by the DIO additives is the most important factor to achieve both highly efficient exciton dissociation and carrier transport.

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3D Ordered Macroporous Inverse-Opal Electrodes Enable High Energy Storage

*This report features the works of Ming-Jay Deng, Jin-Ming Chen, Kueih-Tzu Lu and their co-workers published in Energy Environ. Sci. **6**, 2178 (2013).*

Facing predicaments – a limited availability of fossil fuels but their insatiable demand, climate change and atmospheric pollution, human society actively seeks renewable and clean energy for sustainable living. Although many productions of clean energy from sun and wind have been developed, a great problem is that those natural resources cannot be formed anytime and anywhere. The development of systems to store energy thus becomes an important subject for the efficient storage of solar and wind energy. Supercapacitors are an electrochemical energy storage device but with characteristics different from those of a battery. Whereas existing supercapacitors have energy densities that are approximately one tenth those of a conventional battery, their power density can be thousands of times greater. This greater power density results in much shorter charge/discharge cycles of which the battery is capable, and a greater tolerance for numerous charge/discharge cycles. Supercapacitors have thus attracted intense attention because of their great advantages to meet the demand of both great energy density and power density in many advanced technologies, such as consumer electronics, energy management, memory back-up systems, industrial power and mobile electrical systems.

The current performance of supercapacitors hinges on the design of electrode materials. Three-dimensionally ordered macroporous (3DOM) materials are an active topic for supercapacitors, because they not only create structural interconnectivities with a large surface area,[1-3] but also possess an increased electrical conductivity and maintain improved structural mechanical stability to offer significantly enhanced properties for large energy storage. Direct growth of 3DOM on conductive substrates can facilitate the diffusion of active species and transport of electrons, and hence might broaden further their applications in supercapacitors. Ming-Jay Deng, Jin-Ming Chen and Kueih-Tzu Lu *et al*. from NSRRC, Taiwan, developed a nanoarchitecture comprising a 3DOM metal core–metal oxide shell inverse-opal structure using electrodeposition of a metal within a polystyrene (PS) bead template, which was subsequently anodized in aqueous solution with varied anodization courses to construct a nanoarchitectured pseudocapacitive electrode.[1, 2] The 3DOM metal/metal oxide core–shell structure is expected to produce an electrical conductivity more easily than a conventional chaotic metal-oxide electrode. The periodic pore structure inherent in ordered inverse opals is expected to provide an ionic conduction in the electrolyte-filled pores greater than in the circuitous pore structure in chaotic metal-oxide electrodes. The synthesis strategy is briefly illustrated in Fig. 1(a). The 3D structure of the electrodeposited porous films is particularly dependent on the arrangement of the PS spheres on the substrate; in general, closely packed arrays of PS sphere yield highly ordered porous films. These scientists also compared the capacitive behavior of 3DOM manganese (Mn)/manganese oxide

