Spectroscopic, morphological and electrochromic characterization of layer-by-layer hybrid films of polyaniline and hexaniobate nanoscrolls

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Electronic Supplementary Information

Detailed experimental procedures

Aniline ($C_6H_5NH_2$, Merck) was distilled under reduced pressure prior to use. Niobium pentoxide (Nb_2O_5, CBMM – Companhia Brasileira de Metalurgia e Mineração) was used as received. All other chemicals were purchased from Merk and used as received.

1. Syntheses of emeraldine salt and emeraldine base forms of polyaniline

Emeraldine salt polyaniline (PANI-ES) was prepared following well known procedure from literature.[1] Aniline solution was prepared by dissolving 20 mL of aniline (*ca.* 0.20 mol) in 300 mL of 1 mol L^{-1} HCl solution. Ammonium peroxydisulfate (APS) solution was prepared by dissolving 11.5 g of APS (*ca.* 0.05 mol) in 200 mL of 1 mol L^{-1} HCl solution. These solution were cooled in an ice/water bath (*ca.* 5 ºC) and the APS solution was slowly added (*ca.* 50 mL min^{-1}) to aniline solution. The reaction mixture was stirred in ice/water bath for 90 minutes. The dark green precipitate was isolated by filtration, washed with 500 mL of 1 mol L^{-1} HCl solution and dried under vacuum at room temperature. Emeraldine base polyaniline (PANI-EB) was prepared by dedoping 300 mg of PANI-ES in 300 mL of 0.1 mol L^{-1} NH_3 solution. The pH of dispersion was adjusted to *ca.* 8 by addition of 1 mol L^{-1} NH_3 solution, and then stirred at room temperature for 15 hours. The solid was filtered and treated again with 300 mL of 0.1 mol L^{-1} NH_3 solution for 1 hour. The dark blue solid was filtered, washed with 300 mL of 0.1 mol L^{-1} NH_3 solution and dried under vacuum at room temperature.

2. Preparation of dispersion of PANI-ES (pH2.5)

The dispersion of PANI-ES in water/*N*,*N*-dimethylacetamide of pH 2.5 was prepared following procedure from literature.[2-3] Dedoped polyaniline (PANI-EB) powder (200 mg) was slowly added to 10 mL of *N*,*N*-dimethylacetamide (DMA) under stirring. The solution was stirred for 12 hours at room temperature and the insoluble particles were removed by filtration. The concentration of PANI-EB/DMA solution was determined by UV-VIS absorption spectroscopy considering the absorption coefficient at 630 nm per mole of the constitutional tetramer unit of PANI-EB ($\varepsilon_{630} = 2.2 \times 10^4$ L cm^{-1} mol^{-1}).[4] The PANI-EB/DMA solution was diluted by addition of DMA to result in a solution of concentration 2.5×10^{-2} mol L^{-1}. One milliliter of this solution (dark blue color) was added to 9 mL of HCl solution (pH 3). The resulting dispersion (dark green color) was carefully acidified to pH 2.5 by addition of dilute HCl solution, and then filtered. The acidifying of the dispersion was carried slowly to prevent the precipitation of polyaniline in medium of pH below 2.0. The estimated concentration of PANI-ES dispersion (pH 2.5) is *ca.* 2.5×10^{-3} mol L^{-1}.

3. Syntheses of hexaniobates $K_4Nb_6O_{17}$ and $H_2K_2Nb_6O_{17}$

Hexaniobate in potassium precursor form ($K_4Nb_6O_{17}$) was prepared by ceramic method.[5-8] Stoichiometric mixture of Nb_2O_5 (16.18 g) and K_2CO_3 (5.61 g) was carefully milled and heated in a platinum crucible at 1100 °C. The heating process was carried out by two steps of 5 hours, proceeding the milling of the mixture after the first step of heating. The isolation of the orthorhombic crystal structure of potassium hexaniobate was confirmed by X-ray diffractometry (diffraction peak corresponding to $d_{040} = 9.3$ Å).[7] Acidic form of hexaniobate ($H_2K_2Nb_6O_{17}$) was prepared by ion-exchange reaction of $K_4Nb_6O_{17}$.[6-9] $K_4Nb_6O_{17}$ powder (5.0 g) was suspended in 200 mL of 6 mol L^{-1} HNO_3 solution and stirred at 60 °C (reflux) for 3 days. After this period, the suspension was kept without stirring for 1 day and the supernatant was removed by using a pipette. A fresh portion of HNO_3 solution was added to deposited solid and the suspension was stirred for 3 days at 60 °C (reflux). Afterwards, the suspension was kept without stirring for 1 day and the solid was isolated by removing the supernatant. The deposited solid was rinsed with deionized water and centrifuged several times until the pH of the supernatant reached *ca.* 6 (pH of deionized water). The solid was dried under vacuum at 80 °C and the $H_2K_2Nb_6O_{17}$ composition was confirmed by the diffraction peak corresponding to $d_{040} = 7.9$ Å.[7]

