Development of metal-organic framework-derived nanostructures for supercapacitor applications

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Abstract

The shape, structure, and degree of integration of the electroactive material are important elements to improve the specific capacitance. Many 1D/2D nanostructured materials with unexpected characteristics have been created in the last ten years. Furthermore, it has been shown that multicomponent nanostructured hybrids can inherit the advantages of both nanostructures in addition to gaining from each one's unique traits. This enhances the electrochemical performance of the electrode as a whole and helps to efficiently utilise electroactive species. The synthesis and design of lanthanide compounds have garnered a lot of attention due to the several transition modes involving the 4f shell of their ions. They are widely used as up-conversion materials, phosphors, magnets, catalysts, and time-resolved fluorescence (TRF) tags for biological diagnostics, among other applications, because of their remarkable optical, magnetic, and electrical capabilities. Rare-earth oxide and ions have recently been used as composite electrode materials in supercapacitors and batteries.

Keywords: Metal-organic, framework-derived, supercapacitor, electrochemical

1. Introduction

Nanotechnology has several potential uses that might result in major advancements in renewable energy. One of the NNI's Signature Initiatives, "Nanotechnology for Solar Energy Collection and Conversion," seeks to improve the production of photovoltaic electricity, solar thermal energy, and solar-to-fuel conversions. Through the use of nanoparticle etching technology, the National Renewable Energy Laboratory has produced a roughness that gives photovoltaic cells a black look and improves their ability to absorb solar energy. These "black silicon" solar cells broke the previous record for energy conversion efficiency (18.2%). A method for producing high-performance nanostructured coatings that enable thermal conversion efficiencies of over 90% and extend the temperature range for heat-transfer is inexpensive and scalable, and it is part of a technology intended to boost the efficiency of solar thermal energy conversion.

Charge transfer between the electrode and electrolyte happens as shown in a pseudocapacitor, and the charges are stored by a faradic process. The electrode materials of the

pseudo capacitor experience oxidation and reduction when the voltage is applied. The charge storage methods of pseudocapacitive electrodes include underpotential deposition, redox reactions of transition metal oxides, intercalation pseudo capacitance, and electrochemical doping and de-doping in conducting polymers.

Charges migrate into the double layer as a consequence, creating faradic current in the SC cell. Compared to EDLC, the pseudocapacitor exhibits higher specific capacitance and energy density due to its faradic and redox processes. However, when cycling, the material's power density drops and its stability reduces because of the repeated contraction and expansion. Metal oxides, chalcogenides, nitrides, carbides, phosphates, or conductive polymers as materials for pseudocapacitors

The charge storage mechanism of an electric double-layer capacitor (EDLC) is non-faradaic, which means that electrostatic energy and charge storage are perfectly stored without any electron transport across the electrode interface. Redox chemical processes and lateral repulsion cause electron charges to build up on the electrode surface. These

