질소가 도핑된 그라핀을 이용한 고성능 슈퍼커페시터 구현 : 기저면의 질소 도핑 사이트의 중요성

Nitrogen-Doped Graphene for High Performance Ultracapacitors and the Importance of Nitrogen-Doped Sites at Basal-Planes

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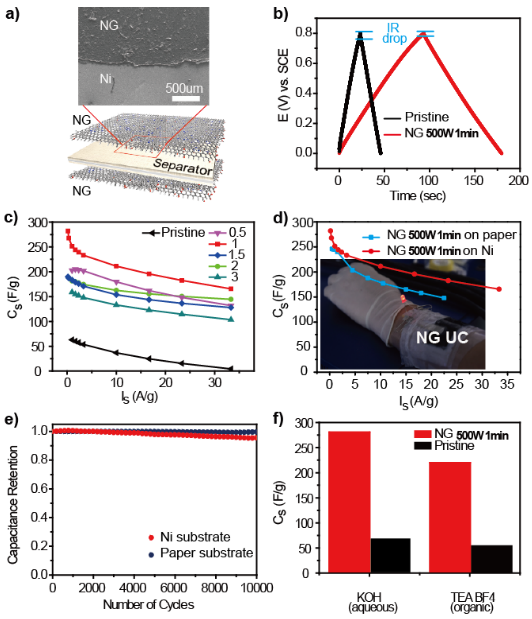
1. 서론

Although various carbon nanomaterials including activated carbon, carbon nanotubes, and graphene have been successfully demonstrated for high performance ultracapacitors, their capacitances need to be improved further for wider and more challenging applications. Herein, using nitrogen-doped graphene produced by a simple plasma process, we developed ultracapacitors whose capacitances (~280 F/$g_{electrode}$) are about four times larger than those of pristine graphene based counterparts without sacrificing other essential and useful properties for ultracapacitor operations including excellent cycle life (>200,000), high power capability, and compatibility with flexible substrates. While we were trying to understand the improved capacitance using scanning photoemission microscopy with a capability of probing local nitrogen-carbon bonding configurations within a single sheet of graphene, we observed interesting microscopic features of N-configurations: N-doped sites even at basal-planes, distinctive distributions of N-configurations between edges and basal-planes, and their distinctive evolutions with plasma duration. The local N-configuration mappings during plasma treatment, alongside binding energy calculated by density functional theory, revealed that the origin of the improved capacitance is a certain N-configuration at basal-planes.

2. 결과 및 고찰



The above figure shows Ultracapacitors based on NGs and their electrochemical testing. (a) A schematic illustration of the assembled UC structure alongside an SEM image showing a top view of the device. (b) Charging and discharging curves measured by galvanostatic characterization. Black and red lines correspond to the pristine graphene and the $NG_{500W,1min}$, respectively. The IR drops at the top cut-off potentials are also denoted. (c) Gravimetric capacitances of UCs based on various NGs and pristine graphene measured at a series of current densities. The numbers in the legend indicate the plasma durations in minute. (d) Gravimetric capacitances of UCs built on nickel and paper substrates measured at a series of current densities. (inset) A photograph showing that a wearable UC wrapped around a human arm can store the electrical energy to light up a LED. (e) The cycling tests for the UCs based on Ni and paper substrates up to 10,000 cycles. (f) The specific capacitances measured in aqueous and organic electrolytes. For both electrolytes, the specific capacitances of NG and pristine graphene are compared.

As an effort to understand the improved capacitance by the N-doping, we have also performed characterization to map the local N-configuration within a single sheet of NG using scanning photoemission microscopy (SPEM). This unique technique led us to detecting a certain N-configuration (pyridine-like) that turned out to be a critical component for the improved capacitance. The detailed data and analyses including density functional theory will be discussed in the poster.

3. 결론

We have developed high capacitance NG UCs using a simple plasma doping process. This simple doping process not only increases the specific capacitance by about four times compared to that of pristine graphene but also preserves excellent cycle life utilizing the intrinsic storage mechanism based on the electrostatic interaction in the EDLs. The improved capacitance is likely resulted from the N-doped sites at basal-planes, according to the integrated analyses using XPS in the microscopic and bulk-scale resolutions as well as the ionic binding energy calculation. Especially, the SPEM technique allows us to observe novel local nitrogen bonding configurations, particularly distinguishing N-configurations at basal-planes and edges, and thus constitute thorough views on the modified graphene structures during the plasma process.

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