

TiO₂ coated carbon nanotubes for electrochemical energy storage

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Supporting Information S-1

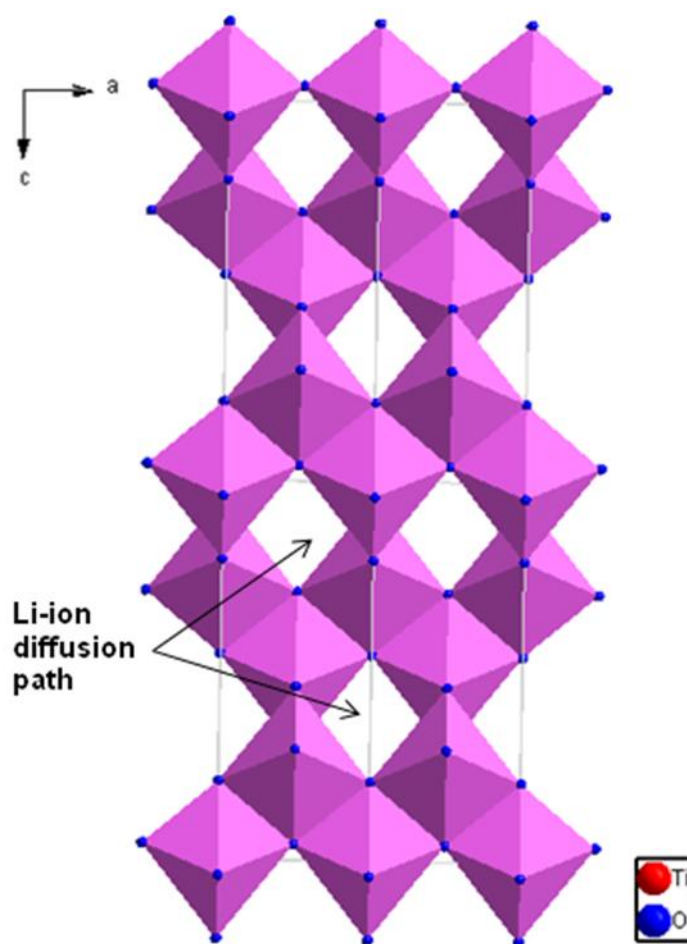


Figure S-1, Structure of Anatase TiO₂

Supporting Information S-2

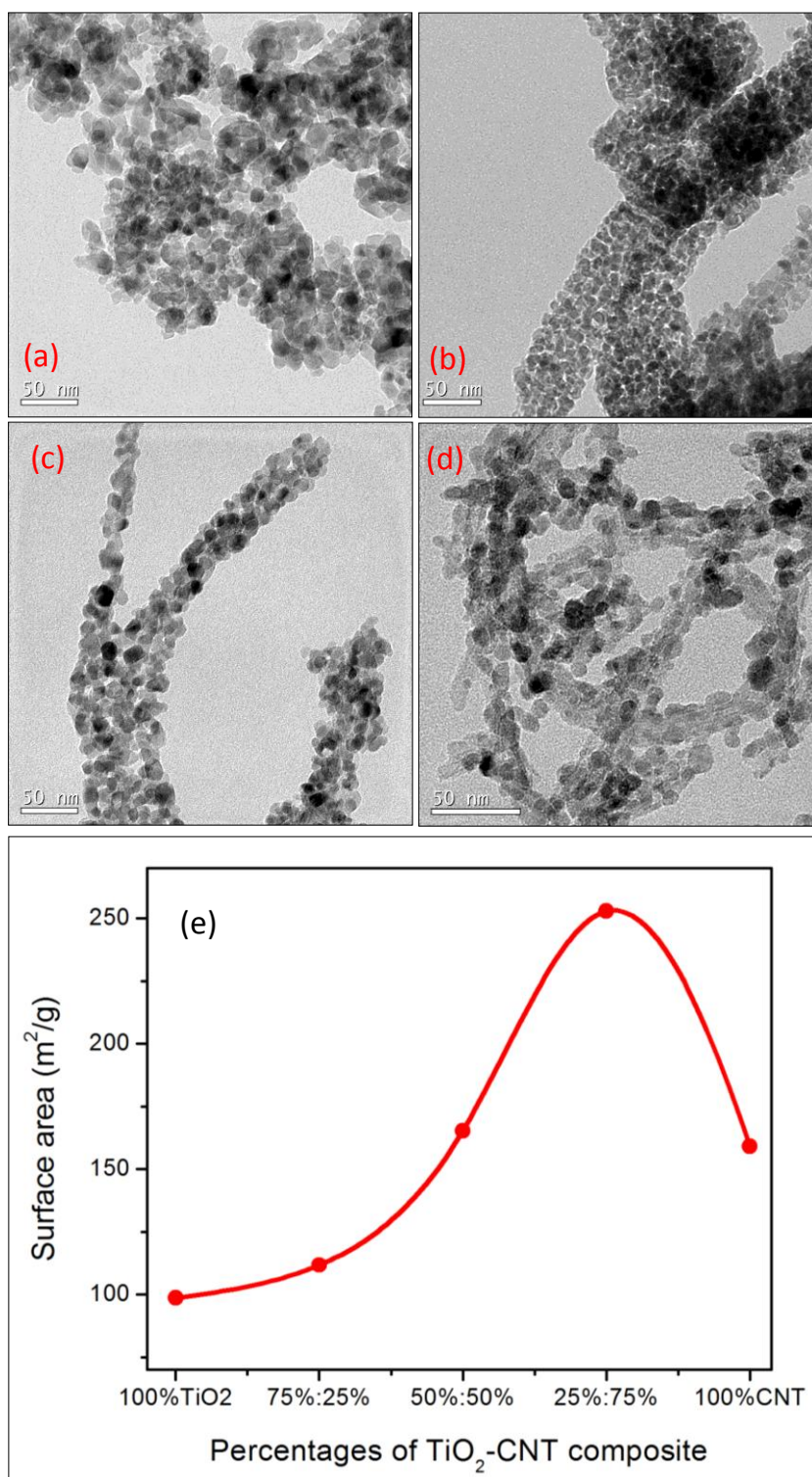


Figure S-2, Transmission electron micrograph of (a) 100% TiO₂, (b) 90% TiO₂/CNT (c) 75% TiO₂/CNT (d) 50% TiO₂/CNT and (e) BET surface area plot

TEM image of pristine unsupported TiO₂, 90% TiO₂/CNT, 75% TiO₂/CNT and 50% TiO₂/CNT composite are shown in Fig. S-2 a-d, respectively. It is seen from the figure that with increase in TiO₂ content beyond 25 % (TEM image of 25% TiO₂/CNT is shown in main text, Fig.3), agglomeration is found to occur and is evidenced from the micrograph shown in the Fig. S-2 (b) and (c). It is also found that average particle size of TiO₂ in 25% loaded sample is less than 10 nm whereas it is about 10-20 nm for pristine TiO₂, 75% TiO₂ and 50% TiO₂ loaded samples. These attributes are further supported with surface area measurements. BET surface area measurements on the different percentages of TiO₂ loading is shown in Fig. S-2(e). The surface area for pure pristine TiO₂ is 98.6 m²/g and functionalised CNT is 158.9 m²/g. The maximum surface area of about 252.9 m²/g is observed for 25% TiO₂ loading. The surface area decreases with increasing percentage of TiO₂ beyond 25 percent. The surface area values for 50% and 75% TiO₂ loading are 165.5 m²/g and 111.7 m²/g, respectively.

