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Supercapacitors of nanocrystalline MOFs outperform activated carbon and graphene

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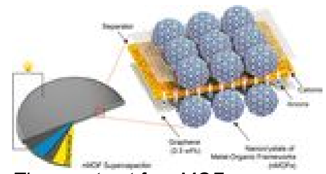
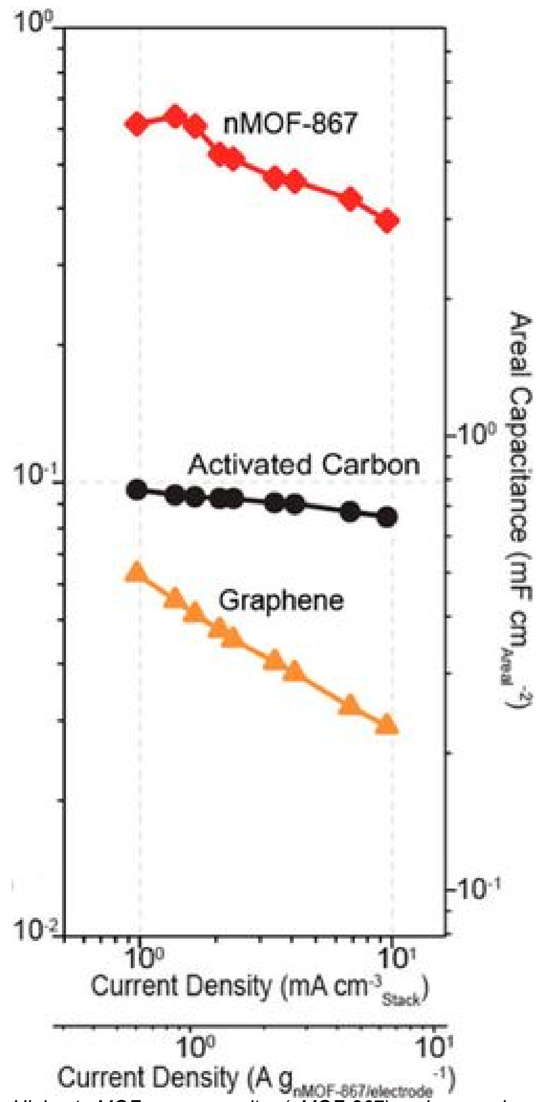
Researchers at UC Berkeley led by Dr. Omar Yaghi and at the Korea Advanced Institute of Science and Technology led by Dr. Jeung Ku Kang have shown that metal–organic frameworks (MOFs) made as nanocrystals (nMOFs) can be doped with graphene and successfully incorporated into devices to function as supercapacitors.



The construct for nMOF Supercapacitors. Credit: ACS, Choi et al. Click to enlarge.

In a paper in the journal *ACS Nano*, the team reported that, among a series of 23 different nMOFs they synthesized, a zirconium MOF (nMOF-867) exhibited exceptionally high capacitance. It has stack and areal capacitance of 0.64 and 5.09 mF cm^{-2}—26 times that of the lowest performing member of the series and about 6 times that of the supercapacitors made from the benchmark commercial activated carbon materials. Performance was preserved over at least 10,000 charge/discharge cycles.

> *In this study, we show how metalorganic frameworks (MOFs) can be integrated into supercapacitor devices and the flexibility with which their metal oxide and organic constituents can be varied and used to uncover their high capacitance and long life cycle behavior; both are desirable features and sought after in supercapacitor research. We examined a series of 23 different MOF compounds, made in their nano-crystalline form, and chosen for their variability in structure type, organic functionality, geometry and size of metal-containing unit, size of pore, and size of the nanocrystals. Thin film devices prepared from these nanocrystalline MOFs (nMOFs) and doped with graphene give a wide range of stack capacitance (0.025 to 0.64 F cm^{-3}).*
>
> —Choi *et al.*



Highest nMOF supercapacitor (nMOF-867) and comparison to activated carbon and graphene. Credit: ACS, Choi et al.

To build their nMOF supercapacitors, the team placed films made from nMOFs doped with graphene on both sides of a separator membrane and soaked the construct in the solution of an electrolyte. By charging the device, the positive and negative ions of the electrolyte move in opposite directions through the separator and into the MOF pores. During discharge, the ions migrate out of the pores and the electrons flow out of the device.

MOFs can perform well in this context because of their high porosity and openness of their structure, which can give high capacity for storage of ions and robust cycling of ions within the cell, respectively.

The series of 23 MOFs had different characteristics; some Click to enlarge.
had the same MOF-5 structure with three-dimensional pores and variously mixed functionalities; others were based on the MOF-74 structure with one-dimensional pores and mixed multimetallic metal oxide units; still others were zirconium(IV) MOFs differing in the length and shape of their links and the size of their nanocrystals; the final members of the series were MOFs with varying nuclearity of the metal containing units.

Among the attributes of the best performing nMOF-867 was:

- Capacitance (0.644 F cm_{stack}^{-3} and 5.085 mF cm_{areal}^{-2} of more than 6 and 10 times that of activated carbon (0.100 F cm_{stack}^{-3} and 0.788 mF cm_{areal}^{-2}) and graphene (0.065 F cm_{stack}^{-3} and 0.515 mF cm_{areal}^{-2}), respectively.
- Gravimetric capacitance of 726 F $g_{nMOF-867/electrode}^{-1}$.
- Maximum energy and power densities of 6.04 104 Wh cm_{stack}^{-3} (3.85 x 10^{-3} mWh cm_{areal}^{-2}) and 1.097 W cm_{stack}^{-3} (8.67 mW cm_{areal}^{-2}), respectively.
- At the power density of 0.386 W cm_{stack}^{-3}, the energy density (2.86 x 10^{-4} Wh cm_{stack}^{-3}) of nMOF-867 is more than three times that of activated carbon (1.00 x 10^{-4} Wh cm_{stack}^{-3}).

> *It is significant that that the charge/discharge profiles, CV curves, and cycling performance of these nMOFs follow the general behavior observed in other supercapacitors. The differences are in the details of the nMOF electrochemical behavior; perhaps their diverse structural and functionality attributes are directly involved in electrochemical processes, and depending on their chemical nature, some undergo redox reactions, which makes several of these nMOFs exceed the capacitance of the benchmark materials. Future work will focus on deciphering the specific impact of these factors on the observed high capacitance of nMOFs.*
>
> —Choi *et al.*

Resources

- Kyung Min Choi, Hyung Mo Jeong, Jung Hyo Park, Yue-Biao Zhang, Jeung Ku Kang, and Omar M. Yaghi (2014) “Supercapacitors of Nanocrystalline Metal–Organic Frameworks” *ACS Nano* 8 (7), 7451-7457 doi: 10.1021/nn5027092
