

# Final report on the Åforsk project “Nanoengineering of functional porous materials by cellulose nanofibers for energy and environmental applications (ref. nr. 19-493)”

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## Summary

The project mainly focused on nanoengineering of functional porous materials, e.g. metal-organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic polymers (POPs), and porous carbons, by cellulose nanofibers (CNFs) for the development of their applications in energy and environment. CNF, a sustainable, renewable, and processable biopolymer was as the substrate to assemble and process porous materials for the preparation of freestanding nanocomposites *via* a bottom-up nanoengineering approach. The synthesis, morphology, dimension, and alignment of the porous materials within the nanocomposites can be controlled at the nanoscale, with the purposes to regulate the overall properties of the hybrid nanomaterials and reach a fundamental understanding of the structure-function relationships. The obtained nanocomposites were studied in a wide range of applications, including flexible energy storage devices, thermal insulator, flame retardant, adsorption and separation, and solar thermal conversion and utilization. This study has overcome the longstanding challenges in processing, shaping and structuring porous material powders and to develop their practical applications. The project has also led to many promising research results and ten papers published in *Energy & Environmental Science*, *ACS Nano*, *ACS Materials Letter*, *Carbon*, *Nano-Micro Letters*, etc. We believe that the results from this project will not only contribute to the fundamental research in nanocellulose, porous materials, and hybrid nanomaterials, but also would greatly promote the development of their practical applications.

The research results are divided into the following five parts:

### 1. Solar thermal energy harvesting and utilization

Harvesting solar energy fits well with the increasing demand for clean sustainable energy. Current technology for solar energy conversion is mostly based on the photovoltaic effect by using solid semiconductors. In fact, most of the solar energy absorbed by the Earth's surface converts into heat. Therefore, it is highly desirable to develop novel materials and technologies to take advantages of the abundant solar thermal resource for energy harvesting. In this contest, we designed freestanding films consisting of nanocellulose and conductive MOF. The films enabled efficient solar-thermal-mechanical conversion, solar thermal steam generation, and water evaporation induced electricity generation.

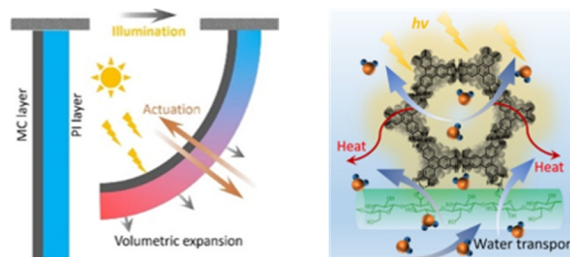
#### 1.1 Efficient solar thermal energy conversion and utilization by a film of conductive metal-organic framework layered on nanocellulose

*ACS Materials Lett.* 2022, 4, 1058

Developing materials for efficient solar thermal energy conversion (STEC) is currently a promising field in energy research. Traditional STEC materials such as carbon and plasmonic nanomaterials have limited efficiency of solar heat utilization, despite their high photothermal conversion efficiency. In fact, the efficiency of current STEC materials is limited by the latter procedure, although the efficient photothermal conversion is often achieved. The main restriction of the effective utilization of the heat by the materials lies in the excessive thermal loss or exchange. Therefore, it is usually imperative that

STEC materials have good thermal management ability with low thermal conductivity and low thermal expansion coefficient, to decrease heat loss in an ambient environment. In addition, STEC materials should be easily processed, mechanically stable, and flexible, so that they can be adapted to different applications.

In this context, we developed a nanoporous film composed of hybrid nanofibers of a conductive MOF layered on nanocellulose (MC film) for efficient solar thermal energy conversion and utilization. The MC film demonstrated excellent thermal management ability with both low thermal conductivity ( $<0.05 \text{ W m}^{-1} \text{ K}^{-1}$ ) and low thermal expansion coefficient ( $3.5 \times 10^{-6} \text{ K}^{-1}$ ). In addition, the freestanding MC film contains abundant micropores and mesopores, and it has a high specific surface area of  $\sim 215 \text{ m}^2 \text{ g}^{-1}$ . The MC film has good mechanical strength, with a tensile strength of up to 300 MPa and a Young's modulus of up to 9.7 GPa.



