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Spontaneous growth of ultra-thin titanium oxides shell on Ag nanowires: an electron energy loss spectroscope observation

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Ag nanowires with a spontaneous ultra-thin TiO₂ shell (~0.5 nm) can be grown on TiO₂ substrate. STEM/EELS results demonstrate that this oxygen-deficient TiO₂ layer is formed through the oxidation of Ti which is released from the substrate and segregated to the nanowire surface simultaneously with crystal growth of the nanowires.

The performance of nanowires is often limited. One of the important solving methods is to synthesize composite nanowires such as core-shell nanowires to enhance functionality and usability. Recently, many studies on core-shell nanowires have been reported [1-4]. The purpose is to combine the materials of the core and shell to produce complementary effects or enhance their properties. With respect to the Ag-TiO₂ core-shell nanowires, the silver nanowires have unique properties of high surface plasmon resonance as well as good electrical conductivity, while TiO₂ is an ideal material as photocatalysts. As tabulated in Table 1, Cheng *et al.*[1] have demonstrated the fabrication of Ag@TiO₂ nanowires through vapor-thermal method using poly(N-vinylpyrrolidone, PVP) as the surfactant. The diameter of the silver core and the thickness of TiO₂ shell are about 50 and 30 nm, respectively. Some studies have suggested to synthesize the Ag nanowires coated with amorphous TiO₂ through sol-gel or chemical reductions [2,3]. However, this method suffers from the sensitivity of synthesizing temperature. When the temperature is not properly controlled, the Ag@TiO₂ nanowires with bristled surfaces would be produced. Moreover, Liu *et al.*[4] used template method combined with the electrodeposition routes to synthesize Pt, Au and Ni nanowires. By manipulating the PH value of solution, the metal-TiO₂ core-shell nanorods could be obtained. They also indicated that low PH value benefits TiO₂ deposition. A small amount of Pt inoculants are needed to produce the metal-TiO₂ core-shell nanorods.

This study aims to develop a universal method for synthesizing ultra-long metal core-oxide shell composite nanowires. In the absence of oxide precursors, templates, inoculants and surfactants, vertically grown Ag/TiO₂ core-shell nanowires were synthesized on TiO₂ substrates using a one step process. The core-shell feature of the nanowires and the TiO₂ valence were observed by scanning transmission electron microscope (STEM) equipped with an electron energy loss spectroscope (EELS). The growth mechanism will thus be proposed.

Table 1 A summary of previous works on the metal-TiO₂ core- shell nanowires.

Metal@oxide	Method	Template (T) Surfactant (S)	Diameter/ Thickness/ Length	Phase	Precursor
Ag@TiO₂ nanowires[1]	vapor-thermal	PVP (S)	50 nm/ 30 nm/ ---	---	TBOT
Ag@TiO₂ nanowiress[2]	sol-gel	PVP (S)	70 nm/ 10 nm/ 10-50 mm	amorphous	TTIP
Ag@TiO₂ nanowiress[3]	chemical reduction	---	40 nm/ 35 nm/ -----	amorphous	TBOT
Pt,Au,Ni@TiO₂ nanowiress[4]	electro-deposition	AAO (T)	---	---	TiCl₃

TBOT(tetrabutyl titanate), TTIP(titanium tetraisopropoxide)

TiO₂ thin films were prepared via sol gel method. Si wafer substrates were dipped into gels and spun at 1000 rpm for 30 s. The solution used was prepared from isopropylalcohol (IPA), titanium isopropoxide (TTIP), and hydrogen chloride (HCl) with a volume ratio of 170:12:0.4 and then stirred for 10 min before aging at room temperature (20 °C) for 2 days. The as-synthesized TiO₂ films were annealed at 500 °C for 8 h in an oxygen atmosphere to obtain well-crystallized anatase TiO₂. Silver nitrate (AgNO₃) was selected as the precursor to grow Ag nanowires. 15 μl of 0.05 M aqueous salt solution was dropped onto the TiO₂ coated substrate. Afterwards, the samples were isothermally