EDLCs have a high degree of cycleability (about ten times) and a high specific power density, but a very low specific energy density since there are no chemical phase or composition changes that occur throughout the charging and discharging process. However, the fundamental mechanism of certain pseudo capacitance-based supercapacitors (redox type of supercapacitors) is faradaic; that is, charge storage is accomplished by an electron transfer.
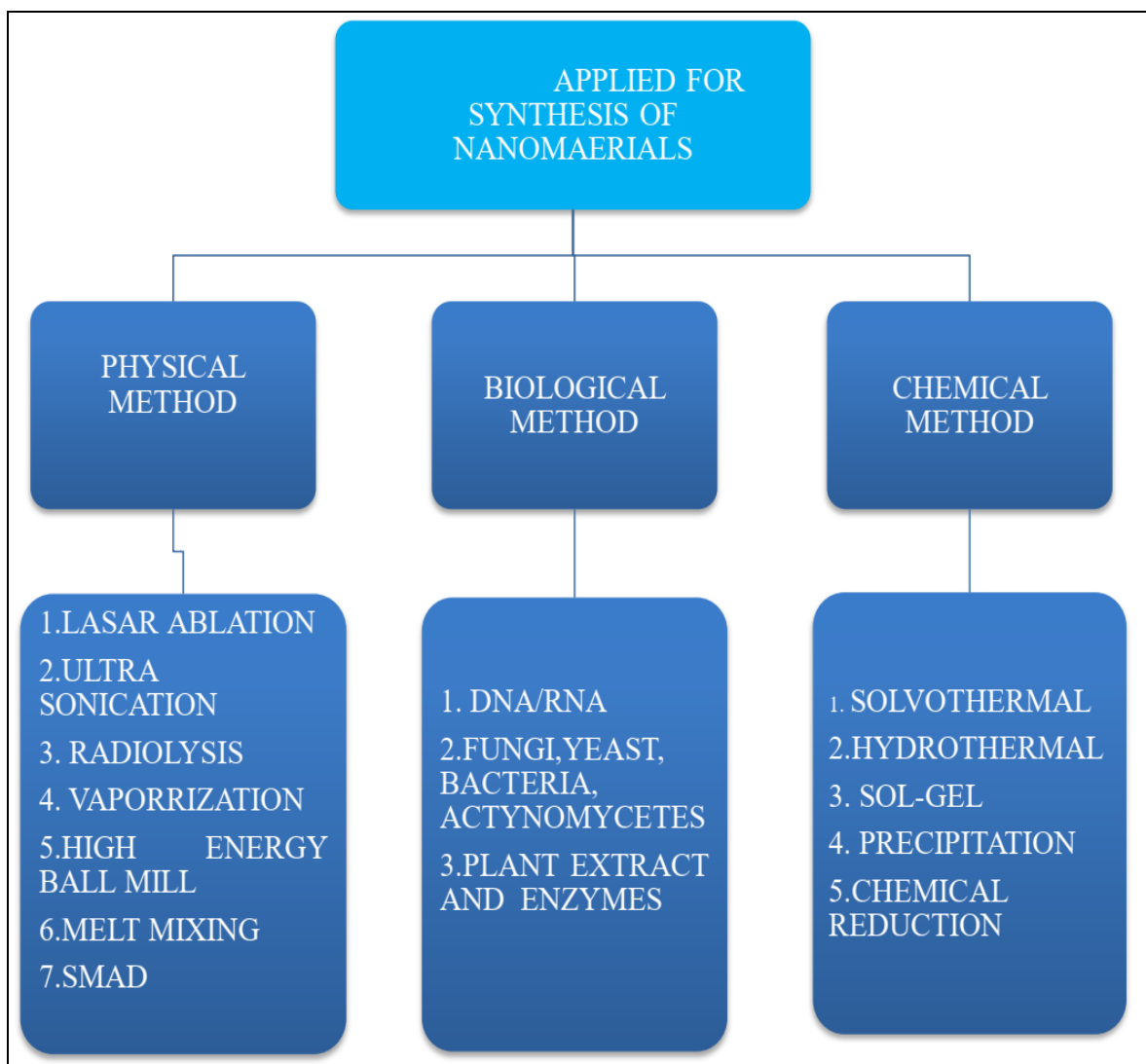

Fig 1: Schematic illustration of several kinds of artificial nanoparticle production techniques

Supercapacitor electrodes include porous matrices and a huge surface area. Batteries, however, are designed with bipolar electrodes for high voltage series combinations. For a battery, the maximum Gibbs energy is equal to G=Q. E, which is the product of the charge Q and the potential difference E between the two electrodes' Nernstian reversible potentials. However, in the case of capacitors, G = 1/2 QV for a given charge Q. It is clear that the energy stored by a two-electrode cell accommodating a given faradaic charge Q at voltage E= V is double that of a capacitor charged with the same Q at the same voltage for a given electrode potential difference, E= V.

Regardless of the quantity of charge Q applied, a charging battery cell should ideally have a thermodynamic potential as long as the two components (oxidised and reduced forms) of the electroactive material remain together. As a result, G= Q. E rather than Q, 1/2 E (or 1/2 V) since the potential difference (electromotive force) of the battery cell is ideally constant during the discharge or recharge half cycles. where an ideal battery's voltage stays constant as long as the two phases are in equilibrium, whereas the voltage of a capacitor drops linearly with increasing charge. Formally, dV/dQ=1/C, or C=Q/V or V= Q/C, causes the supercapacitor voltage to decrease.