**Figure 1.** MOF-cellulose film for applications of solar driven actuator (left) and water evaporation (right).

Based on the unique properties, the MC film has been developed for two proof-of-concept applications (**Figure 1**). Firstly, the MC film enabled solar-thermal-mechanical conversion and it can be designed as a solar-driven actuator, displaying large-angle actuation and high contractile power up to 2.5 times greater than that of human muscle. We emphasized the significance of good thermal management of the MC film, including its low thermal conductivity and low thermal expansion efficiency, in achieving efficient solar thermal energy conversion and utilization. Secondly, the gathered heat by a MC film-based apparatus can be manipulated to drive solar steam generation for highly efficient seawater desalination, generating clean water at rate of  $2.25 \text{ kg m}^{-2} \text{ h}^{-1}$  under one-sun irradiation. We employed in-situ infrared spectroscopy and thermogravimetric analysis coupled with differential scanning calorimetry to demonstrate that confinement of water in the nanopores played an important role for the efficient water evaporation. The water molecules confined in the nanopores tended to evaporate in clusters rather than in monomolecular mode, which resulted in a reduced latent heat of water evaporation and a high water evaporation rate. More importantly, there was almost no salt accumulation on the surface of the MC film after working for a long time. The self-cleaning effect can be explained by the asymmetrical distribution of salt ions in the charged nanoporous channels, which makes it difficult for the salt to form stable nuclei for crystallization on the MC film during the water evaporation.

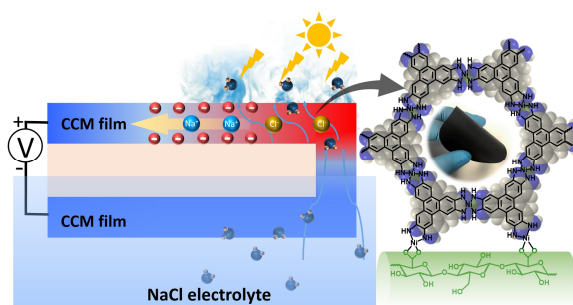
These results not only demonstrate the crucial role of the thermal management ability of the MC materials in the process of STEC and the energy utilization, but also show the various structural advantages (mechanical flexibility, porosity, hydrophilicity, etc.) of the materials, which could improve our fundamental understanding of STEC materials and offer practical guidance for related research in the field of solar energy harvesting.

## 1.2 Solar-driven ionic power generation via a film of nanocellulose @ conductive metal–organic framework

*Energy Environ. Sci.*, 2021, 14, 900.

Water is not only one of the most abundant and sustainable resources on earth but also represents the largest energy carrier. The processes including evaporation, moisture absorption, condensation, precipitation etc. involved in the water cycle are constantly associated with energy exchange with the environment. The total energy carried by water is estimated to be up to  $10^{15} \text{ W}$  per year. However, only a very small portion of the energy carried by water is harvested by traditional hydroelectric power plants that convert the gravitational and kinetic energy of liquid water into electricity. By virtue of the traditional electrokinetic theory and the modern nanotechnology, it opens up new ways to harvest energy from the natural water evaporation for electricity generation. In this context, we have developed a new technology for solar power generation based on ion thermophoresis and electrokinetic effects by

using a hybrid film of nanocellulose @ conductive MOF. The working principle was very different from the mechanisms of traditional photovoltaic or solid-state thermoelectric generation systems. The hybrid film showed integrated properties of hierarchical porosity, low thermal conductivity, high electronic conductivity, and efficient photothermal conversion. As a result, a large thermal gradient can be produced on the surface of the film under light illumination. This gradient induced fast water evaporation in an aqueous electrolyte (NaCl). More importantly, the thermal gradient and the water evaporation could drive selective ion transport through the charged nanochannels, which generated ionic thermoelectric and streaming potentials, respectively. The assembled device can produce a sustained voltage output of 1.1 V, with a high power density of up to  $15 \text{ W m}^{-2}$  under one sun illumination. The unprecedented concept of “solar-driven ionic power generation” developed in this study should be able to provide an alternative way for solar energy utilization. In addition, the described technology could find applications in solar steam generation, seawater desalination, and self-powered wearable electronics (Figure 2).



**Figure 2.** Solar steam generation and water evaporation induced electricity generation via a film of nanocellulose @ conductive metal–organic framework

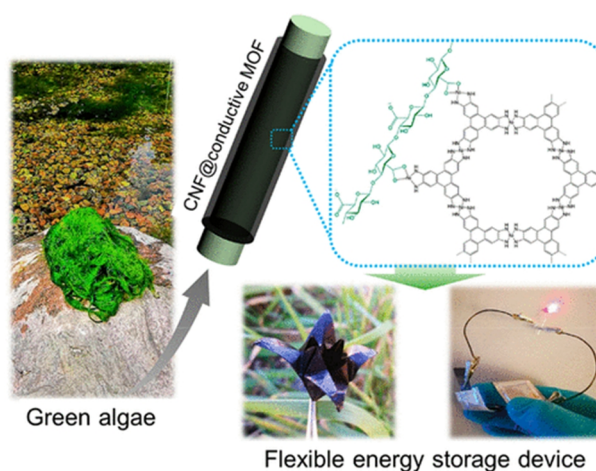
## 2. Nanocomposites consisting of porous materials and cellulose for flexible energy storage devices

MOFs and COFs are a new family of crystalline and porous materials. The building blocks are connected in a periodic manner via strong coordination or covalent bonds that form crystalline frameworks with ordered porous channels. Their unique properties such as highly accessible surface areas, tuneable pore sizes, built-in redox-active centres, and versatile functionalities make them as suitable candidates for studies in electrochemical energy storage. However, the intrinsic low electrical conductivity of MOFs and COFs hampers charge transfer in the frameworks that significantly limits their electrochemical performances. In addition, the difficulty in processing MOFs and COFs largely hampers their practical applications, especially in flexible energy storage devices. In this context, we developed nanocomposites consisting of conductive MOFs/COFs and nanocellulose with good processability that can be assembled into flexible and foldable electrochemical energy storage devices.

