

Biomass Derived Porous Carbonaceous Materials

Robin J. White, Maria-Magdalena Titirici, and Markus Antonietti*

*Max-Planck-Institute for Colloids and Interfaces,
Wissenschaftspark Golm, D-14424 Potsdam Germany*

Introduction

The production of porous nanostructured functional carbons from inexpensive naturally occurring precursors using environmentally friendly processes is a hot topic in modern materials science.[1] One practical efficient approach is the thermal dehydration / transformation of carbohydrate-based biomass in H₂O under autoclave conditions at relatively low temperatures (e.g. 180 - 200 °C) and pressures (< 10 bar); termed Hydrothermal Carbonization (HTC).[2] This process yields spherical particles with functionally rich surfaces.[3] HTC has clear advantages, being totally green, economical, mild and fast. In this regard, the use of microwave assisted HTC leads to carbonaceous materials in much shorter reactions times, therefore enhancing further the green credentials. The synthesis of a variety of HTC materials will be presented, including high volume mesoporous materials prepared from naturally occurring inorganic / carbohydrate composites (e.g. crustacean shells) and macroporous hollow carbon sphere materials prepared via latex nanoparticle templating. The preparation of nitrogen-doped carbon aerogels (“*carbogels*”) derived from carbohydrate / protein mixtures as well as ordered mesoporous carbons prepared via soft-templating (data not shown) will also be presented. Furthermore, post modification strategies are also discussed, demonstrating the efficacy of HTC materials for the preparation of wide range of chemically interesting materials.

Experimental

Synthesis of prawn shell derived nitrogen doped carbon[4]

“*Wet*” prawns shells (2.4 g (dry mass: 1.5 g)) and 14 mL deionised water were mixed and sealed in a Teflon lined steel autoclave and hydrothermally treated at 180 - 200 °C for 24 h. The resulting yellow / brown material was then washed thoroughly with deionised water and oven dried under vacuum overnight at 80 °C. The dried product was carbonised to the desired temperature (e.g. 750 °C) under N₂ to yield the inorganic / carbon composite material. The recovered black solid was then added to 30 mL acetic acid (aq) (2 M) and stirred for 24 h at RT. The suspension was filtered and washed extensively with deionised water, before drying at 80 °C overnight under vacuum to yield purified carbon material.

Synthesis of carbohydrate/protein-derived nitrogen doped carbons[5]

In a representative synthesis, D-Glucose(Glu)/Ovalbumin(alb)/H₂O (1.5:0.3:13.5 (g:g:g)) were mixed and sealed in a Teflon-lined steel autoclave and hydrothermally treated at 180 °C for 5.5 h to yield an aqueous carbonaceous monolith gel. The “*carbogel*” is then washed with ethanol until washings were clear. Supercritical CO₂ drying was employed to produce highly functional low density nitrogen-doped carbon aerogel ($\rho < 0.1 \text{ cm}^3\text{g}^{-1}$). Further carbonisation (under N₂) was conducted to direct surface chemistry / textural properties.

Synthesis of carbonaceous hollow spheres[6]

In a typical synthesis, 6 mL of distilled H₂O was mixed with 2 mL (1.85 g) of 100 nm -OH terminated polystyrene (PS) latex nanoparticles (18.5 wt% dispersed in aqueous SDS) in a glass autoclave insert. PS latex nanoparticles were prepared as reported elsewhere.[7] To this suspension, 0.80 g of Glu was added and mixed until sugar dilution was complete. The glass insert was then sealed in a steel autoclave. Hydrothermal carbonisation was performed at 180 °C for 20 h. The resulting hydrothermal carbon / latex composite was then washed thoroughly with distilled water followed by particle isolation via centrifugation, and drying under vacuum at 80 °C for 12 h. To produce carbon hollow spheres, the composite material was heated in a carbonisation oven (using ceramic crucibles) to 550 °C (or above) under N₂.

