

Supporting Information for

Hierarchical Tube-in-tube Structures Prepared by Electrophoretic Deposition of Nanostructured Titanates into TiO₂ Nanotubes Array.

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Estimation of molar fraction of titanate nanotubes (TiNT) inside the pores of TiO₂ nanotubes array (TiO₂ NT)

The method is based on the large difference in adsorption of methylene blue (MB) on the surface of TiNT and TiO₂. This adsorption can be approximated to a Langmuir type isotherm with maximum coverage of the surface (a_s) being 8×10^{-3} mol(MB) and 6×10^{-5} mol (TiO₂) (see reference ¹).

To estimate the molar ratio $n_{\text{TiNT}}/n_{\text{TiO}_2}$, two samples of TiO₂ NT and TiNT/TiO₂ NT were soaked overnight in 10^{-2} mol dm⁻³ aqueous solution of MB at room temperature (293 K) followed by washing with water and drying in air. Using a UV-Vis spectrometer with full integrating sphere, the diffuse reflectance spectra of both samples were recorded. The absorbance of dye was measured for both samples at its maximum absorption of 654 nm. The ratio $n_{\text{TiNT}}/n_{\text{TiO}_2}$ could be estimated using following equation:

$$\frac{\Delta A}{A_{\text{TiO}_2 \text{ NT}}} = \frac{a_s^{\text{TiNT}}}{a_s^{\text{TiO}_2}} \times \frac{n_{\text{TiNT}}}{n_{\text{TiO}_2}} \quad (\text{s1})$$

where ΔA is the difference in absorbance between MB coated TiNT/TiO₂ NT composite and MB coated TiO₂ NT ($A_{\text{TiO}_2 \text{ NT}}$)

Measurements

SEM images of electrode surfaces were obtained using a JEOL 6500 FEG-SEM scanning electron microscope. TEM images were obtained using a JEOL 3010 transmission electron microscope operating at 300 kV; the electrode surface was scratched and the powder was sonicated in ethanol for 3-5 min then the solution was transferred onto a copper grid covered with a perforated carbon film. UV-Vis diffuse reflectance spectra of electrodes were recorded using Neosys – 2000 (Scinco) spectrometer.

EPD of long nanotubes

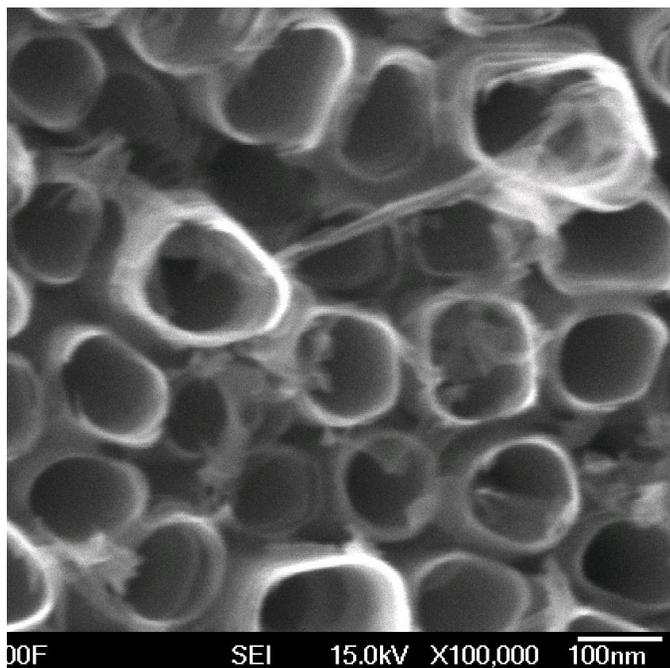


Figure S1. SEM image of neat (long) TiNT deposited on the surface of TiO₂ NT by EPD from ethanol solution.

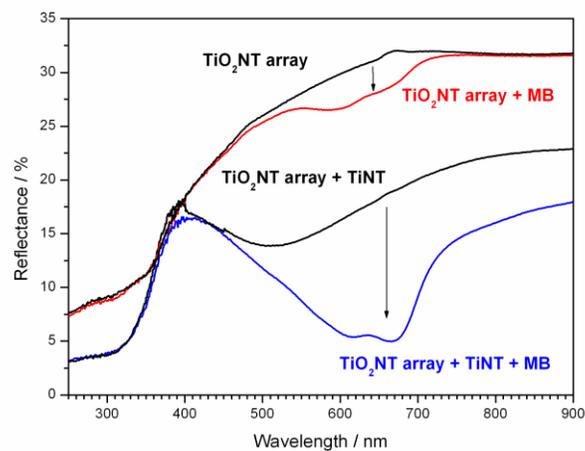


Figure S2. Diffuse reflectance spectra of methylene blue (MB) after adsorption on the surface of TiO₂ NT array (red) or the surface of TiNT incorporated in pores of TiO₂ NT (blue) from aqueous solution.