### 2.1 Cellulose nanofiber @ conductive metal–organic frameworks for high-performance flexible supercapacitors

*ACS Nano, 2019, 13, 9578*

We have applied interfacial synthesis approach to fabricate conductive MOF (c-MOF) nanolayers on CNFs for the preparation of freestanding and flexible CNF@c-MOF nanopapers (Figure 3). The nanopapers demonstrated high electrical conductivity of up to  $100 \text{ S cm}^{-1}$  which was significantly higher than the values of the bulk c-MOF pellet and the composite prepared by direct mixing of c-MOF powder and CNFs. In addition, the CNF@c-MOF nanopapers displayed high surface areas (up to  $203 \text{ m}^2/\text{g}$ ), hierarchical micro-/mesoporosity and excellent mechanical properties. The high conductivity and hierarchical porous structure of the CNF@c-MOF nanopaper electrodes endowed fast charge transfer and efficient electrolyte transport, respectively.



**Figure 3.** Flexible energy storage device based on cellulose nanofibers and conductive MOF

Remarkably, the nanopaper electrodes were further assembled into supercapacitors, which displayed relatively high gravimetric capacitances of up to 141.5 F/g and high volumetric capacitance of up to 2800 mF/cm<sup>3</sup>. Given the unique nanostructures of CNF@c-MOF nanopapers, the assembled electrochemical supercapacitor device shows excellent flexibility. Bending (90, 120°) or even folding (180°) the device had no significant influences on its electrochemical performances. In addition, the device showed extremely high cycle stability with capacitance retentions of >99% after 10000 continuous charge–discharge cycles.

This study integrates advantages and versatile functionalities of cellulose and c-MOFs by the nanoengineering approach for the development of novel hybrid nanomaterials of CNF@MOF. In addition, the relationships between the nanostructures, physical properties and electrochemical performances of the CNF@c-MOF nanopapers have been revealed, which may guide the exploration of cellulose and c-MOF-based nanomaterials with optimal structural design for next generation flexible electronics.

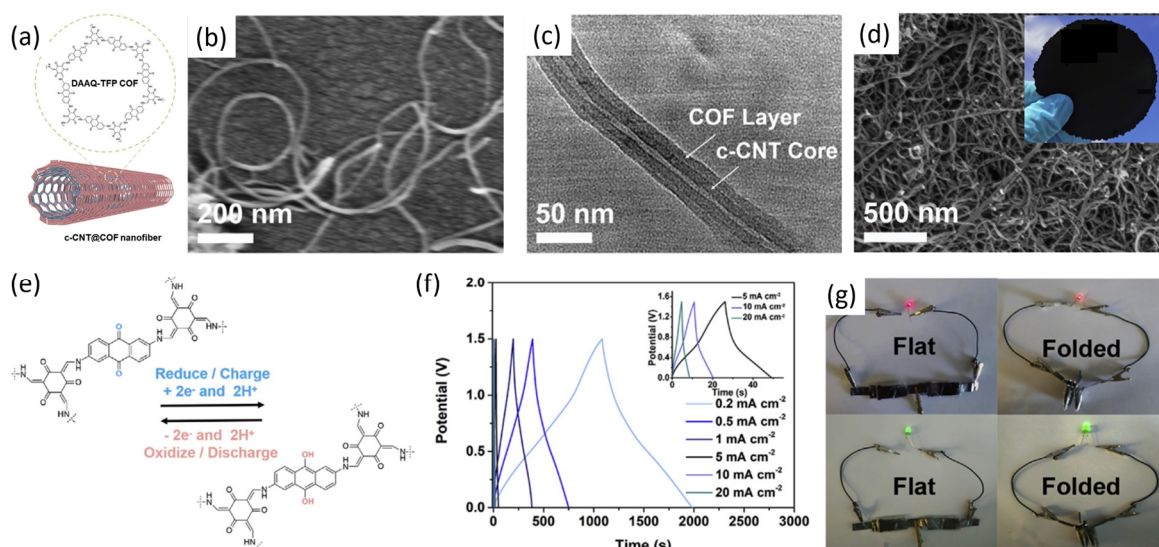
## **2.2. Redox active covalent organic framework-based conductive nanofibers for flexible energy storage device**