Supporting Information S-3

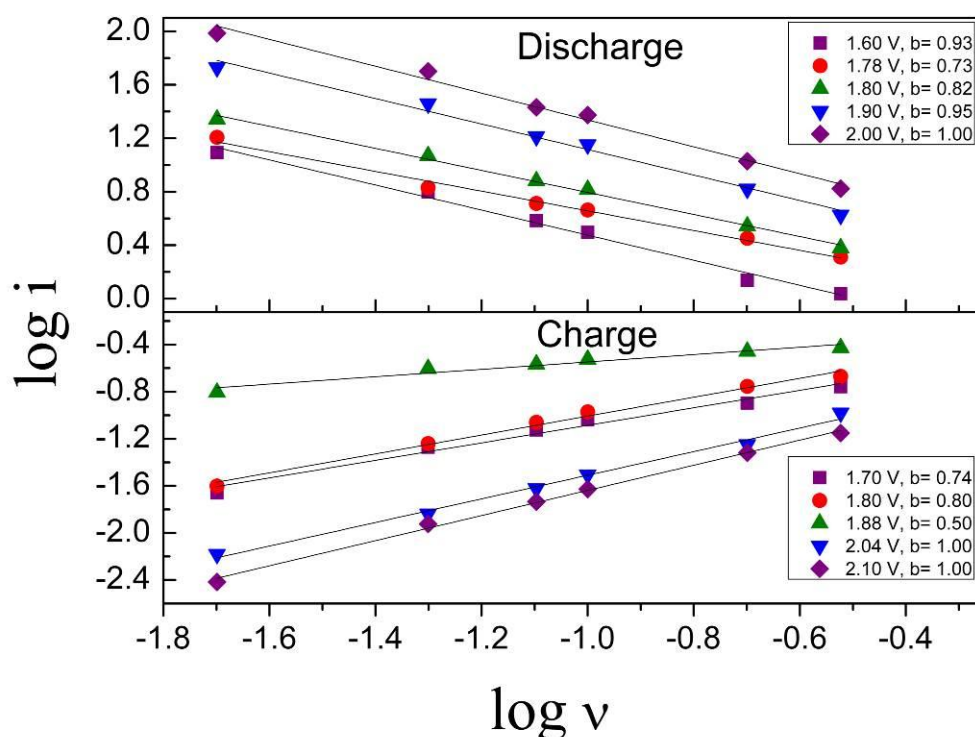


Figure S-3. Plot showing linear relationship of $\log v$ vs $\log i$ for cathodic (discharge) and anodic (charge) sweeps of cyclic voltammogram of 25% TiO_2/CNT composite.

Cottrell equation is given as $i = nFAC_j^0 \sqrt{D_j} / \sqrt{(\pi t)}$. In practice, the simplified equation can be written as $i = at^{-1/2}$ where 'a' represents constants such as n, F, A, C_j^0 , D_j . Since scan rate (v) and t are related, $(v)^{1/2}$ is used instead of $t^{-1/2}$ in the Cottrell equation. As a result, current response for the voltammetric sweep complies the power law relationship, $i = av^b$, where a and b are variable parameters. This can also be written as, $\log i = \log a + b \log v$ and the value of b can be defined from the slope of linear curve obtained by plotting $\log i$ vs. $\log v$.

For a non diffusion limited processes, the value of slope would be unity, $b = 1$ (i.e, $i = a_1v$) and for a diffusion limited processes, slope $b = 0.5$, ($i = a_2v^{1/2}$). The current values at different potentials (V) of cyclic voltammograms recorded at various scan rates were plotted as a function of scan rate. The slope, 'b' for the cathodic and anodic sweeps is obtained from the slope of the straight line.

