Selective Preparation of MoO_3 and H_xMoO_3 Nanobelts in Molybdenum–Hydrogen Peroxide System

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In this letter a new synthetic strategy has been established for MoO_3 nanobelts by oxidizing Mo powders with H_2O_2 in neutral water at 70 °C and a subsequent hydrothermal treatment at 140 °C. By introducing alcohol into this system, we can selectively prepare blue H_xMoO_3 nanobelts. The photoluminescence (PL) property can be greatly altered before and after hydrogen incorporation into MoO_3 nanobelts. The mechanism on formation process of nanobelts has also been addressed.

Orthorhombic α-MoO_3 is characteristic of its layered structure along [010] crystallographic direction, and among adjacent layers van der Waals interactions are the major binding means.[1] Owing to its unique structure and variable oxidation states of Mo, molybdenum trioxide possesses many physical and chemical properties. For example, MoO_3 exhibits electrochromism and photochromism after intercalating with appropriate cations (such as H^+, Li^+, and Na^+), making it suitable for their use in display devices, smart windows, and storage batteries.[2] The colored amorphous H_xMoO_3 films can be obtained via applying an electric field or UV light illumination on amorphous MoO_3 films, which are fabricated by many techniques such as vacuum deposition and pulser laser deposition.[3–6] In the case of MoO_3 nanomaterials, the nanobelts and nanowires have been synthesized by several ways.[7,8,16] However, as far as the chemical ways are concerned, nanofamily materials of MoO_3 are commonly prepared by acidification of molybdate and a subsequent hydrothermal treatment.

Herein, we report a new route for preparing MoO_3 nanobelts by directly oxidizing metallic molybdenum powders with H_2O_2 in neutral water and a subsequent hydrothermal treatment (For detailed procedure, see Supporting Information[17]). The introduction of ethanol into this system can color MoO_3 nanobelts from white to blue, which is attributed to the formation of hydrogen molybdenum bronze (H_xMoO_3). To our knowledge, this is the first report on the preparation of H_xMoO_3 nanobelts.

Figure 1 is the XRD pattern of the white products, in which all peaks can be indexed as orthorhombic MoO_3 phase, with the lattice constants of $a = 3.966$, $b = 13.858$, $c = 3.693$ Å (JCPDS 05-0508). As compared to other peaks, the surprising intensity of (0k0) reflections arises from the fact that almost all nanobelts lie on the holder with (010) planes.

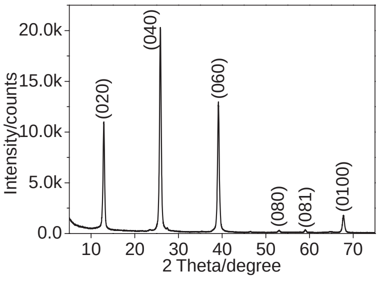

Figure 1. The XRD pattern of as-synthesized white MoO_3 nanobelts.

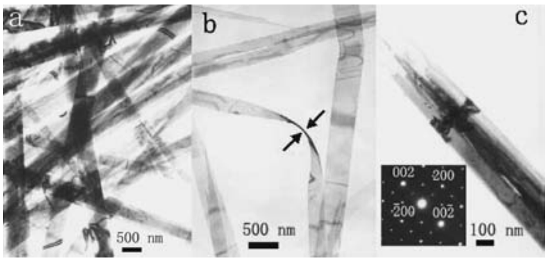

Figure 2. (a,b) TEM images of MoO_3 nanobelts and bending parts; (c) TEM images of a single nanobelt and the corresponding SAED patterns.

Figure 2 shows the TEM images of MoO_3 nanobelts, which have a width from 200 to 800 nm and a length of several micrometers. The nanobelts are so thin that they are electron-beam transparent and can be easily bended. From the observation of bending parts of nanobelts (indicated by arrows in Figure 2b), their thickness can be estimated to be about 30 nm. The selected area electron diffraction (SAED) recorded perpendicularly to the upper surface of a single nanobelt can be assigned to the [010] zone axis diffraction of orthorhombic MoO_3 and suggests that the nanobelts are single crystals growing along [001] direction.

If a little amount of ethanol is introduced into our system, interestingly, the resultant nanobelts present blue in color. The XRD analysis, TEM images, SAED, and Raman spectra all conclude that the blue nanobelts are still single crystal with almost the same structure as MoO_3 nanobelts (Figures S1–S3 in Supporting Information).[17] Furthermore, there is no difference in morphology as compared to white MoO_3 nanobelts.