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heated at 300 and 600 °C respectively for a certain period of time in air using an infrared furnace, and cooled down to ambient temperature. The structure and phase of the nanowires were characterized using a transmission electron microscope (TEM) equipped with electron energy loss spectroscope (EELS, USTEM Nion) and operated at 100 keV. The core loss was done using 0.6 eV per channel spectra dispersion and energy domain ranging from 450 to 480 eV in order to collect the Ti-L edge. In addition, inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine the solubility of Ti in molten $AgNO_3$ salt.

Fig. 1(a) shows the as-synthesized Ag nanowires subjected to heating at 300 °C for 3 h. It reveals that the Ag nanowires have an average diameter and length of about 65±8 nm and 8.3 μm, respectively. The selected-area electron diffraction pattern (SADP) inserted in Fig. 1(a) confirms that the Ag nanowires are single-crystalline with $[1\bar{1}0]$ growth direction, and the EDS spectrum verified the purity of Ag nanowires without any detectable impurities. The EELS mapping was done to have a better understanding on the structure of the nanowires. Fig. 1(b) shows the presence of ultra-thin spontaneously-grown oxide shell enriched with Ti (0.5±0.05 nm) on the surface of the Ag nanowire. This shell layer is continuous, compact and firmly attached to the nanowire surface. The chemical composition and elemental distribution of Ag nanowires analyzed by EELS are shown in Fig. 1(c). The elemental line-scanning reveals that the Ti concentrates at the edge of the Ag signal, indicating a core–shell structure. The oxygen signal is overlapped with Ti but narrower. It locates at the outer surface region of Ti peak, which proves that the oxide layer is formed through inward diffusion of oxygen and thus oxidation of Ti.

The XRD patterns of the Ag nanowires heated at different time and temperature have been shown in Fig. 2(a). Only Ag is identified. The amount of Ti oxide layer is too small to be detected. Figs. 2 (b)(c)(d) illustrate high resolution TEM images of the corresponding Ag nanowires. The interval of lattice fringes, 0.23nm, exactly matches the interplanar distance of Ag(111). Those data all demonstrate that the cores of the nanowires are pure Ag crystals instead of silver oxides, Ag-Ti alloys or solid solutions.

Fig. 3 shows the experimentally obtained Ti $L_{2,3}$-edge EELS spectra of the oxide layer in different heating conditions (300 °C-3 h, 300 °C-9 h and 600 °C-3 h) and the standard anatase TiO_2 as a reference. The Ti L-edge possesses two groups of peaks of Ti 2p core level consisting of $2p_{1/2}$ (L_2 -edge) and $2p_{3/2}$ levels (L_3 -edge). For standard TiO_2, the Ti 3d band can be split into four sublevels including $2p_{3/2}t_{2g}$ (A_1), $2p_{3/2}e_g$ (A_2), $2p_{3/2}t_{2g}$ (B_1) and $2p_{3/2}e_g$ (B_2) symmetry [5-8]. For TiO_2 systems, Calvert *et al.*[8] reported that when the valence of Ti ions is reduced from Ti^{4+} (TiO_2) to Ti^{3+} (Ti_2O_3), Ti L-edge peak positions shift to lower energy and the intensity of A_1 peak for Ti L_3-edge becomes weaker while the A_2 peak becomes stronger. As shown in Fig. 3, it is remarkable that no A_1 signal is visible in the EELS spectra of the oxide shell, but a distinct A_1 signal can be seen from the TiO_2 reference. Furthermore, the positions of A_2 and B_2 signals from all the samples are identical with the signals from TiO_2 reference. These differences in Ti $L_{2,3}$-edge EELS