Supporting Information S-4

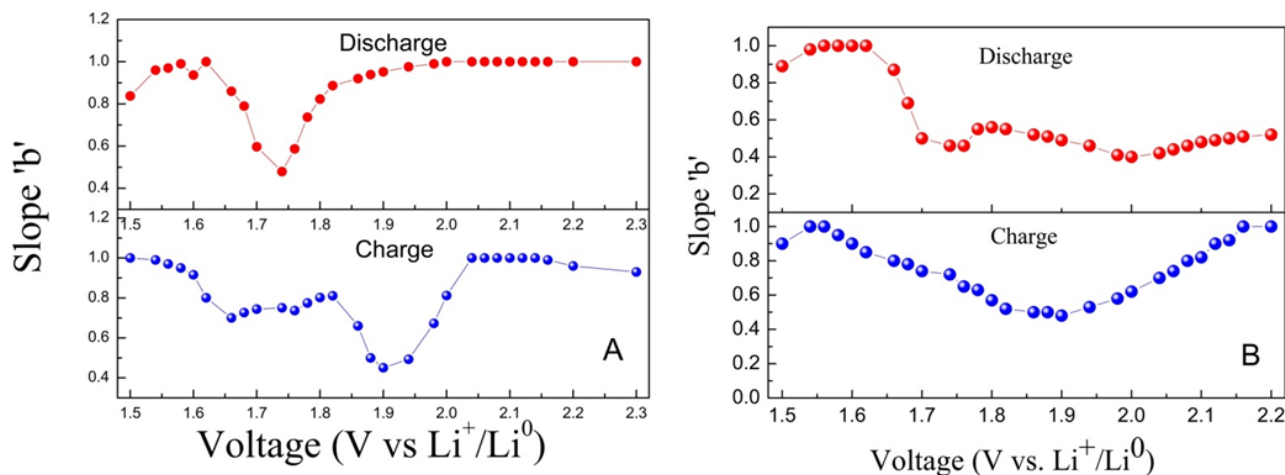


Figure S-4. Dependence of slope 'b' (slope value obtained from linear fit of $\log i$ vs $\log v$) as a function of cell voltage for (A) 25% TiO₂/CNT composite (B) 100% TiO₂.

As explained in Fig S-3, the value of b is obtained and plotted as a function of voltage V . It is seen from the Fig. S-4 (A) that the b value is close to ≈ 0.5 at peak potentials and it is closer to one at all other potentials. This indicates that diffusion limited intercalation process dominates at peak potential whereas capacitive contribution is prominent at other potentials. On the other hand, the value of b is closer to 0.5 at most of the potentials for unsupported TiO₂ indicating the dominance of intercalation capacity to charge storage in unsupported TiO₂. The percentage contribution from diffusion controlled intercalation towards total stored charge is 98% for pristine anatase TiO₂ (See Fig. 10).

