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ALD Alumina Passivated Silicon Nanotrees electrodes for new Ultrastable Microsupercapacitors

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The current trend towards miniaturized and autonomous electronic devices requires innovative energy storage solutions. For instance, autonomous micro-sensor networks or implantable medical devices would need a robust power source with high cyclability and a large power density, which might be out of the scope of conventional battery technologies. For such applications, microsupercapacitors (μ SCs) are promising alternatives, and their integration “on-chip” could allow significant innovations.¹ However, finding a suitable “on-chip” μ SCs technology implies addressing key challenges, such as temperature resistance, silicon industry compatibility and good electrochemical performances on a small footprint.

Following this trend, our work focuses on μ SCs using highly doped silicon nanowires (SiNWs) and nanotrees^{2,3} (SiNTs) as current collector. The fine morphological tuning of the nanostructure allowed by the bottom-up approach permits a careful design of the electrodes architectures, with a considerable liberty compared to other techniques. Such latitude allows optimizing porosity and ionic and electronic pathways while keeping robust mechanical performances, depending on the target application or other parameters like surface modification, functionalization by pseudo-capacitive material, electrolyte...

Nanostructures such as SiNWs and SiNTs demonstrated excellent cyclability with more than 1 million cycles of galvanostatic charge/discharge under a 4 V wide electrochemical windows in EMI-TFSI ionic liquid, with large power densities and good capacitance values.^{3,4} Moreover, the use of silicon for electrode material allows extremely interesting developments towards “on-chip” integration and potential scale-up production using standard silicon industry processes for small micro-sized energy storage devices.

Furthermore, we have also investigated the impact of the addition of a high-k dielectric layer, such as Al_2O_3 as protective films on silicon nanotrees. The electrochemical performances was enhanced, allowing symmetric 2 electrodes device to reach an unprecedented cell voltage of 5.5 V, improving energy and maximum power densities compared to unmodified nanostructured silicon. The cyclability was also largely enhanced, with only 3% capacitance fade after 10^6 galvanostatic charge/discharge cycles at 4 V, and no degradation even after several 10^5 cycles over 5 V⁵. In addition, the protective alumina layer makes it possible to use aqueous electrolytes, not usable with crude silicon, in order to significantly increase the capacities of the μ SCs from $1\text{mF}/\text{cm}^2$ to $10\text{mF}/\text{cm}^2$ and open the door to use metal oxides.

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