for the nanowire growth kinetics.

The mass transport mechanism of cobalt ions during the growth was schematically proposed in Fig. 2C. The nanowires were generally thought to form on the grains rather than from the grain boundary regions [23,38]. The vertically aligned grain boundaries provide critical path for the outward transfer of cobalt ions (Fig. 2C, left). The large lattice mismatch at the interface of Co/CoO and $\text{CoO/Co}_3\text{O}_4$ ensures difficulty for the local volume accommodation [22,23], which

generates enough stress at the interface serving as the driving force for the diffusion of cobalt ions from the high-concentration Co foil side to the low-concentration nanowire root region [38]. Similar stress-driven mechanism was also mentioned by Z. Dong et al [24] to explain the formation of Co_3O_4 nanowires in the edge area of the substrate. With the presence of water vapor, above thermodynamic analysis indicates that the formation of CoO bottom layer is largely inhibited (see Fig. S2A and B in Supplementary Information). This leads to the shortening of diffusion path for cobalt ions and thus the growth of Co_3O_4 nanowires with high spatial density becomes possible. Meanwhile, the authors also observed that the grain size of both CoO and Co_3O_4 decreased when water vapor was fed, which would provide more diffusion path for cobalt ions (Fig. 2C, right). Since the nanowires were thought to mainly grow on the grains of the top layer [22,37], refined grain size would also lead to more possibilities for the growth of Co_3O_4 nanowires. In addition, it is necessary to mention here that the presence of water vapor was reported to be able to promote the formation of oxygen vacancies [29,39], which also facilitate the diffusion of oxygen ions along the grain boundaries. A representative SEM image for the structure of cobalt oxide underlayer and the diffusion of cobalt ions was shown in Fig. 2D.

3.2. Influence of substrate treatment and additives

From above comments, one can understand that the existence of stress also takes a critical role in the growth of metal oxide nanowire in such thermal oxidation process [27,37,38]. Thus, creation of extra surface stress before the growth would be another promising approach to increase the spatial density of grown nanowires. Several substrate treatment methods were used in this paper for the generation of surface stress. These include surface polishing, substrate bending, surface

denting/scratching and sand-blasting. The corresponding product morphologies after the thermal oxidation were shown in Fig. 3A-D. The substrate polishing was conducted using a 120-grit Al_2O_3 sand paper however no obvious increased growth was observed (Fig. 3A). This is probably because the abrasive sand paper generated a lot of local heat which released the surface strain during the polishing. Bending of the substrate (see inset in Fig. 3B) led to the growth of Co_3O_4 nanowires with significant increased spatial density. However, the stress was mainly accumulated in the regions where the bending occurred (see Fig. S3A in Supplementary Information) meanwhile scalable stress creation is difficult. With this regard, surface denting/scratching (see inset in Fig. 3C) was found to be a simple, scalable, and reproducible method, which also led to high-density growth of Co_3O_4 nanowires (Fig. 3C, D and Fig. S3B-D in Supplementary Information).

Another surface-treating method is regarded as work hardening. For instance, S. Jin et al. [27] found that the work hardening of the steel substrate by shot-peening significantly improved the growth of Fe_2O_3 nanowires. In this study, we treated the Co foil with a sand blaster for various durations however no positive improvement of the growth was observed on these samples (see Fig. 3E and Fig. S4 in Supplementary Information). This is probably because the sand particles are much lighter than the stainless-steel beads (used by S. Jin et al.) and meanwhile the generated local heat released the surface strain. The morphology and shape of the substrate were also reported to have remarkable influence on the thermal growth of metal oxide nanowires [20,40]. Here we conducted the growth on chemically synthesized Co particles (Fig. 3F) and sputtered Co films (Fig. 3G) however no nanowires were observed grown on these two types of substrates (see Fig. S5 and S6 in Supplementary Information for details). Moreover, the influence of additives in DI-water on the morphology and spatial density of Co_3O_4 products [41] were further

demonstrated in Fig. 3G and H. One can observe that addition of KI in DI-water led to the formation of Co_3O_4 “nano-cookies” (Fig. 3H) meanwhile the addition of NH_4F resulted in rough surface with growth of Co_3O_4 nanorods (Fig. 3I). The morphology evolution mechanism for these two nanostructures is still unclear, however this is beyond the scope and aim of this paper and will be further studied in future.