*Carbon, 2021, 171, 248.*

Owing to their unique properties of long-range ordered nanopores, good physicochemical stability, tunable porosity, and predesignable structure, COFs have been studied for applications in gas storage and separation, catalysis, sensing, as well as electrochemical energy storage. However, COFs encounter similar drawbacks as MOFs featuring low electrical conductivity and poor processability that have limited their applications in electrochemical energy storage. In addition, the short distance between the COF layers (~3–4 Å) results in the difficulty of electrolyte infiltration into the internal skeletons and thus leads to a low utilization of the active sites during the electrochemical processes. Therefore, it is worthwhile to develop new strategies to design highly conductive, accessible and processable COFs or COF-based nanocomposites for the design of high performance and flexible energy storage devices.

In order to overcome the above-mentioned drawbacks, we applied interfacial synthesis method to grow few layered two-dimensional (2D) redox-active DAAQ-TFP COF (DAAQ: 2,6-diaminoanthraquinone; TFP: 1,3,5-triformylphloroglucinol) on the surface of carboxylated carbon nanotubes (c-CNTs), which aimed at developing conductive, processable and flexible COF-based electrode materials (**Figure 4**). The obtained c-CNT@COF nanofibers showed a typical tube-type core-shell nanostructure where the morphology and thickness of the COF nanolayers can be finely controlled at the nanoscale. The strong  $\pi$ - $\pi$  interactions between the COF nanolayers and the conductive CNT backbones promote the electron transfer throughout the entire nanofibers, while the nanolayer structure of the COF significantly increases the electrolyte ion diffusion and charge/discharge rate. As a result, the synergetic effects lead to an efficient utilization of the redox active sites. More significantly, the nanofibrous structure of the c-CNT@COFs greatly favors the materials processing that allows for the formation of freestanding nanopaper with the assistance of CNFs via a bottom-up interweaving approach. The obtained flexible nanopapers of c-CNT@COF/CNT/CNF can be used as electrodes for the assembly of flexible and foldable hybrid capacitors.

The composition and the nanostructure of the hybrid nanofibers and the assembled nanopapers were fully characterized by infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM),



**Figure 4.** (a) Schematic illustration of the structure of c-CNT@COF nanofibers; (b) SEM and (c) TEM images of c-CNT@COF nanofibers; (d) SEM image of c-CNT@COF/CNT/CNF nanopaper. The inset shows the optical image of the nanopaper; (e) The reversible quinone to hydroquinone transformation in DAAQ-TFP COF showing its redox charge/discharge mechanism; (f) Galvanostatic charge-discharge (GCD) curves of device at different current densities; (g) Photo of red and green LEDs powered by the flat or folded devices.

and  $N_2$  sorption measurement. The IR and XPS studies suggested that the COF nanolayers were chemically bonded to the surface of c-CNTs via the formation of amide bonds at the interface. The TEM image of the nanofiber showed typical tube-like core-shell nanostructures, in which the COF nanolayers compactly wrapped the c-CNT backbones. SEM image of the c-CNT@COF/CNT/CNF nanopaper showed that the c-CNT@COF-3 nanofibers were interwoven by CNF and CNTs with the formation of a homogeneous and completely connected nanostructure.  $N_2$  sorption analysis indicated that the c-CNT@COFs and the assembled nanopapers had hierarchical porous structures, which could enable fast transport of the electrolyte ions during the electrochemical processes.

The electrochemical performances of the c-CNT@COF electrodes were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy measurements. Given the high conductivity, few layered nanostructure, and the presence of redox-active species, the c-CNT@COF electrodes demonstrated high gravimetric capacitances (up to 418.7 F/g at 0.2 A/g), good rate capability, and high Coulombic efficiency. Furthermore, a hybrid capacitor was fabricated by using the c-CNT@COF-3/CNT/CNF nanopaper and CNT/CNF nanopaper as the negative and positive electrode, respectively. Despite of the low COF loading of  $\sim 0.32$  mg/cm<sup>2</sup>, the device could reach high areal capacitances of up to 123.2 mF/cm<sup>2</sup> at a current density of 0.2 mA/cm<sup>2</sup>. The hybrid capacitor could operate at a wide operational window of 1.5 V, which resulted in high energy densities and power densities of up to 30.7  $\mu$ Wh/cm<sup>2</sup> and 591.9  $\mu$ W/cm<sup>2</sup>, respectively. In addition, the device showed good recyclability that 94.0 % of its original capacitance was retained after 10000 GCD cycles at a current density of 10 mA/cm<sup>2</sup>. The good recyclability can be attributed to the high stability of the COF, CNT, CNF in the electrode. More importantly, the interwoven nanostructure endowed excellent flexibility and foldability for the device.