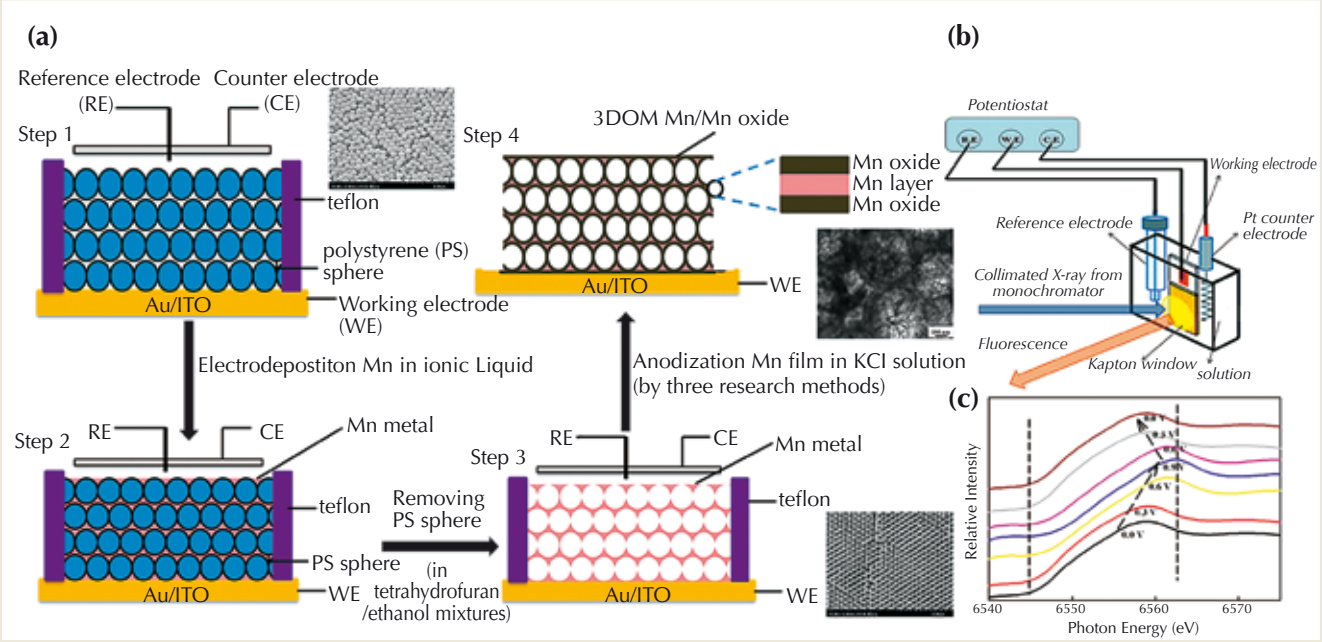

Fig. 1: (a) Scheme of preparation of a highly porous 3DOM metal/metal oxide core/shell electrode. (b) Schematic illustration of the electrochemical cell used for XAS studies *in situ*. (c) Mn K-edge XANES spectra of the 3DOM Mn/Mn oxide-CV electrode measured *in situ* in KCl solution with applied potential, respectively. (Courtesy of M. J. Deng with the figure adapted from Ref. 1)

(MnO_2) and 3DOM MnO_2 electrodes in potassium chloride (KCl) solution.

With a comprehensive understanding of an electrochemical characterization of electron transfer and future practical applications, they recorded synchrotron-based X-ray absorption spectra (XAS) *in situ*, X-ray diffraction (XRD) and X-ray photoelectron spectra *ex situ* at **BL01C2**, **BL07A1**, **BL17C1** and **BL20A1** of the TLS to elucidate the mechanism of charge storage and the variation of the oxidation state of the metal in the 3DOM metal/metal oxide electrode in electrolytes during charge and discharge cycles.[1, 2] Figure 1(c) shows Mn X-ray absorption near-edge structure spectra (XANES) of the 3DOM Mn/Mn oxide–cyclic voltammetric (CV) electrode measured *in situ* under three applied potentials in a sequence + 0.0 V, + 0.3 V, + 0.6 V, then + 0.9 V and + 0.6 V, + 0.3 V, and finally + 0.0 V. The rising edge of absorption of the Mn K-edge spectra of the 3DOM Mn/Mn oxide–CV electrode shifted toward greater energy with increasing applied potential, and returned to nearly the initial position when the potential was reversed. The variation of the Mn oxidation state between 0.0 V and + 0.9 V with a 3DOM Mn/Mn oxide–CV electrode is nearly 0.9. These results confirm that the 3DOM structure minimizes the distances of both ionic and electronic transport in the 3DOM Mn/Mn oxide–CV, and thus improves the electrode kinetic performance, contributing the significant capacitance observed in Fig. 1(c), which is a crucial concern for high-performance supercapacitor applications.

In summary, a facile, cost-effective, and potentially scalable method was demonstrated to fabricate 3DOM metal/metal oxide core–shell inverse-opal electrodes for high-performance supercapacitors. Having a larger surface area, higher hydrous state and lower Mn valence state, this unique 3DOM Mn/Mn oxide core–shell electrode showed an excellent rate capability and long-term cycle stability. Such method of metal/metal oxide core–shell electrodes would open new opportunities for the next generation of high-performance supercapacitors.

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