TiO$_2$ coated carbon nanotubes for electrochemical energy storage

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Supporting Information S-1

Figure S-1, Structure of Anatase TiO$_2$
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 TiO$_2$, 90% TiO$_2$/CNT, 75% TiO$_2$/CNT and 50% TiO$_2$/CNT composite are shown in Fig. S-2 a-d, respectively. It is seen from the figure that with increase in TiO$_2$ content beyond 25 % (TEM image of 25%TiO$_2$/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 TiO$_2$ in 25% loaded sample is less than 10 nm whereas it is about 10-20 nm for pristine TiO$_2$, 75% TiO$_2$ and 50% TiO$_2$ loaded samples. These attributes are further supported with surface area measurements. BET surface area measurements on the different percentages of TiO$_2$ loading is shown in Fig. S-2(e). The surface area for pure pristine TiO$_2$ is 98.6 m$^2$/g and functionalised CNT is 158.9 m$^2$/g. The maximum surface area of about 252.9 m$^2$/g is observed for 25% TiO$_2$ loading. The surface area decreases with increasing percentage of TiO$_2$ beyond 25 percent. The surface area values for 50% and 75% TiO$_2$ loading are 165.5 m$^2$/g and 111.7 m$^2$/g, respectively.
Figure S-3. Plot showing linear relationship of log υ vs log i for cathodic (discharge) and anodic (charge) sweeps of cyclic voltammogram of 25% TiO₂/CNT composite.

Cottrell equation is given as \( i = nFAC_0^Dj/\sqrt{Dj/\pi t} \). In practice, the simplified equation can be written as \( i = a\sqrt{\nu} \) where ‘a’ represents constants such as n, F, A, C₀, D. Since scan rate (ν) and t are related, (ν)\(^{1/2}\) 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, \( i = a\nu^b \), where a and b are variable parameters. This can also be written as, log \( i = \log a + b \log \nu \) and the value of b can be defined from the slope of linear curve obtained by plotting log i vs. log \( \nu \).

For a non diffusion limited processes, the value of slope would be unity, \( b = 1 \) (i.e, \( i = a1\nu \)) and for a diffusion limited processes, slope \( b = 0.5 \), \( i = a2\nu^{1/2} \). 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% TiO\textsubscript{2}/CNT composite (B) 100% TiO\textsubscript{2}.

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 \approx 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 TiO\textsubscript{2} indicating the dominance of intercalation capacity to charge storage in unsupported TiO\textsubscript{2}. The percentage contribution from diffusion controlled intercalation towards total stored charge is 98% for pristine anatase TiO\textsubscript{2} (See Fig. 10).
Supporting Information S-5

![Plot of $v^{1/2}$ vs. $i/v^{1/2}$](image)

**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.

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

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 $\alpha$ 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 $1.4534 \times 10^{-14}$ cm$^2$/s and $4.7385 \times 10^{-14}$ cm$^2$/s, respectively. Thus diffusion coefficient of Li$^+$ is higher in 25% TiO$_2$/CNT than TiO$_2$. 

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Figure S-7. Ragone plot of 25% TiO$_2$/CNT composite

Ragone plot of specific power vs. specific energy was derived from constant power experiments. The data indicates that 25% TiO$_2$/CNT offered higher energy and power densities than pure pristine TiO$_2$. 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.