Surface Capacitive and Ion-Diffusion-Limited Capacitive Effects in High Energy Density Quantum Dot Nanopores Supercapacitors

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Achieving high energy and power density values are the aims of designing high-performance energy storage devices, including supercapacitor (SC). Since the capacity of an electric double layer supercapacitor (EDL-SC) is strongly determined by the interaction between the electrode surface and the electrolyte, significantly enhancing the surface area of the electrodes is vital. Electrode nanostructuring and the utilization of solution-processable nanomaterials can be effective solutions. However, the inadequate accessible surface by the ions would reducing the efficient capacitive area and the inefficient charge transport in the nanomaterials-based electrodes would hamper the energy storage capability than expected. Recently, assembling small diameter colloidal semiconductor quantum dots into hierarchical nanoporous structures and applying them as electrodes allow the demonstration of ultrahigh volumetric energy density supercapacitor devices, reaching 95.8 Wh L^{-1}. In this structure, electrolytes (i.e., ionic liquid) could access all surfaces of the QDs via the created ion "highway" while maintaining the efficient electronic coupling for charge transport.

Here, we report the electrochemical kinetic analysis of the supercapacitor based on the QD hierarchical nanopore (QDHN) electrodes to understand their charge storage mechanism. Detailed evaluation of the cyclic voltammetry and electrochemical impedance spectroscopy measurements of different devices with thickness variations reveal that there are mixed contribution of diffusion-controlled capacitive effect and the surface capacitive (EDL) effect. It suggests that the supercapacitor devices have not worked as a full EDL supercapacitor, but still limited by the capability of the ions moving inside the QDHNs. We found out that ligands that bridge and modifies the surface of the QDs also play roles in controlling the ionic mobility when diffusing in and out the QDHNs. Reducing the ion diffusion limited capacitive ratio and enhancing the EDL ratio to the device operation will enable further enhancement of the QDHN-based supercapacitor devices.

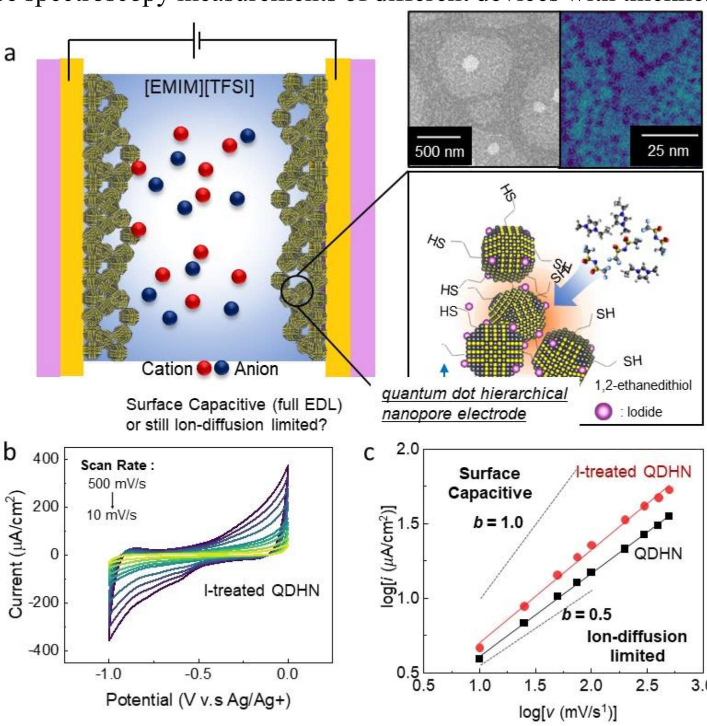

Figure 1 (a) Schematic of supercapacitor device based on PbS quantum dot hierarchical nanopore electrodes (right images) (b) The cyclic voltammetry of the supercapacitors at different scan rate, (c) A plot showing the linear correspondence between the anodic current and the scan rate of different types of QDHN samples suggesting that the capacitive mechanism in the device is still also influenced by ion-diffusion limited process of the electrolyte. Improving the device to work in full surface capacitive (EDL) mode will further enhance the supercapacitor performance.

References:

1. R.D. Septianto, S. Z. Bisri, et al. *NPG Asia Mater.* 12, 33 (2020).
2. M. A. Irham, S. Z. Bisri, et al. *submitted*