# Vertically Aligned Graphene/$MnO_2$ Nanosheets for Ultracapacitor Applications

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Graphene is an excellent electrode material for energy storage applications, such as ultracapacitors, because of its outstanding material properties. It is a two-dimensional structural material with very large specific surface area of excellent electrical conductivity, chemically and mechanically stable, and can be fabricated economically. As an electrochemical double layer capacitor, pure graphene has shown high specific capacitance. On the other hand, transition metal oxides such as $MnO_2$ have very high theoretical specific capacitance due to pseudocapacitive behavior involving rapid, reversible faradaic reactions where the oxidation state of Mn varies between +3 and +4 in conjunction with the intercalation and deintercalation of the electrolyte cation. Also, $MnO_2$ is inexpensive, readily available and environment friendly. Recently, various phases of $MnO_2$ with different nanostructural morphologies have been synthesized and characterized for supercapacitor electrode applications [1].

This paper reports a novel approach that exploits and integrates the unique advantages of these materials by impregnating vertically aligned graphene nanosheets with $MnO_2$ nanoparticles to form hybrid electrodes thereby boosting their energy density and power performance. We present fabrication and characterization of vertically aligned Graphene/$MnO_2$ nanosheets ultracapacitor electrode by direct *in-situ* electrochemical deposition of $MnO_2$ from $KMnO_4$ solution on vertically aligned graphene nanosheets which provides excellent control over the $MnO_2$ film thickness while ensuring maximum usage of the high specific surface area of the graphene.

Vertically aligned graphene nanosheets were grown on a highly doped silicon substrate by thermal CVD at 900°C in a gas mixture of methane and argon with a flow rate of 5:100 sccm. The height of the graphene was controlled by varying the $CH_4$ flow time. The Raman spectra in Figure 1 shows that the as-deposited graphene film has the 2D peak at ~2700 $cm^{-1}$ with sharp FWHM of 60 $cm^{-1}$, the intensity ratio of 2D:G is larger than 4, and the D peak is minimal. Hence, confirming the as-grown film is single layer graphene. Figure 2(a) is a top view SEM image of ~2μm tall of vertically aligned graphene nanosheets grown on the silicon substrate. Controlled electrochemical deposition of $MnO_2$ on the graphene nanosheets was achieved by direct reduction of $KMnO_4$ in de-ionized water. This novel deposition process is extremely efficient, green, and low-cost. The tilted view SEM image seen in figure 2(b) shows the $MnO_2$ coated on vertically aligned graphene nanosheets.

Electrochemical characterization was performed in a flat cell using 0.1M KCl as the supporting electrolyte. Cyclic voltammograms were recorded in a 0-1V potential window at different scan rates and $MnO_2$ film thicknesses. The capacitance was calculated by using area under the curve and incorporating that into equation.

$$C\left(V_f - V_i\right) = q = \frac{1}{\vartheta}\int_{V_i}^{V_f} I(V)\,dV$$

The capacitance increased with decrease in scan rates. For a fixed scan rate, we saw an increase in the pseudo-capacitive current as we increased the $MnO_2$ thickness up to a certain limit. Figure 3 shows CVs recorded at 50mV/s; before and as a function of $MnO_2$ deposition thicknesses. The current of the electrode increases and reaches a maximum as $MnO_2$ deposition increases. A drastic reduction in current due to increased thickness is observed upon further $MnO_2$ deposition. The high values of capacitance obtained were ***50mF/cm²*** and ***140 mF/cm²*** at scan rates of 50mV/s and 2mV/s, respectively, each representing > ***50x*** enhancement in the electrode capacitance due to the addition of $MnO_2$.

Fabrication and characterization of the novel graphene/$MnO_2$ hybrid ultracapacitor and its enhanced performance in terms of specific energy and power densities, cyclic stability, and the effect of the $MnO_2$ thickness on the graphene/$MnO_2$ hybrid electrode will be discussed.

**References:**

1. S. Wei, W. P. Kang, J. L. Davidson, B. R. Rogers, and J. H. Huang, *ECS Transactions*, 28 (8) 97-103 (2010).

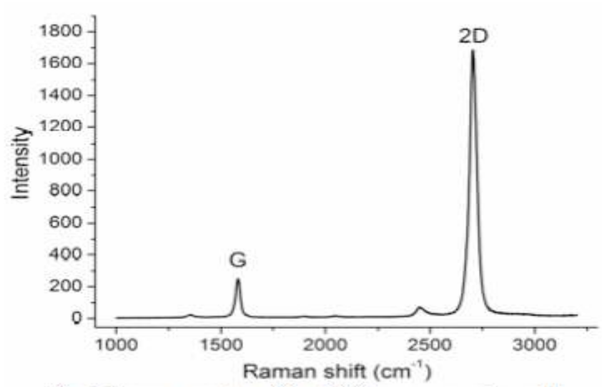


Fig 1 Raman spectra of the CVD grown graphene film .

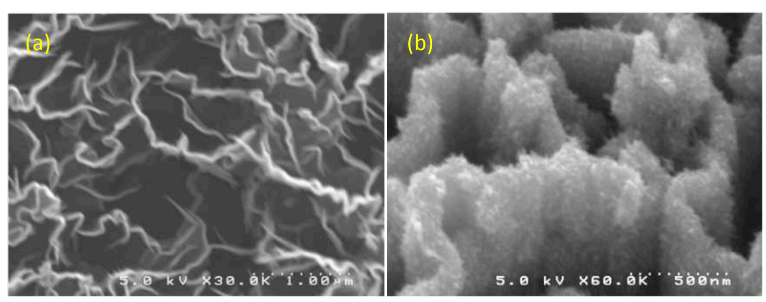


*Figure 2. (a) Top view SEM image of vertically aligned graphene nanosheets electrode grown on silicon substrate; (b) Tilted view SEM image of the electrode with $MnO_2$ coating on the graphene nanosheets.*

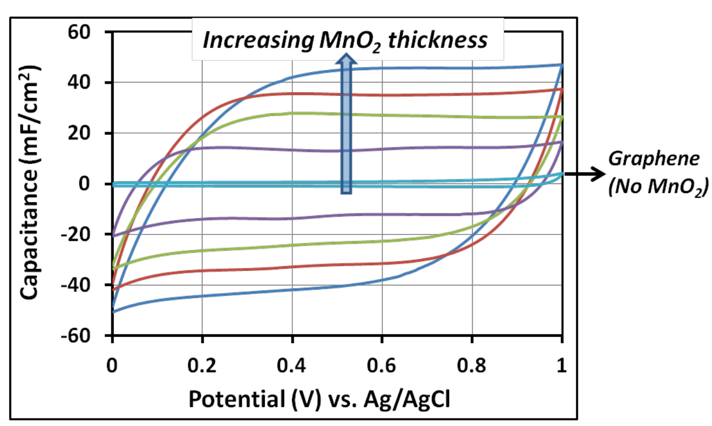


*Figure 3. CV scans recorded at 50mV/s in 0.1M KCl, using as-grown graphene nanosheeets and different thickness of $MnO_2$ coating on graphene nanosheets, showing capacitance enhancement variation as a function of the $MnO_2$ thickness.*