spectra leads us to believe that Ti ions are predominantly in between Ti^{3+} and Ti^{4+} oxidation states. Strictly speaking, the oxide shell should be denoted as TiO_{2-x}.
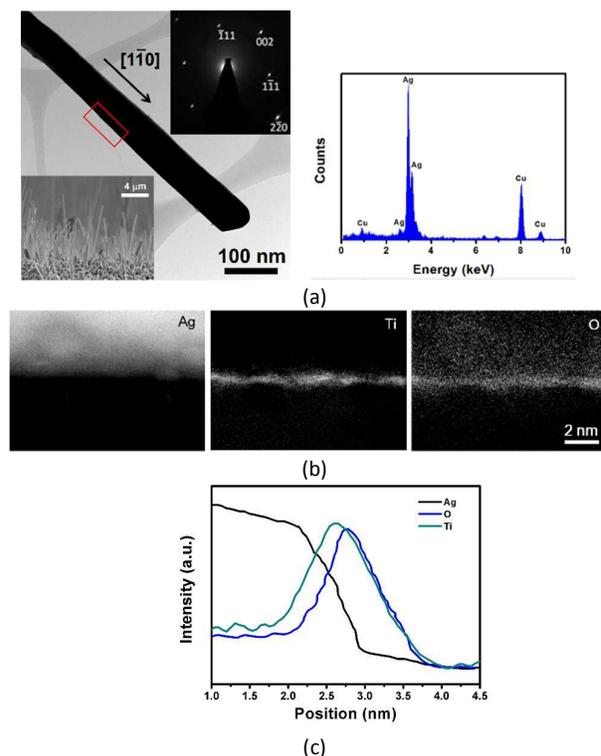
Fig. 1 (a) TEM image and EDS spectrum of Ag nanowire synthesized on the TiO_2 substrate after heating at 300 °C for 3 h (Insets: SEM image of vertically-grown Ag nanowires and SADP)(the Cu signal in EDS spectrum comes from the Cu grids), (b) EELS mapping and (c) elemental line-scans.
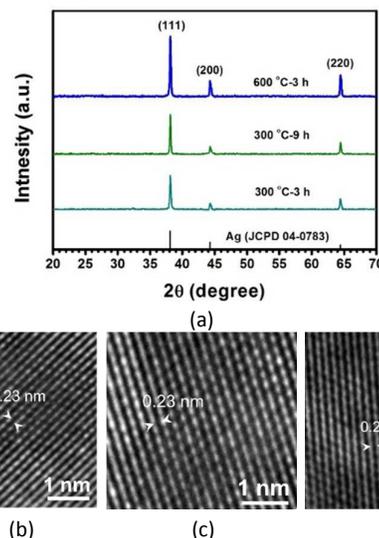
Fig. 2 XRD patterns (a) and high resolution TEM images of the Ag nanowire samples heated at different time and temperature: (b) 300 °C-3 h, (c) 300 °C-9 h and (d) 600 °C-3 h

(b)
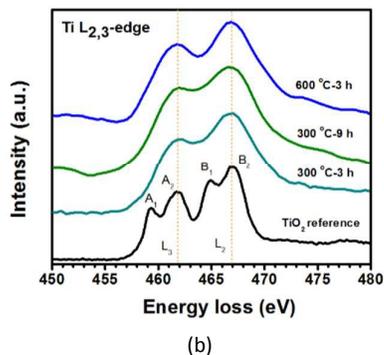
Fig. 3 STEM-EELS of oxides layer on Ag nanowire samples heated at different time and temperature.