This study provides a new pathway for the development of next generation sustainable and flexible energy storage devices based on COFs and cellulose materials. In addition, the transfer of the nanoengineering techniques developed in this study to COF processing may lead to the development of freestanding, flexible and sustainable COF-based nanomaterials for the promotion of their practical applications in energy storage, nanofiltration, sensing, heterogeneous catalysis, etc.

### 3. Elastic aerogels of cellulose nanofibers @ metal-organic frameworks for thermal insulation and fire retardancy

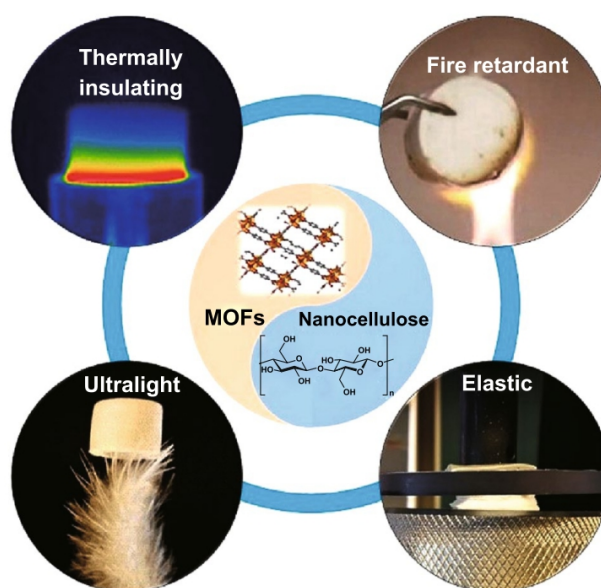
The highly porous and thermally stable MOFs are potentially thermal insulation and flame retardant materials. The abundant micro-/mesopores in the MOFs could suppress gas movement and reduce the mean free path to a few nanometers, thus reducing the thermal conductivity, while the structure stiffness and the existence of strong coordination or covalent bonds could lead to high thermal stability and efficient flame retardancy. However, their applications in these areas have rarely been exploited, probably because of the difficulty in shaping and processing of the brittle and insoluble MOF and POP powders.

In this study, we have developed interfacial synthesis and stepwise assembly approach for the design of a hybrid aerogel based on CNFs and an aluminium-based MOF (CNF@Al-MIL-53; CAM). Individual CNFs are coated and further cross-linked with continuously nucleated Al-MIL-53 nanolayers. The resultant lightweight aerogels showed low thermal conductivity, moisture resistance, superelasticity, and good fire retardancy (**Figure 5**).

The crosslinked nanostructure endows the CAM aerogel high mechanical strength and superelasticity. It showed 80% maximum recoverable strain, high specific compression modulus of  $\sim 200 \text{ MPa cm}^3/\text{g}$ , and specific stress of  $\sim 100 \text{ MPa cm}^3/\text{g}$ . In addition, the aerogel displayed good compression stability. It shrank only 8.3% in volume and retained over 70% of the original modulus after 800 loading–unloading cycles.

The aerogel displayed interconnected cellular networks with a pore diameter of  $\sim 10 \mu\text{m}$ . The walls of the network are constructed by entangling and weaving of the CAM nanofiber. Due to the highly porous structure and low density ( $\sim 0.2\text{--}3.0 \text{ mg/cm}^3$ ), the aerogel demonstrated low thermal conductivity of  $43 \text{ mW/m/K}$ , which was significantly lower than the value of Al-MIL-53 pellet ( $485 \text{ mW/m/K}$ ), and comparable with the value of pure CNF aerogel ( $41 \text{ mW/m/K}$ ). More importantly, the thermal conductivity of the CAM aerogel only increased from 41 at 5% RH to  $55 \text{ mW/m/K}$  (34% increase) at 80% RH. In contrast, the thermal conductivity of the pure CNF aerogel significantly increased from 44 at 5% RH to  $\sim 76 \text{ mW/m/K}$  (72% increase) at 80% RH. The increased moisture resistance of CAM aerogel can be explained by the fact that the hydrophobic Al-MIL-53 layer reduced the moisture adsorption.

The high thermal stability of the aerogels inspired us to evaluate their potential applications in fire retardancy. Interestingly, the CAM aerogel did not ignite and the flame did not self-propagate under the flame of an alcohol lamp ( $\sim 500 \text{ }^\circ\text{C}$ ). More significantly, the CAM aerogel displayed excellent fire retardancy and remained intact even under the flame of a butane blowtorch ( $\sim 500 \text{ }^\circ\text{C}$ ). SEM studies revealed that the aerogel maintained the cellular network and cross-linked nanofibrous structures after the burning test. Meanwhile, XRD studies indicated the formation of aluminium oxide in the residual. These findings strongly support the notion that the special core–shell structure of the CAM nanofibers plays a key role in the fire retardancy of the aerogel. It is suggested that the Al-MIL-53 nanolayers and the thermally decomposed aluminium oxide efficiently protected the wrapped CNFs from ignition upon exposure to flames. The newly developed aerogels based on MOFs and sustainable celluloses (and



