Confinement of Single Polyoxometalate Clusters in Molecular-Scale Cages for Improved Flexible Solid-State Supercapacitors

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Introduction

Polyoxometalates (POMs) have been suggested as economically and chemically viable replacements for noble metal oxide as pseudo-capacitive material in energy storage fields recently. Our work realize supramolecular confinement of single POM cluster precisely in polypyrrole (PPy) hydrogel-wrapped CNT framework with molecular-scale cages for enhanced flexible solid-state supercapacitors performance.

Material Design

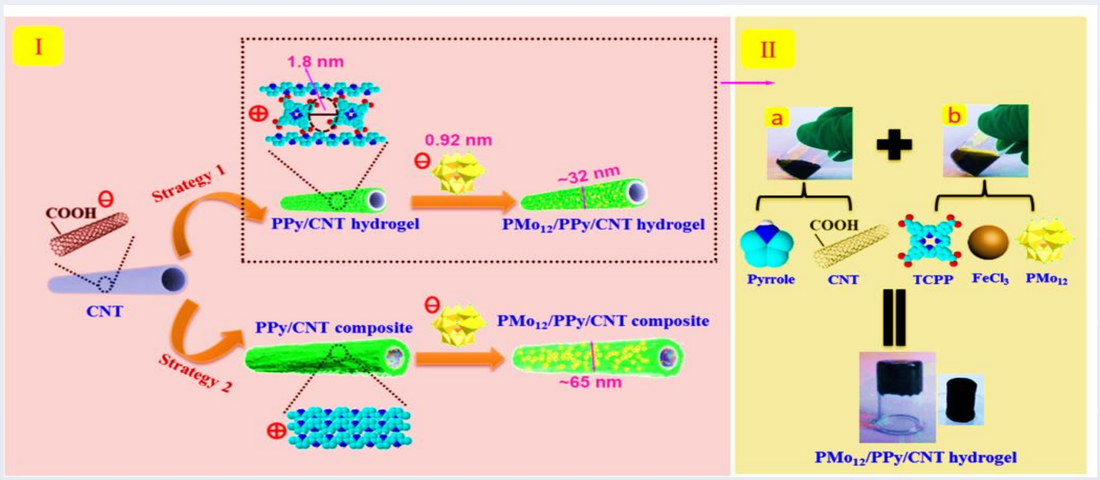


Figure 1. (I) Electrostatic capture of PMo_{12} molecules by fishnet-like PPy hydrogel (strategy 1) or blanket-like PPy chains (strategy 2)-wrapped CNT. (II) The fabrication process of PMo_{12}/PPy/CNT ternary hybrid hydrogel, Inset: photographs of the PMo_{12}/PPy/CNT hybrid hydrogel.