Supporting Information S-5

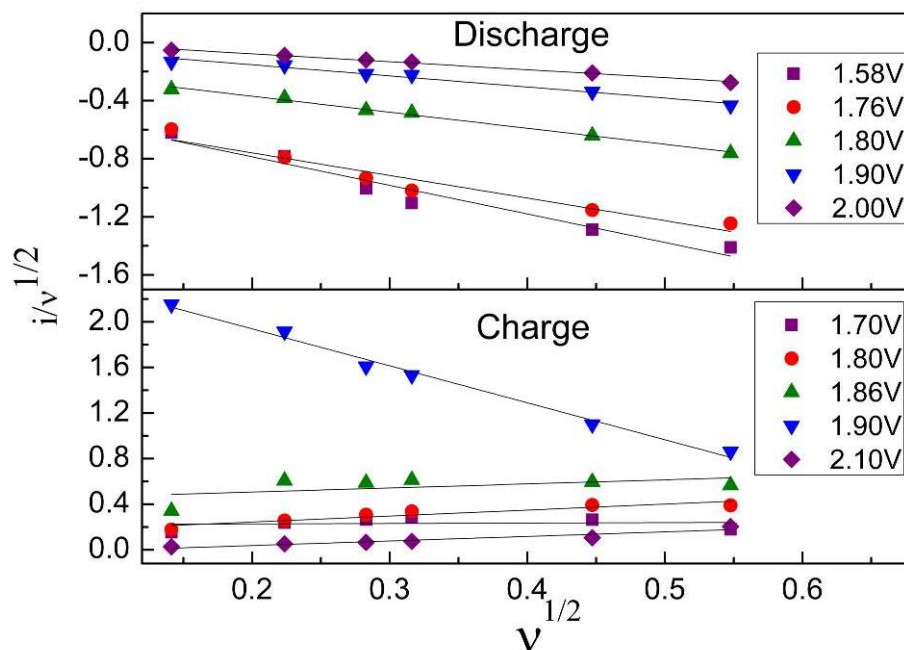


Figure S-5. The plot of $v^{1/2}$ vs. $i/v^{1/2}$ used for calculating constants a_1 and a_2 at different potentials of 25% TiO_2/CNT composite.

The overall current response to charge storage can be represented by $i = a_1v + a_2v^{1/2}$ where the first part, a_1v indicated current contribution from non diffusion process and the second part, $a_2v^{1/2}$ to diffusion process. The above equation can be rearranged as $i(V)/v^{1/2} = a_1v^{1/2} + a_2$ to determine the constants a_1 and a_2 from the linear plot of $i/v^{1/2}$ vs. $v^{1/2}$. Current values at different potentials were obtained from cyclic voltammograms at different scan rates. Plots of $i/v^{1/2}$ vs. $v^{1/2}$ (Fig. S-5) are drawn at different potentials and the values of a_1 and a_2 are derived from the slope and intercept, respectively.

Supporting Information S-6

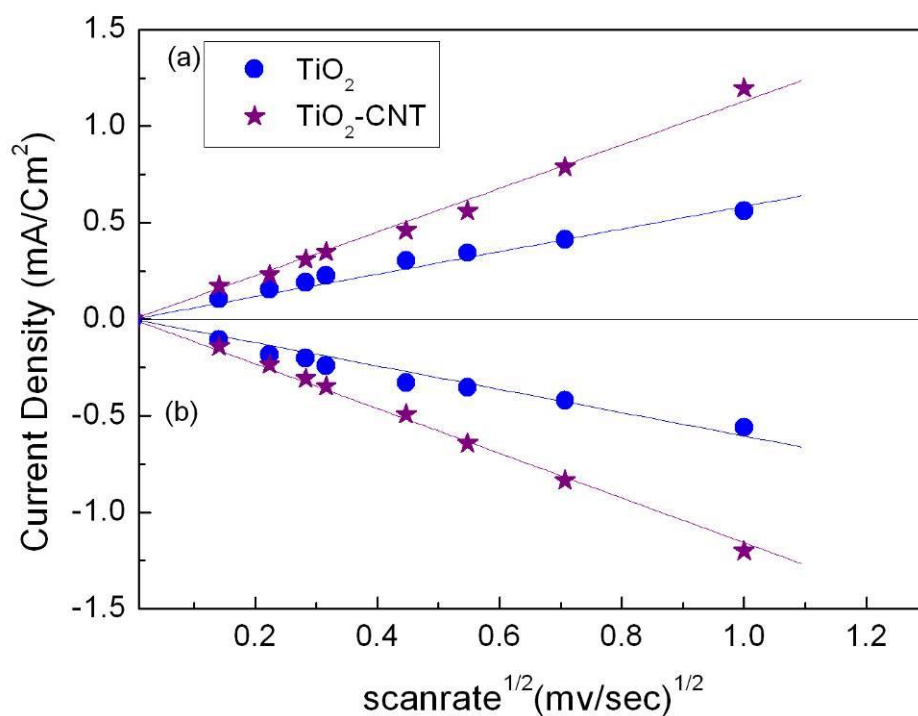


Figure S-6. Plot of i_p vs. $v^{1/2}$ for the cathodic and anodic peaks

For irreversible redox process, the effect of scan rate on peak current (i_p) is expressed by the following equation.