3.3. Variation of growth parameters for process improvement

Fig. 4 demonstrates the influence of various growth parameters on the morphology and spatial density of obtained Co_3O_4 nanostructures. SEM images of representative samples after thermal oxidation with different water vapor feeding rate were shown in Fig. 4A-C. When the water vapor was fed either too fast or too slow, no high-density nanowires were formed on the substrate. Thus, it is reasonable to select a moderate feeding rate (12 ml/h) for the following studies. The influence of water vapor feeding rate on the dimension of Co_3O_4 nanowires as well as on the thickness of $\text{CoO}/\text{Co}_3\text{O}_4$ underlayer will be further discussed below. Fig. 4D-F show the SEM images of samples after thermal oxidation with flowing of various oxygen sources. One can observe that with a lower flow rate of air, the nanowires grown on the substrate resulted a low spatial density. However, this could be improved by slightly increase the air flow rate. More interestingly, when the oxygen source was changed from air to 5% O_2/Ar , significantly increased spatial density of Co_3O_4 nanowires were further observed. This is probably because the decreased oxygen content (with no influence on water vapor feeding rate) provided more driving force for the nucleation process [23] and meanwhile flowing of high-purity O_2/Ar effectively prevented possible contaminations from air (CO_2 , H_2 , and other dusts).

As further shown in Fig. 4G-I, the growth temperature was observed to have a dominant influence on the morphology of Co_3O_4 products. Lower temperature (375°C) led to the growth of vertically aligned Co_3O_4 nanoflakes (Fig. 4G). Further increase of growth temperature (425°C) resulted in the formation of nanotrapezoids (Fig. 4H). When the temperature was above 475°C , the Co_3O_4 products presented nanowire morphology. This observation can be well-explained by above thermodynamic analysis (see Fig. 2). Low temperatures were favorable for the formation of $\text{Co}(\text{OH})_2$ however its further conversion to CoO was inhibited. This actually gave large amount of nucleation while the growth of these nuclei was slow, as a result, formation of horizontally grown nano-flakes with high spatial density was observed. This finding has a good consistent with several studies reported previously [42-44]. With the increase of growth temperature, nucleation of $\text{Co}(\text{OH})_2$ was inhibited while its conversion to CoO became facilitated, which resulted in the continuous growth of one-dimensional nanowire structure. It is worth noting that when the temperature was beyond 625°C , no significant nanowire growth was observed due to the instability of Co_3O_4 nanostructures at high temperature. Further, the influence of growth duration on the morphology of Co_3O_4 nanowires was shown in Fig. 4J-L. Growing for 10 min and 30 min gave very less Co_3O_4 nanowires on the substrate. With the increase of growth duration (1-10 h), the density of nanowires obvious increased (Fig. 4K, L). However, when the growth was processed beyond 20 h, most of the nanowires were observed disappeared. This is probably due to the re-fuse and fracture of Co_3O_4 nanowires under long-time high-temperature process.

The influence of these growth parameters on the spatial density, diameter, length of these Co_3O_4 nanostructures as well as the thickness of the $\text{CoO}/\text{Co}_3\text{O}_4$ underlayer were further estimated from SEM demonstration and summarized in Fig. S7-S9 (see Supplementary Information). Fig. S7A

indicates that the highest spatial density of Co_3O_4 nanowires was obtained at a moderate feeding rate of water vapor. Either higher or lower flow rate led to decreased spatial density. This observation is consistent with above thermodynamic analysis since the presence of excess water vapor eliminated the oxygen content and thus nucleation of $\text{Co}(\text{OH})_2$ was reduced. In Fig. S7B, one can observe that the highest Co_3O_4 spatial density was obtained with the feeding of 5% O_2/Ar . Moreover, the spatial density was obviously decrease with the increase of temperature and growth duration (Fig. S7C and D) due to the fracture and re-fuse of nanowires.

Fig. S8 (Supplementary Information) shows the variation of length and diameter according to the growth parameters. The feeding of water vapor at 9 ml/h and 12 ml/h resulted in the highest nanowire length, further increasing the feeding rate led to decreased nanowire length (Fig. S8A) as described above. For the air flow rate set, 0.8 SLM of air flow gave the longest nanowire, however, this length was further increased when using 5% O_2/Ar (Fig. S8B). The growth temperature exhibited the most significant influence on the length of nanowires since it affected the morphology of the Co_3O_4 products (Fig. S8C). Fig. S8D shows that the nanowire length increased with the increase of growth duration (when < 20 h). In addition, one can also observe that the variation of growth conditions has no significant influence on the diameter of Co_3O_4 nanowires except the temperature. The relatively low temperatures (475°C and 525°C) resulted in smaller diameter of the nanowires, while the diameter increased at higher temperature due to the faster mass transportation during growth.