Material Characterization

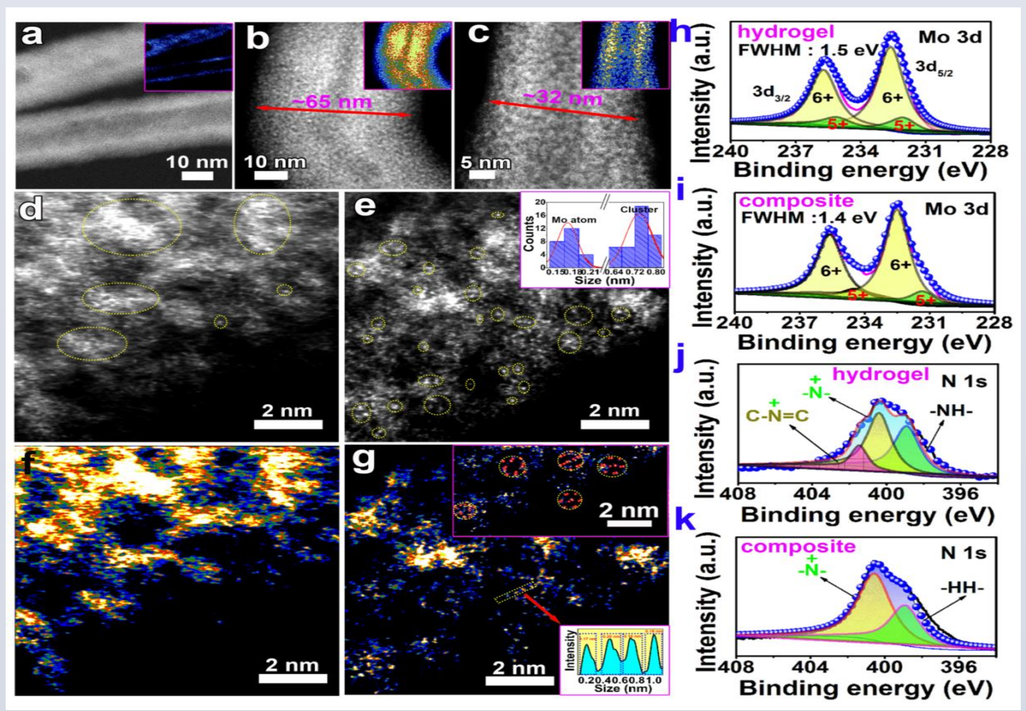


Figure 2. HAADF-STEM images of CNT (a), PMo_{12}/PPy/CNT conventional composite (b, d, f) and PMo_{12}/PPy/CNT hybrid hydrogel (c, e, g), respectively; Selected examples of Mo atoms were mapped in yellow circles (e). Note: The raw STEM images were processed using the Gatan Microscopy Suite Digital Micrograph software to generate color-enhanced Z-contrast images (f, g and inset of a-c); XPS curve fits of Mo 3d and N 1s spectra of hybrid hydrogel (h, j) and composite (i, k); Inset: Histogram of cluster size distribution in hybrid hydrogel (e) and the profile of integrated pixel intensities of reprehensive single Mo atom (bottom right corner of Figure 3g).

Performance Comparison

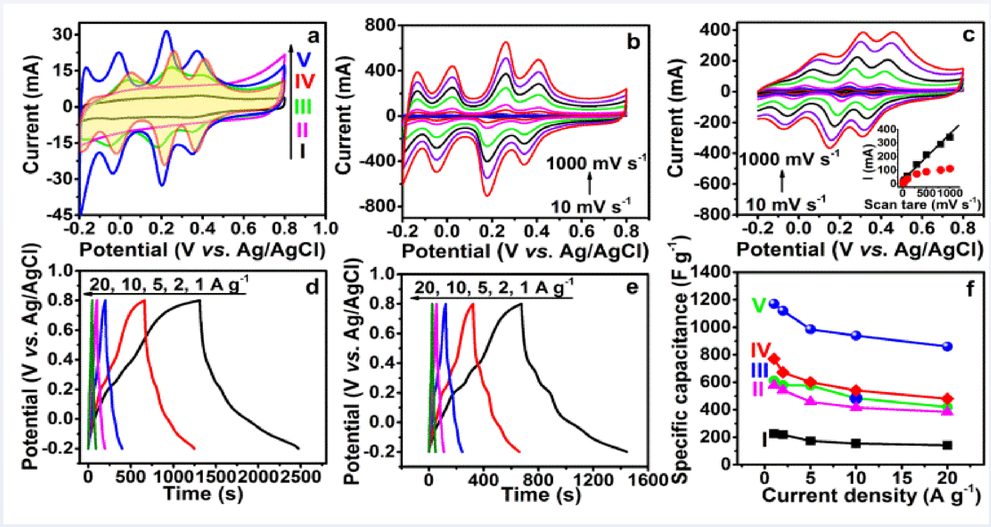


Figure 3. (a) CV curves of CNT (I), PPy/CNT hydrogel (II), PMo_{12}/PPy hydrogel (III), PMo_{12}/PPy/CNT composite (IV) and PMo_{12}/PPy/CNT hybrid hydrogel (V); CV curves of (b) PMo_{12}/PPy/CNT hybrid hydrogel and (c) PMo_{12}/PPy/CNT hybrids electrodes at different scan rates; GCD curves of (d) hydrogel and (e) hybrids electrodes; (f) Specific capacitance values.