Fig. 4 depicts the quantitative data of the Ag core diameter and the thickness of the TiO_{2-x} shell with different heating time and temperature. As illustrated, after a prolonged heating at 300 ^{o}C from 3 h to 9 h, the thickness of TiO_{2-x} shell remains almost same (0.5±0.05 nm for 3h and 0.52±0.06 nm for 9h). However, when the sample is heated at 600 ^{o}C for 3 h, the thickness of TiO_{2-x} shell significantly increases to 1.5±0.1 nm. Similarly, the Ag wire diameter increases from 65 nm (300 ^{o}C) to 110 nm (600 ^{o}C). Ti segregates at the nanowire surface probably through two routes, one is Ti diffusion from the TiO_2 substrate through the Ag wire surface, and the other is the repelling of Ti in molten salt to the nanowire surface during the single crystal growth. In the second route, it can be speculated that Ti from TiO_2 substrate dissolves into molten salt (melting point of $AgNO_3$: 212 ^{o}C) in the very early stage of heating prior to nanowire growth. The fact that thin oxide shell covers the whole nanowires as well as the pronounced effect of heating temperature compared with holding time suggests that Ti is repelled during nanowire crystallization instead of long-distance diffusion from the substrate. The solubility of Ti in molten $AgNO_3$ salt at different heating time and temperature is estimated from the ratio of TiO_{2-x} shell thickness/Ag wire radius, and experimentally obtained by measuring the Ag and Ti concentrations in nitric acid aqueous solution using ICP. Table 2 shows the ICP results and estimated values of Ti/Ag (wt %), which corresponds with each other to some extent. As can be seen, when the sample is heated at 600 ^{o}C, the Ti solubility is two times higher than that at 300 ^{o}C. Holding time has no significant effect since the saturation has been reached.

Fig. 5 presents schematic illustration of the formation of Ag/TiO_{2-x} core-shell nanowires. As illustrated, Ti is from the dissolution of TiO_2 substrate into molten silver nitrate salt. The dissolved Ti, which can be regarded as impurities due to its limited solubility in solid Ag at the heating temperature range [9], migrates to the crystal surface during the single-crystal growth of the Ag nanowires. The subsequent oxidation turns Ti into oxygen-deficient TiO_{2-x}.
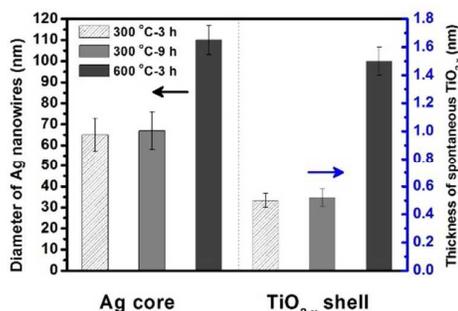
Fig. 4 The thickness of spontaneous TiO_{2-x} in the samples heated at different time and temperature.

Table 2 Solubility of Ti in $AgNO_3$ salt (given as Ti/Ag) at different time and temperature

Samples	ICP Ti /Ag (wt. %)	Estimated values Ti /Ag (wt. %)
300 ^{o}C-3 h	1.6	1.3
300 ^{o}C-9 h	1.6	1.3
600 ^{o}C-3 h	3.3	2.3
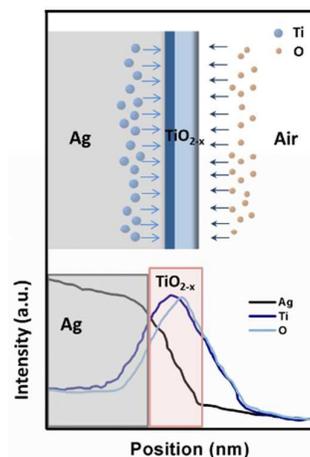
Fig. 5 Schematic illustration of Ag/TiO_{2-x} core-shell nanowires.

In summary, a one-step synthesis of Ag/TiO_2 core-shell nanowires was proposed in this study. Spontaneously-grown TiO_2 shell with a thickness of about 0.5 nm was found to cover the whole surface of Ag nanowires. Experimental results confirm that the TiO_2 shell is formed from the oxidation of Ti which is repelled from single-crystalline Ag during the crystallization of Ag nanowires. It is also verified that Ti is from dissolution of TiO_2 substrate in molten salt. The higher the heating temperature, the thicker the TiO_2 shell. The EELS spectra suggest that the valence of Ti ions in this spontaneous oxide layer is between Ti^{3+} and Ti^{4+}.

Acknowledgements

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