With respect to the thickness of $\text{CoO}/\text{Co}_3\text{O}_4$ underlayers, increased water vapor feeding rate led to decreased underlayer thickness because the absorption of water molecules on the substrate prevented the formation of oxide (Fig. S9A in Supplementary Information). This demonstrates a

good consistence with our thermodynamic prediction that the presence of water vapor inhibits the formation of cobalt oxide film and further confirms the new nanowire formation mechanism we proposed above. Moreover, we observed that the variation of air flow rate has no significant influence on the underlayer thickness (Fig. S9B) while the temperature contributes the most (Fig. S9C). The thickness was significantly increased due to the temperature increase. High temperature (500-800 °C) leads to the formation of more Co_3O_4 film but less nanowires as described above. In addition, the underlayer thickness increased at the first stage of growth (0-10 h) however no significant increase was observed afterwards (Fig. S9D). As a summary, the influence of various growth conditions on the morphology, length, and diameter of the obtained Co_3O_4 nanostructures as well as their influence on the thickness of the underlayers were schematically summarized in Fig. S10 (Supplementary Information).

From above demonstration one can observe that the growth temperature has the most significant influence on the Co_3O_4 products, leading to the evolution of interesting nanostructures including nanoflakes (375 °C), nanotrapezoids (425 °C), and nanowires (475 °C). TEM analysis was conducted to demonstrate their structure and morphology (Fig. 6). The average size of the nanoflakes is $\sim 158.6 \pm 20.3$ nm (Fig. 6A), with a lattice spacing of ~ 0.25 nm, which indicates the growth plane of (311). The nanotrapezoids (Fig. 6C) were observed to have an average width of $\sim 210.7 \pm 28.4$ nm at the bottom and $\sim 112 \pm 16.4$ nm at the top. The average height of these nanotrapezoids is $\sim 2.2 \pm 0.7$ μm . High resolution TEM image (Fig. 6D) indicates that their crystal plane is (311), too, with a lattice spacing of ~ 0.24 nm. The Co_3O_4 nanowires obtained at 475 °C exhibit a uniform shape (Fig. 6E) and good single crystalline structure (Fig. 6F). The average diameter of these nanowires is 109.5 ± 10.3 nm, with a length of 4.2 ± 1.4 μm . In addition, the lattice spacing of 0.23 nm indicates their growth direction is also (311). It is worth

mentioning here that such (311)-induced crystal plane of Co_3O_4 nanostructures has been widely proposed before for favorable charge transfer in many electrocatalytic, photovoltaic and electronic devices [27,45,46].

3.4. Properties characterization

Raman spectra were collected for understanding the chemical and phase composition of various Co_3O_4 nanostructures demonstrated in Fig. 6. As shown in Fig. 6A, the obtained Raman signals for all three samples are regards to spinel Co_3O_4 [47,48]. These include F_{2g} at $\sim 194\text{ cm}^{-1}$, $\sim 518\text{ cm}^{-1}$ and 617 cm^{-1} , E_g at $\sim 475\text{ cm}^{-1}$, and A_{1g} at $\sim 682\text{ cm}^{-1}$. The A_{1g} mode is assigned to the octahedral sites (CoO_6) in spinel Co_3O_4 while the E_g and F_{2g} modes are related to the combined vibrations of tetrahedral sites (CoO_4) and octahedral oxygen motions. One can observe that the nanowire and nanotrapezoid samples show similar spectra geometry while the F_{2g} mode (at 518 nm) of the nanoflake sample is obviously increased. This is probably attributed to the exposure of CoO underlayer since very few Co_3O_4 film was observed on this sample (see Fig. S9C in Supplementary Information). In addition, all of these Raman peaks are slightly shifted to the negative position as compared with bulk Co_3O_4 , which is probably due to the optical phonon confinement effect in such nanostructured materials, which causes uncertainty in the phonon wave vectors and then a downshift of the Raman peaks [49,50].

XRD patterns in Fig. 6B further confirmed the presence of different phases and elements in these nanostructured substrates. Crystallographic planes for CoO, Co_3O_4 and Co were constantly observed for all three samples. The presence of CoO peaks is due to the formation of CoO underlayer during the thermal growth, which is consistent with above SEM demonstration. The

peaks for the Co_3O_4 are attributed to both the Co_3O_4 underlayer and the standing nanostructures. The dominant (311) peaks of spinel Co_3O_4 for all three samples indicate the main growth direction of these nanostructures, which has a good consistence with the lattice spacing observed in above TEM demonstrations (Fig. 5).

Band gap energy of these three samples was evaluated using the Tauc plots converted from the UV-vis reflectance spectra in Fig. S11 (Supplementary Information). Considering Co_3O_4 is an indirect band gap semiconductor, basically two band gap energies were evolved for these Co_3O_4 nanostructures [51]. The former one located from 1.5 eV to 2.0 eV is regarded to the transitions from O^{2-} to Co^{3+} while the latter one observed at ~ 2.6 eV is for the transitions from O^{2-} to Co^{2+} . In general, the estimated band gap energies are consistent with previous literature [52,53], however, it does need to mention the band gap energies of the Co_3O_4 nanowire sample in Fig. 6C is slightly different from the sample in our previous report [27], which, probably, can be attributed to the inevitable error of this calculation method as well as the influence of sample geometry.