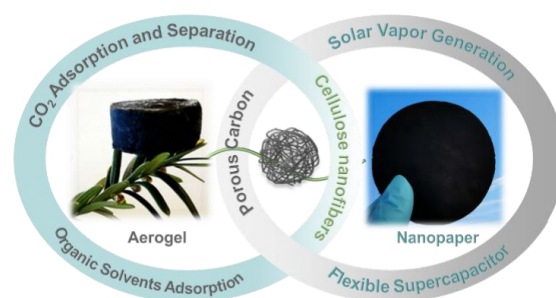
**Figure 5.** Nanocompositing of MOFs with cellulose formed ultralight and elastic aerogels demonstrating good thermal insulation and fire retardancy performances.

perhaps other biopolymers) are expected to find application in energy-efficient buildings, structural materials, packaging and storage of food, and pharmaceuticals.

#### 4. All-cellulose-based freestanding porous carbon nanocomposites and their versatile applications

*Composites Part B 2022, 232, 109602*

Porous carbons are key functional materials in a range of chemical processes. Developing porous carbons from renewable biomass resources is greatly important from a sustainability perspective. On the other hand, engineering and processing of porous carbons using facile binder-free techniques presents significant challenges. Therefore, it is highly desirable to develop fully sustainable porous carbons and advanced engineering techniques that would broaden the field of use and improve the application performance of porous carbons.



**Figure 6.** All-cellulose-based freestanding porous carbon nanopaper and aerogel

Inspired by our previous studies on processing MOFs and COFs by nanocellulose for energy harvesting and storage applications, this project presents a nanoengineering approach to the preparation of all-cellulose-based, freestanding porous nanocomposites based on interweaving cellulose-derived porous carbon particles with cellulose nanofibers (**Figure 6**). *Cladophora* cellulose (CC), a natural cellulose nanofiber extracted from green algae, has been used as both a bioprecursor and a flexible substrate in nanoengineering procedures. The obtained nanopapers and aerogels have shown versatile applications, including CO<sub>2</sub> separation, adsorption of organic liquids, solar vapor generation, and flexible electrochemical energy storage.

The aerogels, which have cellular networks, low density and high mechanical strength, were investigated as sorbents for CO<sub>2</sub> capture and removal of various organics. The presence of rich ultramicropores allows the aerogels to adsorb relatively high amounts of CO<sub>2</sub>, with high selectivity of CO<sub>2</sub>-over-N<sub>2</sub> (up to 111). More importantly, the sorbents have high CO<sub>2</sub> working capacities and excellent recyclability under temperature swing adsorption conditions. In addition, the aerogels can adsorb various organic solvents remarkably well, corresponding to 100–217 times their own weight. The nanopapers are active photothermal materials that can be applied as solar absorbers for interfacial solar vapor generation, providing a high evaporation rate (1.74 kg m<sup>-2</sup> h<sup>-1</sup> under one sun illumination). The nanopapers were also employed as electrodes in flexible, foldable supercapacitors with high areal capacitances.

The highlights of this study include:

- (a) The all-cellulose-based porous carbon nanocomposites demonstrated obvious advantages from the perspectives of sustainability and manufacturing cost.
- (b) Natural cellulose nanofibers were used as a flexible substrate to interweave porous carbon materials for the formation of freestanding nanocomposites. The binder-free materials processing technique enables the porous channels and high surface area of the porous carbons can be easily accessed.
- (c) The flexible and freestanding form of the porous carbon nanocomposites facilitated the study of their practical applications in a range of chemical processes, for instance, interfacial solar vapor generation and flexible electrochemical energy storage, which cannot be easily achieved by using porous carbons in conventional powder form.

The transfer of knowledge from this study into a broader area of materials processing and manufacturing could promote the development of fully sustainable, freestanding functional materials with specifically tailored compositions and connectivity for application in energy and environmental fields.