Previously, much work on MoO_3 has shown that when MoO_3 is injected with alkaline metal ions and electrons they will likely turn blue in color, which is generally ascribed to the formation of molybdenum bronzes.[1,3,6,9,10] Hydrogen molybdenum bronzes (H_xMoO_3, $0 < x \leq 2$) are characteristic of different colors produced with varied hydrogen incorporation into MoO_3 layered structure. Similarly in our process, MoO_3 nanobelts have been reduced to H_xMoO_3 nanobelts by ethanol (see below).[9]

Figure 3 demonstrates the XPS results of MoO_3 and H_xMoO_3 nanobelts. The two peaks of Mo 3d spectrum in Figure 3a are at 235.8 and 232.65 eV, which are characteristic of spin–orbit coupling doublets of $3d_{3/2}$ and $3d_{5/2}$ of Mo^{6+}.[5] In Figure 3b, the peaks of Mo 3d spectrum are at 235.6 and 232.4 eV. The binding energy of Mo 3d electron in H_xMoO_3

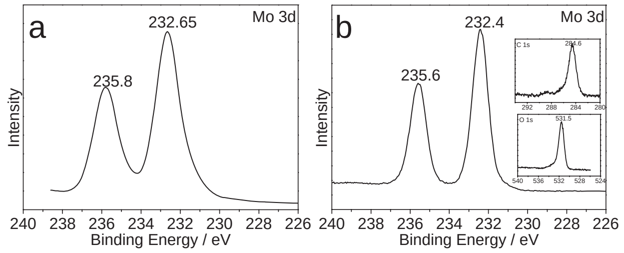

Figure 3. XPS spectra of Mo 3d electron in MoO_3 nanobelts (a) and H_xMoO_3 nanobelts (b). Insets in (b) depict the XPS spectra of C 1s and O 1s available when measuring the spectrum of H_xMoO_3 nanobelts.

nanobelts is about 0.2 eV lower than that in MoO_3 nanobelts. Many tests prove that the binding energy of Mo 3d electron in H_xMoO_3 is always lower than that in MoO_3. The decrease of binding energy of Mo 3d electron shows that there are some Mo^{5+} ions in H_xMoO_3 nanobelts,[4,11] though the additional electron in Mo^{5+} relative to Mo^{6+} may not be strictly localized,[12] and the inter valence charge-transfer transition between Mo^{5+} and Mo^{6+} makes H_xMoO_3 nanobelts blue.[3,6] In fact, H_xMoO_3 exhibits some metallic characteristics,[1] probably owing to these additional nonlocalized electrons.[10]

Considering the standard electrode potentials between Mo oxidation states and H_2O_2, we conclude that zero-valent Mo can be eventually oxidized to H_2MoO_4 by H_2O_2. In fact the resulting solution has a low pH value of about 1.7, showing that H^+ is produced during the oxidation reaction. The yellow color of solution comes from peroxomolybdate complex that are formed from molybdate ions and excessive H_2O_2.[13] When the solution is further heated in a hydrothermal way, a polymerization reaction occurs among peroxomolybdate acids accompanied by the release of H_2O and O_2, and as a result, MoO_3 is formed. The belt-like morphology is likely determined by crystallographic nature of α-MoO_3 such as different surface energy among (010), (100), and (001) planes.[8] In the presence of ethanol, some of Mo(VI) species have been reduced to Mo(V) species by ethanol under hydrothermal heating,[14] then protonated Mo(V) species and Mo(VI) species condense all together releasing H_2O and O_2 to form Mo–O–Mo frameworks, in which some protons are intercalated at the same time, and hydrogen molybdenum bronze is formed. H_xMoO_3 retains the parent orthorhombic structure of MoO_3.[1] Because of the small hydrogen atoms and great MoO_3 lattice, incorporation of hydrogen brings no obvious variation on lattice parameters,[9,10] thus the diffraction patterns and Raman spectrum of H_xMoO_3 nanobelts are closely analogous to those of MoO_3 nanobelts.

The photoluminescence spectra of nanobelts are demonstrated in Figure 4. The emission peaks at 420 and 440 nm are detectable only in MoO_3 nanobelts whereas in H_xMoO_3 nanobelts there is no obvious peak. Hydrogen incorporation into MoO_3 does not disturb energy bands of MoO_3 except that some trapping states in the forbidden band are created.[15] The two peaks are contributed from interband radiative recombination of photogenerated electrons and holes. Because there are trapping states in H_xMoO_3 nanobelts, most electrons are trapped and the recombination is nonradiative.

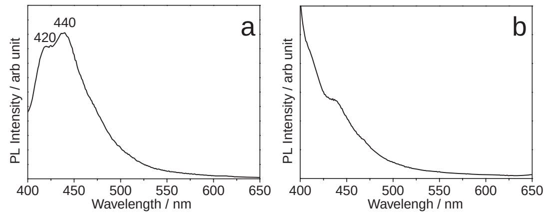

Figure 4. Photoluminescence spectra of MoO_3 nanobelts (a) and H_xMoO_3 nanobelts (b). The high signal at about 400 nm comes from the influence of incident beam of 370 nm.

In summary, a new strategy has been established to prepare selectively MoO_3 and H_xMoO_3 nanobelts in molybdenum–hydrogen peroxide system. H_xMoO_3 nanobelts remain almost the same crystal structure as MoO_3 nanobelts. The XPS spectra display that there exist some Mo^{5+} in H_xMoO_3 nanobelts. The PL spectra further suggest that there are great differences in optical property between MoO_3 and H_xMoO_3 nanobelts. It should be noted that the value of x in this work has not been determined and further work is being attempted.

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17 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.