$$i_p = 0.4958nFAC (D\alpha nFv/RT)^{1/2}$$

Where n is the number of electrons transferred in the redox event, A is electrode area in cm^2 , D is the diffusion coefficient in cm^2/s , C is the concentration in mol/cm^3 , v is the scan rate in V/s and α is the charge transfer coefficient. According to this equation the plot of i_p versus $v^{1/2}$ is linear and the diffusion coefficient can be calculated from its slope. Figure S-7 shows the i_p versus $v^{1/2}$ plot for TiO_2 and 25% TiO_2/CNT . From the plot, the values of Diffusion coefficient (D) for TiO_2 and 25% TiO_2/CNT were calculated to be $1.4534 \times 10^{-14} \text{ cm}^2/\text{s}$ and $4.7385 \times 10^{-14} \text{ cm}^2/\text{s}$, respectively. Thus diffusion coefficient of Li^+ is higher in 25% TiO_2/CNT than TiO_2 .

Supporting Information S-7

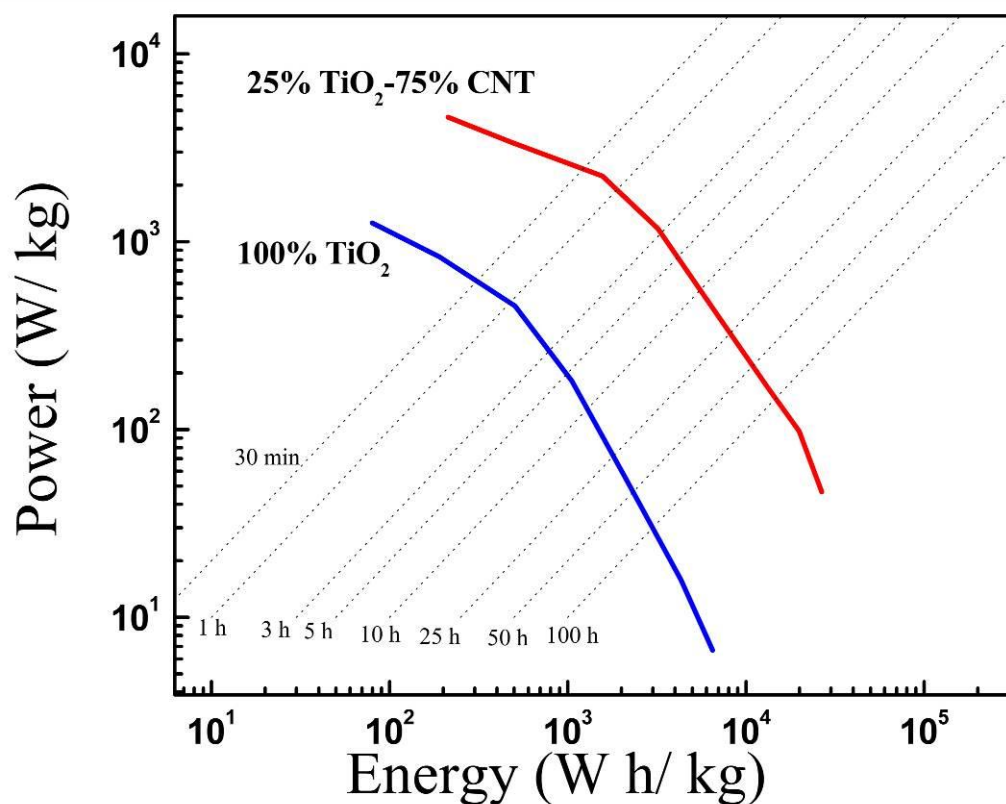


Figure S-7. Ragone plot of 25% TiO₂/CNT composite

Ragone plot of specific power vs. specific energy was derived from constant power experiments. The data indicates that 25% TiO₂/CNT offered higher energy and power densities than pure pristine TiO₂. These results further confirm that these composites offer superior capacity in terms of energy and power density as the total capacity contributions come from individual diffusion controlled lithium intercalation and non-diffusion controlled pseudocapacitance.