## 5. Synthesis of porous organic polymers for environmental applications

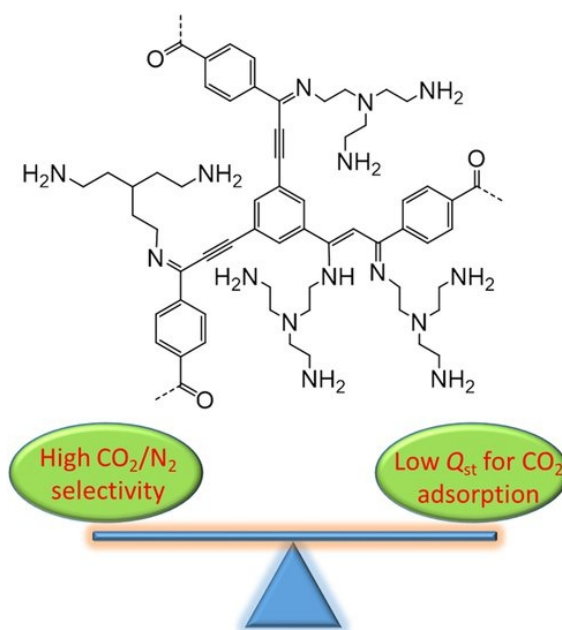
POPs with high surface areas, rich microporosity and tuneable pore sizes have been widely studied for CO<sub>2</sub> capture and separation, catalysis and pollutant removal. We have synthesized a range of novel functional POPs, including amine-modified POPs, POPs with ionic structures, and POPs with highly conjugated structures. The functional POPs showed excellent performances in highly selective CO<sub>2</sub> capture, precious metal recovery, heterogeneous catalysis, and photocatalytic degradation of organic dyes.

### 5.1 Synthesis of porous organic polymers with tunable amine loadings for CO<sub>2</sub> capture: balanced physisorption and chemisorption

*Nanomaterials*, 2019, 9, 1020

POPs show advantages of synthetic diversity and ease of modification. For example, introducing alkyl amine groups onto the pore surface could induce chemisorption of CO<sub>2</sub> and thus significantly increase the CO<sub>2</sub> adsorption capacity and the CO<sub>2</sub>-over-N<sub>2</sub> selectivity. However, the strong chemisorption requires high-energy input to reactivate the sorbents in the process. Therefore, it would be great of interest to balance the trade-off between the separation efficiency and energy efficiency.

In this study, we design a method to tune the amine density on a ynone-linked POP by post-modification approach, which enables balancing of the effects of physisorption and chemisorption of CO<sub>2</sub> and optimization of the CO<sub>2</sub> adsorption capacity, CO<sub>2</sub>-over-N<sub>2</sub> selectivity and heat of adsorption of CO<sub>2</sub> (Figure 7). The ynone-linked POP was prepared by the cross-coupling reaction of 1,3,5-triethynylbenzene with terephthaloyl chloride. Tethering tris(2-aminoethyl)amine molecules onto the polymeric framework led to the formation of amine-modified POPs. As expected, the amine-modified POPs showed much higher CO<sub>2</sub> adsorption capacity (0.65–1.11 mmol/g at 0.15 bar, 273 K), CO<sub>2</sub>-over-N<sub>2</sub> selectivity (239–4154) and heat of adsorption of CO<sub>2</sub> (46.8–76.5 kJ/mol) than those values for the unmodified POP. The *ex situ* IR results revealed that the amine species on the polymers could induce chemisorption of CO<sub>2</sub> with formation of ammonium carbamate ion pairs. Remarkably, tuning the amine density on the polymer allows balancing the physisorption and chemisorption of CO<sub>2</sub> to reach a high separation efficiency, excellent recyclability, high-energy efficiency for CO<sub>2</sub> capture and separation. This study provides a new way for the development of highly efficient sorbents for post-combustion capture of CO<sub>2</sub>. Future studies may focus on the nanoengineering of such POPs by CNFs for the design of freestanding and flexible CNF-POP nanopapers as efficient membranes for practical CO<sub>2</sub> separation.



**Figure 7.** Tuning the amine density on the POP could balance the physisorption and chemisorption effects for the design of highly efficient CO<sub>2</sub> sorbents.

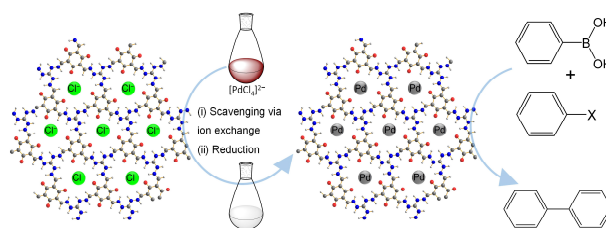
### 5.2 Dual-functional ionic porous organic framework for palladium scavenging and heterogeneous catalysis