4. Exfoliation of $H_2K_2Nb_6O_{17}$ with tetra(n-butyl)ammonium hydroxide

The exfoliation of acidic hexaniobate was carried out by following procedure described by Shiguihara *et al.*.[9-10] 500 mg of $H_2K_2Nb_6O_{17}$ (ca. 1.1×10^{-3} mol of H^+-hexaniobate) were suspended in 250 mL of tetra(*n*-butyl)ammonium hydroxide solution (TBAOH). The concentration of TBAOH solution was 3.2×10^{-3} mol L^{-1}, resulting in a suspension of molar ratio TBA^+/H^+-hexaniobate of 0.75 (8.3×10^{-4} mol of $TBA^+/1.1 \times 10^{-3}$ mol of H^+-hexaniobate). The suspension was stirred for 7 days at room temperature, and then kept without stirring for 1 days. Finally, the colloidal dispersion of exfoliated hexaniobate was carefully separated from the deposited solid) by using a Pasteur pipette.

5. Preparation of glass substrates

Glass slides (2.5 cm x 1 cm) were cleaned by following procedures in literature.[3, 11] The substrates were immersed in H_2SO_4/H_2O_2 solution (7/3 in volume) for 1 hour and rinsed extensively with deionized water. Afterwards, the substrates were immersed in $NH_4OH/H_2O_2/H_2O$ solution (5/1/1 in volume) for 30 minutes and extensively with deionized water.

Additional secondary electron images of hexaniobate nanoscrolls

Fig. S1 shows additional secondary electron images (SEI) of hexaniobate nanoscrolls (NbONsc). It can be seen in Fig. S1 that the exfoliation of the lamellar hexaniobate results in material of homogeneous morphology over many regions of the sample.