This study explores the synthesis, characterization, and electrochemical performance of nanostructures derived from metal-organic frameworks (MOFs) for use in supercapacitor applications. MOFs, with their tunable porosity and high surface area, serve as excellent precursors for creating advanced electrode materials. By transforming MOFs into nanostructured metal oxides, metal sulfides, and carbon composites, we achieve materials with high specific capacitance, excellent rate capability, and superior cycling stability. These findings highlight the potential of MOF-derived nanostructures as promising candidates for next-generation energy storage devices.
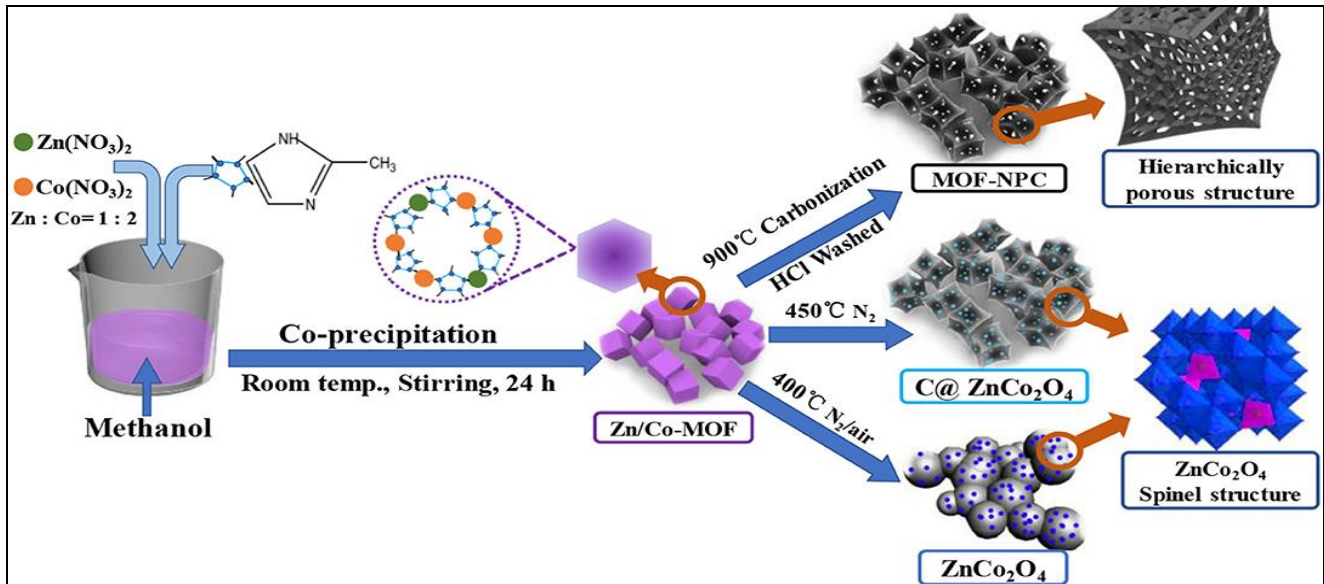
Fig 2: Nonporous Carbon

With the growing demand for efficient and sustainable energy storage systems, supercapacitors have emerged as a promising technology due to their high power density, rapid charge/discharge rates, and long cycle life. The performance of supercapacitors is largely dependent on the properties of the electrode materials. Metal-organic frameworks (MOFs), known for their high surface area, tunable porosity, and diverse chemical compositions, offer a unique platform for the development of advanced nanostructured materials. This study focuses on the transformation of MOFs into nanostructured metal oxides, metal sulfides, and carbon composites, and evaluates their potential as supercapacitor electrodes.