DFT calculations

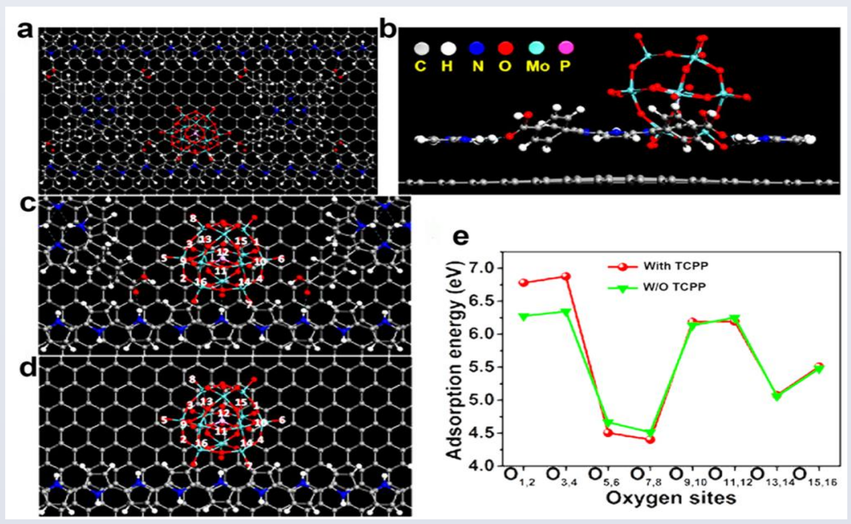
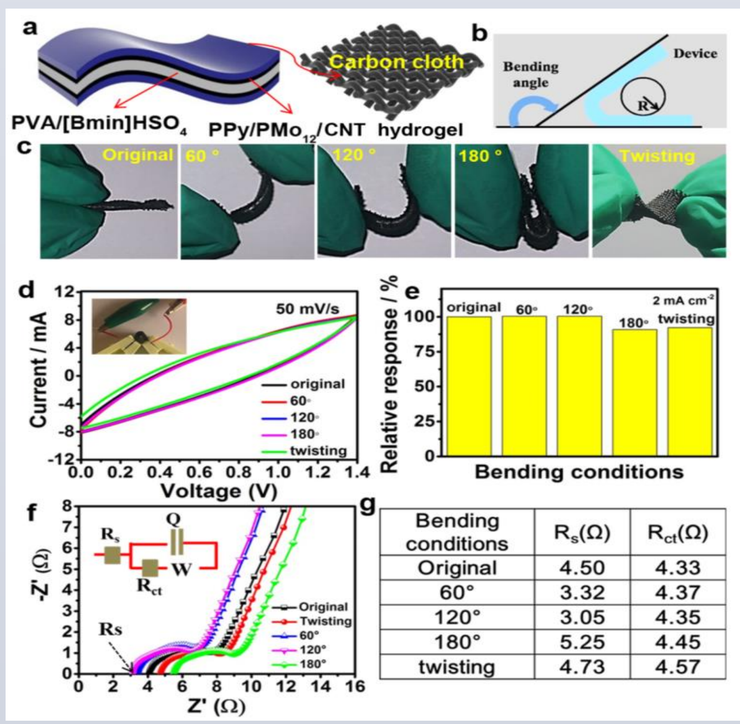


Figure 4. Optimized structural models of PMo_{12}/PPy/carbon mono layer doped by TCPP: top view (a) and side view (b); enlarged structural model of PMo_{12}/PPy/carbon mono layer doped by TCPP (c) and TCPP-free PMo_{12}/PPy/carbon mono layer (d) in both of which sixteen different O sites are numbered; DFT calculated adsorption energies of two H atoms on sixteen different O sites of two samples (e).

Application



Bending conditions	R_s(Ω)	R_{ct}(Ω)
Original	4.50	4.33
60°	3.32	4.37
120°	3.05	4.35
180°	5.25	4.45
twisting	4.73	4.57

Figure 5. Schematic diagram of the flexible SSC made by PMo_{12}/PPy/CNT hydrogel electrodes (a); Photographs of the flexible SSC in various flexible conditions (c); CVs of the assembled SSC in normal, bended or twisted states at 50 mV s^{-1} (D); Capacitance retention as a function of bending state (e); Nyquist plot (f, g) of the SSCs with different flexible conditions.