Pseudocapacitive Charge Storage in Two-Dimensional Materials

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The recent development of methods for manipulating graphene has ignited intense interest in 2D layered materials for both fundamental studies and potential applications. A large family of layered materials in which atoms within each layer are held together by covalent bonds, while van der Waals interactions hold the layers together, has been isolated into single or few-layered nanosheets through various exfoliation methods. Because of the reduced dimensionality, these 2D nanosheets can exhibit distinctly different properties from their 3D bulk counterparts. These 2D materials are of considerable interest for energy-storage devices[1-4], as the van der Waals gap between the 2D sheets provides a network of empty lattice sites that can be occupied by a large number of guest species. The ability of these 2D layered materials to support fast ion transport of Li^+ and Na^+ is well established as the electrochemical properties of many transition metal oxides[5-7] and transition metal dichalcogenides[8, 9] in bulk form were determined in the 1970's and 80's.

In our research, we have been synthesizing functional inorganic nanomaterials with atomic scale thickness and infinite planar lengths. These layered materials have been prepared by either direct synthesis in solution (bottom up) or bulk-exfoliation (top down). Among the materials we have prepared are TiO_2, Nb_6O_{17}, Nb_2O_5, $TiNbO_5$, Ti_2NbO_7, TiS_2, MoS_2 and WS_2. In the case of oxides, we synthesized single layer materials by bulk-exfoliation of micron particles size synthesized by solid state reactions. For example, TiO_2 nanosheets are obtained by bulk-exfoliation of $Cs_xTi_{2-x/4}O_4$ protonate phase with tetrabylammonium hydroxide (TBAOH) in solution. The $Cs_xTi_{2-x/4}O_4$ powder is prepared by solid state reaction of Cs_2CO_3 and TiO_2 anatase at 800°C. In contrast, single layers of dichalcogenides were prepared by direct synthesis in solution at ambient atmosphere. In the case of MoS_2, for example, the single nanosheets are prepared by reflux under N_2 flow of $(NH_4)_2MoS_4$ in oleylamine at 360°C during 30 min. Figure 1 shows some of the typical nanosheets that we have synthesized.

While the electrochemical properties of transition metal dichalcogenides have been characterized as bulk materials, there are very few instances where single sheets of these materials produced by direct synthesis have been reported. We fully expect that 2D sheets of these materials will have interesting charge storage properties. The open ion pathways within 2D layers coupled with the thin morphology and high electrical conductivity may well produce the combination of high ion and electron transport which is essential for rapid charge storage. In our work to date, the properties of single layer and bulk are compared, to better understand the reactions kinetics. In fact, MoS_2 single sheets materials, in comparison to MoS_2 multi-layers, exhibits the highest capacitance at high sweep rate (Figures 1e).

While our research at this time is just starting, it is apparent that single layer 2D materials exhibit different properties from the corresponding bulk. The combination of having high electrical conductivity, large surface area, and redox-active constituents suggests that these materials have great potential for pseudocapacitive charge storage.

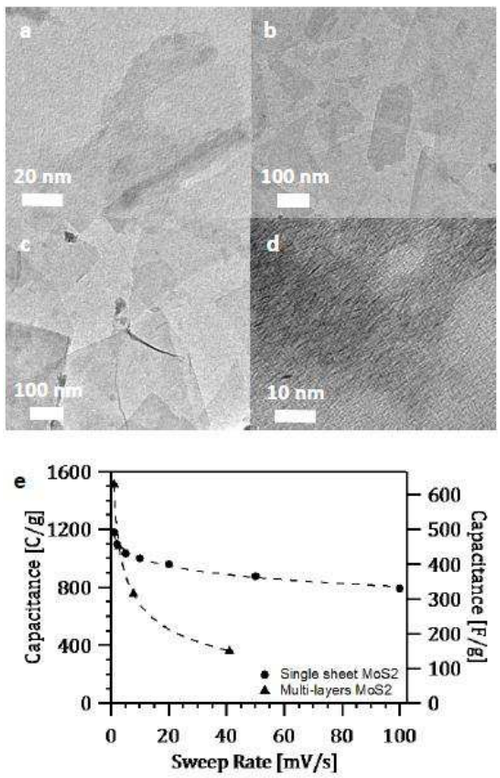

Figure 1: Example of typical nanosheets (a) TiO_2, (b) Nb_6O_{17}, (c) $TiNbO_2$, (d) MoS_2. (e) Capacitance for MoS_2 single sheet (this work) and multi-layers[10] (5-10 layers) materials in function of the sweep.

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