Appearance of TiNT/TiO₂ NT composites stained with MB

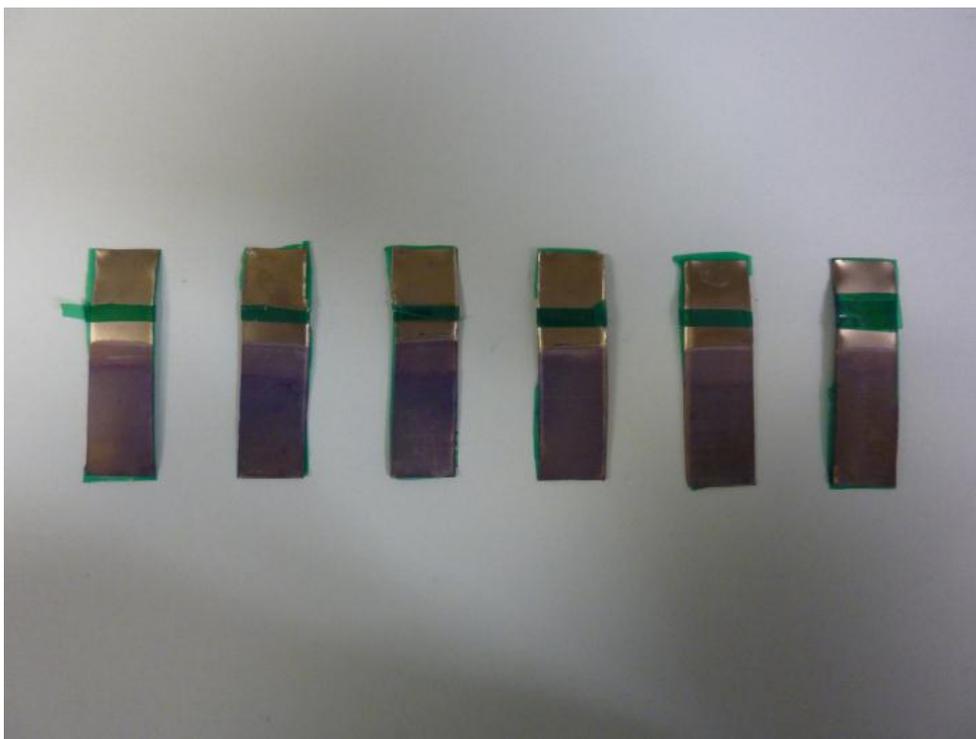


Figure S3. Photographic image of TiO₂ NT with incorporated TiNT using EPD with variable stirring rate in ethanol solution and stained by MB. From left to right the stirring rate is 60, 120, 180, 300, 360 and 480 rpm.

Estimation of linear velocity from the stirring rate of electrolyte.

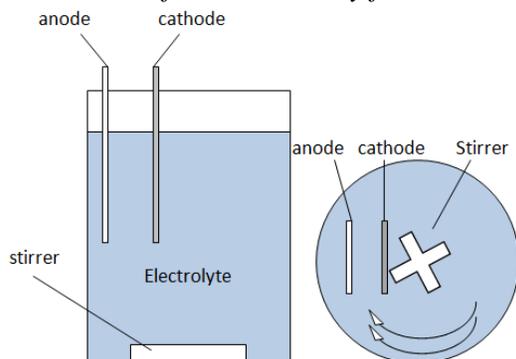


Figure S4. Schematic set up for electrophoretic deposition under shear flow of electrolyte.

The introduction of the electrolyte flow in the parallel to the surface of electrode direction was achieved using set up shown in Figure S4. PTFE coated magnetic stirring bar was located in the middle of the beaker and had a cross shape and 1 cm size. The distance between the beaker center and the anode R was 1.5 cm. Assuming that rotation speed of

the magnetic stirrer is equal to that of the electrolyte, the linear velocity u can be estimated using formula

$$u = \frac{2\pi R}{60} \times rpm = 0.157 \times rpm \quad [cm \ s^{-1}]$$

Note however that obtained value of the linear velocity is probably overestimated due to neglecting of the drag and non-uniform distribution of the flow.

Estimation of TiNT concentration in the solution

The concentration of TiNT C_{TiNT} in the colloidal solution was estimated by measuring optical absorbance A at 280 nm and using Lambert – Beer equation.

$$A = \varepsilon \times C_{TiNT} \times l$$

where ε an extinction coefficient of TiNT (earlier determined as $5900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and l is the optical length of the cuvette.

Distribution of TiNT inside the pores of TiO₂ NT.

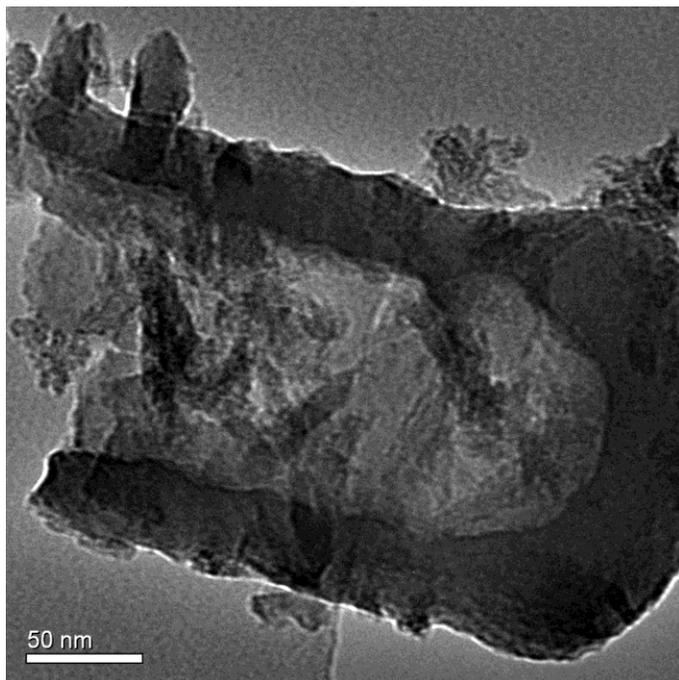


Figure S5. TEM image of close end (which face the Ti substrate) of TiO₂ NT after deposition of TiNT using EPD. Image shows no significant quantities of TiNT indicating low mobility of TiNT inside the pores during EPD.

References

¹ D.V. Bavykin, K.E. Redmond, B.P. Nias, A.N. Kulak, F.C. Walsh, Aust. J. Chem. 2010, 63, 270–275.