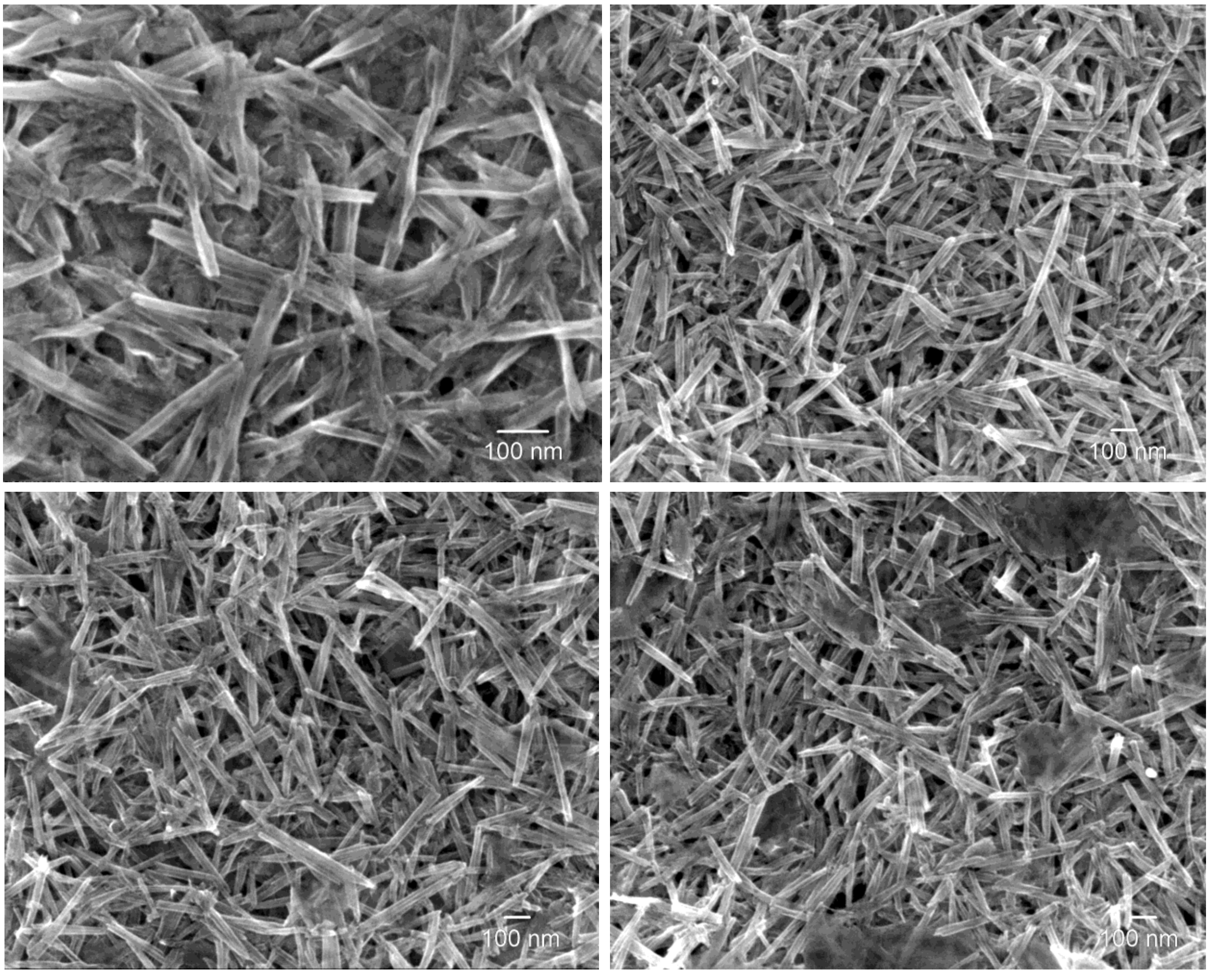

Fig. S1. SEI images of hexaniobate nanoscrolls. These images show the reproducibility of the nanoparticules obtained by exfoliation process.

Considering over one thousand hexaniobate nanoscrolls of SEI images of many regions of the sample, the calculated value of the mean external diameter of the NbONsc is 26 ± 5 nm. The histogram in Fig. S2 shows that the distribution of measured external diameters is broad, in accordance with SEI images.

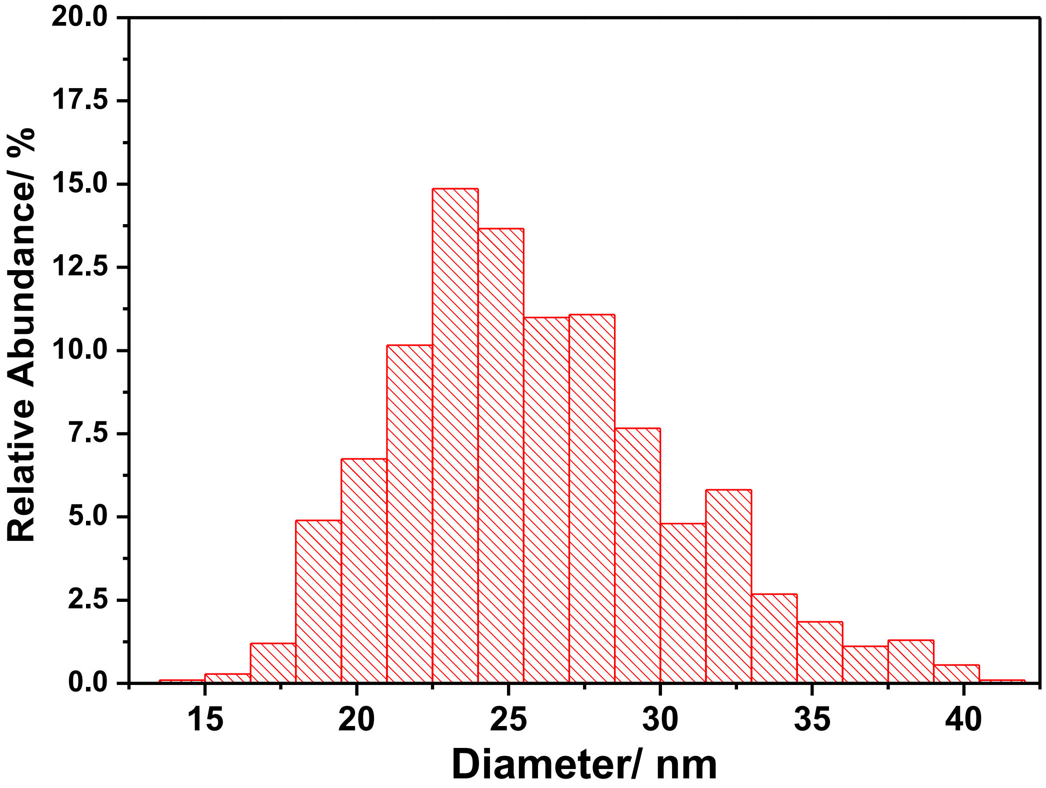

Fig. S2. Histogram of measured external diameters for over one thousand nanoscrolls. The calculated value of the mean external diameter of the NbONsc is 26 ± 5 nm.

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