*Nanoscale*, 2021, 13, 3967

Palladium catalysts are widely used in a range of important organic transformations. However, traditional homogeneous palladium catalysts usually suffer from significant recovery problems, which not only cause a waste of precious metal resource but also lead to heavy metal contamination in the products. In order to overcome these problems, it is highly desirable to develop efficient palladium



scavengers and heterogeneous palladium catalysts. POPs with tuneable nanoporous channels and predesigned structures that may find potential applications in adsorption and heterogeneous catalysis. In addition, introducing ionic structure into the framework endows POPs with new functionalities that may extend their applications. Therefore, we developed new applications of scavenging and heterogeneous catalysis for a guanidinium-based ionic POP (IPOP-Cl) (**Figure 8**). The IPOP-Cl displays fast adsorption kinetics and high adsorption capacities (up to 754 mg/g) of  $[\text{PdCl}_4]^{2-}$  in aqueous solutions via a chemisorption (ion exchange) process. In addition, it shows excellent scavenging activity towards trace amount of  $[\text{PdCl}_4]^{2-}$  in aqueous solution. It could reduce the Pd concentration in aqueous solution from 100 ppm to <0.1 ppm in 60 min. More significantly, the loaded  $[\text{PdCl}_4]^{2-}$  species on the IPOP substrate can be further reduced into ultrafine Pd nanoparticles with size of ~2–5 nm. The obtained IPOP-Pd(0) nanocomposite containing uniformly distributed Pd nanoparticles and hierarchical porous structure demonstrates high activity and good recyclability in catalyzing a range of Suzuki coupling reactions. This study may boost the research of ionic porous organic materials in recovering precious metal ions, removing heavy metal pollutants, scavenging trace amount of metal ions, and immobilizing homogeneous catalysts that may lead to their practical applications in mining, water treatment, synthesis and handling of pharmaceuticals, industrial catalysis, and organic synthesis.

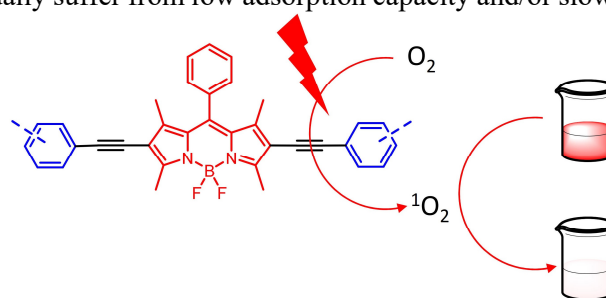


**Figure 8.** IPOP enabled removal trace amount of  $[\text{PdCl}_4]^{2-}$  from aqueous solution. The Pd loaded IPOP showed high catalytic performance for Suzuki coupling reactions.

### 5.3 BODIPY-linked conjugated porous polymers for dye wastewater treatment

*Microporous and Mesoporous Materials* 2022, 332, 111711

Dyeing process in textile and fashion industry has been generating a large amount of polluted water containing various organic dyes. Conventional water treatment process usually relies on adsorption technique that removes the dye molecules by using porous materials such as activated carbon, silica, and natural polymers. However, these sorbents usually suffer from low adsorption capacity and/or slow adsorption kinetic. Recently, photocatalysis technique has been developed for the treatment of dyestuff wastewater, which showed great advantages such as low energy consumption, sustainability and high efficiency in comparison with the adsorption technique. Therefore, it is greatly desired to develop novel materials to achieve dual functions of adsorption and photodegradation of dyes that could significantly increase the efficiency of treating dyestuff wastewater. In this project, we described the integration of strong visible-light absorbing BODIPY skeletons into conjugated porous polymers (CPPs) via Sonogashira coupling reactions. The obtained CPPs showed synergetic properties of high surface area, hierarchical porous structures and strong visible-light absorption. As a result, the dual functional CPPs showed relatively high adsorption capacity and high photocatalytic degradation effectivity towards Rhoadmine B dyes. Mechanism studies revealed that the CPPs acted as photosensitizers to generate singlet oxygen species that drove the dye degradation process (**Figure 9**). This study may lead to the development of multifunctional porous organic materials for environmental applications.



**Figure 9.** BODIPY-linked CPPs could efficiently remove organic dyes from aqueous solution via synergetic effects of physical adsorption and photocatalysis

In addition, we have published a review paper to summarize recent studies (2014-2019) on the potential of use of POPs as  $\text{CO}_2$  sorbents and  $\text{CO}_2$ -selective membranes. The advances, opportunities and

challenges of using POPs for CO<sub>2</sub> capture are discussed in the review paper. (*Materials Today Advances, 2020, 6, 100052*)

## **Conclusions**

The present project aimed at using sustainable cellulose nanofibers as substrates to process various functional porous materials in a facile and scalable approach. Most importantly, it provided a new strategy to overcome the longstanding challenges in processing, shaping and structuring porous material powders for the development of their practical applications. The bottom-up nanoengineering approach enabled controlling their morphology, dimensions, and alignment at the nanoscale, which allow us to reach a fundamental understanding of structure-property-function relationship of the obtained nanocomposites. In addition, the project would lead to the development of novel cellulose-based nanomaterials and their versatile applications in flexible electrochemical energy storage devices, thermal insulation and flame retardancy, solar-thermal steam generation, adsorption and separation.

Collectively, the present project not only developed novel nanomaterials based on cellulose and porous materials and gained a fundamental understating of the structure-property-function relationship, but also would develop their practical applications in energy and environment areas and contribute to build a sustainable society in the future.