In regard to the magnetic properties, the room-temperature hysteresis loops for the three Co_3O_4 nanostructures were measured using an AGM system. As we know, the bulk Co_3O_4 is antiferromagnetic [54]. However, a little ferromagnetic property with un-saturated magnetization was observed on the Co_3O_4 nanowire sample (Fig. 6D). Such hysteresis is probably caused by the surface spins [13,24]. The Co_3O_4 nanoflake sample and nanotrapezoid sample exhibit increased magnetic properties with a saturation magnetization of $\sim 1.1 \times 10^{-3}$ emu, and $\sim 0.9 \times 10^{-3}$ emu, respectively. Besides, low remanent magnetization (see inset in Fig. 6D) were also observed for the latter two samples. Such modified ferromagnetic behaviors are probably due to

the nano-scale size and thin-flake geometry of the latter two Co_3O_4 nanostructures [55-57]. According to these demonstrations, one can expect that these Co_3O_4 nanostructures with controllable nanoscale geometry and interesting optical and magnetic properties may lead to promising opportunities for their applications in photo-/electro-catalysis, sensors and other micro-electronic devices.

4. Conclusions

In summary, we developed a facile and single-step approach for the scalable growth of free-standing Co_3O_4 nanowires. The process was achieved by the water vapor-assisted direct thermal oxidation of stress-enriched cobalt foil. Thermodynamic calculation indicates the incorporation of water vapor in the growth system takes a critical role in improving the spatial density of Co_3O_4 nanowires. The authors found that the presence of water vapor not only modified the formation path of Co_3O_4 nanowires but also refined the grain size of the $\text{CoO}/\text{Co}_3\text{O}_4$ underlayers, which significantly facilitated the diffusion of cobalt and oxygen species. Meanwhile, the authors realized that various interesting Co_3O_4 nanostructures can be obtained by simply modifying the growth parameters. These include the structural evolution of Co_3O_4 nanocookies by adding KI into the water vapor source, growth of Co_3O_4 nanorods by feeding NH_4F in the system, and preparation of Co_3O_4 nanoflakes and nanotrapezoids by slightly varying the growth temperature. Interesting optical and magnetic properties were also observed for these nanostructures. We believe such unique Co_3O_4 materials will open new insight for developing novel metal oxide nanocomposites or heterostructures for catalysis, sensors and energy conversion/storage devices.

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Figures

Fig. 1. (A) SEM and (B, C) TEM images of the Co_3O_4 nanowires obtained by thermal oxidation in air environment. (D) SEM and (E, F) TEM images of the Co_3O_4 nanorods obtained in water vapor environment. (G) SEM and (H, I) TEM images of the Co_3O_4 nanowires obtained in air & water vapor environment.

Fig. 2. (A, B) Thermodynamic calculation of possible cobalt oxidation reactions in the absence and presence of water vapor. (C) Schematic showing the growth mechanism of Co_3O_4 nanowires in the absence (left) and presence (right) of water vapor. (D) SEM image of the $\text{CoO}/\text{Co}_3\text{O}_4$ underlayer and the mass transport of cobalt ions.

Fig. 3. (A-F) SEM images showing the influence of substrate treatment on the growth of Co_3O_4 nanowires: (A) polished Co foil, (B) bended Co foil, (C, D) scratched Co foil, (E) sand-blasted Co foil, (F) Co powders and (G) sputtered Co film. (H, I) SEM images showing the influence of additives in water vapor on the growth of Co_3O_4 nanowires: (H) KI, (I) NH_4F .

Fig. 4. SEM images showing the influence of growth parameters on the structure and density of Co_3O_4 nanostructures: (A-C) water feed rate - (A) 6 ml/h, (B) 12 ml/h, and (C) 18 ml/h; (D-F) oxygen flow rate - (D) air of 0.1 SLM, (E) air of 1.2 SLM, and (F) 5% O_2/Ar of 1.2 SLM; (G-I) growth temperature - (G) 375 °C, (H) 425 °C, and (I) 475 °C; (J-L) growth duration: (J) 10 min, (K) 1 h, and (L) 20 h.

Fig. 5. TEM images of various representative Co_3O_4 nanostructures: (A, B) nanoflakes for Fig. 4G, (C, D) nanotrapezoids for Fig. 4H, and (E, F) nanowires for Fig. 4I.

Fig. 6. (A) Raman spectra and (B) XRD patterns of various nanostructures: Co_3O_4 nanoflake (grown at 375 °C), Co_3O_4 nanotrapezoid (grown at 375 °C), Co_3O_4 nanowire (grown at 375 °C). (C) Tura plots obtained from the absorbance spectra in Fig. S11 (Supplementary Information) for the evaluation of band gap energies of various Co_3O_4 nanostructures. (D) Magnetic hysteresis curves measured at room temperature (~ 25 °C) for various Co_3O_4 nanostructures.