2. Materials and Methods
2.1 Synthesis of MOF-Derived Nanostructures
The synthesis process involves three main steps: preparation of the MOF precursor, thermal transformation, and post-synthesis treatment.
1. **MOF Precursor Preparation:** MOFs such as ZIF-8 (Zeolitic Imidazolate Framework-8) and MIL-101(Cr) are synthesized using solvothermal methods. For ZIF-8, zinc nitrate and 2-methylimidazole are dissolved in methanol and subjected to solvothermal treatment at 120 °C for 24 hours. For MIL-101(Cr), chromium nitrate and terephthalic acid are used under similar conditions.
2. **Thermal Transformation:** The synthesized MOFs are subjected to pyrolysis under an inert atmosphere (argon or nitrogen) at various temperatures (500-800 °C) to transform them into metal oxides, metal sulfides, or porous carbon structures. For instance, ZIF-8 can be converted into zinc oxide (ZnO) or zinc sulfide (ZnS) by adjusting the pyrolysis conditions.
3. **Post-Synthesis Treatment:** The obtained nanostructures are further treated with sulfur or ammonia gas to form metal sulfides or nitrides if needed. Additionally, carbonization in the presence of a carbon source can be performed to enhance conductivity.

2.2 Characterization
The MOF-derived nanostructures are characterized using various techniques:
- **X-ray Diffraction (XRD):** To determine the crystalline structure.
- **Scanning Electron Microscopy (SEM):** To analyze the morphology.
- **Transmission Electron Microscopy (TEM):** To observe the nanoscale structure.
- **Brunauer-Emmett-Teller (BET) Analysis:** To measure the surface area and pore size distribution.
- **Raman Spectroscopy:** To confirm the presence of graphitic carbon structures.

2.3 Electrochemical Measurements
The electrochemical performance of the MOF-derived nanostructures is evaluated using a three-electrode system in 1 M KOH electrolyte. The working electrode is prepared by mixing the active material with a binder (e.g., PVDF) and conductive carbon (e.g., Super P) and coating it onto a nickel foam substrate. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) are performed to assess the capacitive behavior, specific capacitance, rate capability, and cycling stability.

3. Results and Discussion
3.1 Structural and Morphological Analysis
XRD patterns confirm the successful transformation of MOFs into their respective metal oxides and sulfides. SEM and TEM images reveal well-defined nanostructures with uniform size distribution and high porosity. BET analysis shows a significant increase in surface area and pore volume, which are critical for electrochemical performance. Raman spectroscopy indicates the presence of graphitic carbon in carbonized samples, enhancing their electrical conductivity.

3.2 Electrochemical Performance
CV curves exhibit typical pseudocapacitive behavior with rectangular shapes and redox peaks, indicating high

capacitive performance. GCD tests show that the specific capacitance of MOF-derived nanostructures is significantly higher than that of conventional materials. For example, ZnO derived from ZIF-8 exhibits a specific capacitance of 320 F/g at a current density of 1 A/g, while ZnS shows even higher capacitance due to improved conductivity and ion transport. EIS measurements reveal lower charge transfer resistance for carbonized samples, attributed to the presence of conductive carbon frameworks. The cycling stability tests demonstrate excellent performance, with capacitance retention over 90% after 5000 cycles.

4. Conclusion

Energy needs must be met by using electrochemical energy storage devices, which are essential in a world where the energy landscape is rapidly changing every day as a result of increased energy use. The vast amount of research being done at the cutting edge of materials science and technology has greatly benefited these electrochemical energy storage systems. Due to battery technology's dominance in portable electronic devices, the area of electronics has been revitalised by the rebirth of materials science. Batteries are weak in the area of power density, though, therefore SCs have added exceptional power density to batteries in this situation, boosting their expansion across a range of industrial sectors.

MOF-derived nanostructures exhibit exceptional electrochemical performance, making them suitable for supercapacitor applications. The unique properties of MOFs, combined with their versatile transformation into various functional nanomaterials, enable the development of high-performance supercapacitor electrodes. Future research will focus on optimizing the synthesis parameters, exploring other MOF precursors, and integrating these materials into practical supercapacitor devices.

5. References

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