Results and Discussion

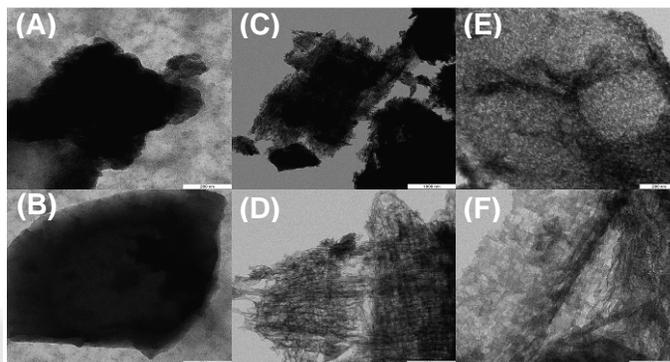


Figure 1: TEM images of prawn shell-derived carbon materials; (A) and (B) before and (C) to (F) after CaCO₃ removal.[4]

Naturally occurring inorganic/polysaccharide composites (e.g. crustacean shells) can be used for the fabrication of mesoporous nitrogen doped carbon materials. The polysaccharide chitin here provides the C and N source, whilst the nanoscopically organized inorganic CaCO₃ component provides a ready made template, which can be removed using another waste product, acetic acid. The resulting carbons possess large surface areas ($S_{\text{BET}} > 300 \text{ m}^2\text{g}^{-1}$), mesopore volumes ($V_{\text{meso}} > 0.6 \text{ cm}^3\text{g}^{-1}$), and a high N content (e.g. > 6 %wt) interdigitated texture with some linear structuring. TEM images obtained of prawn shell-derived material before CaCO₃ removal indicate no discrete mesoporous structuring (Fig. 1 (A) and (B)). Acid treatment results in the opening up of a well defined mesoporous structure, reflecting the former texture of chitin strands in the shell nanocomposite structure (Fig. 1 (C) – (F)). Mesoporous entrances, of spherical / elliptical apertures, can clearly be seen, varying in diameter from 5 – 20 nm. From a carbon perspective, such structures are very promising, as they combine large pore volume and good accessibility with good mechanical stability and rather linear (nitrogen-doped) electronic conduction pathways. The use of the weak acid allows material preparation over a broad carbonization temperature range, allowing direction of surface chemistry and nitrogen chemical state.

The introduction of surface stabilising globular proteins (e.g. alb) to the HTC of Glu results in the formation of a stable gel. Exchange of H₂O for ethanol, followed by supercritical

CO₂ drying, yields a carbon aerogel possessing high surface area ($S_{\text{BET}} > 250 \text{ m}^2\text{g}^{-1}$) and total pore volume ($> 0.4 \text{ cm}^3\text{g}^{-1}$). Post carbonisation results in an increase in (meso) pore volume ($> 0.5 \text{ cm}^3\text{g}^{-1}$).

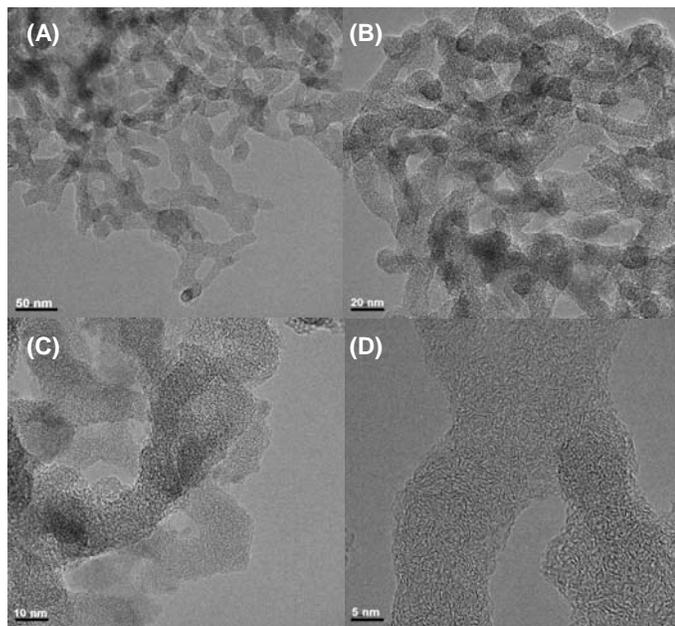


Fig. 2: HR-TEM images of Glu/Alb-derived aerogels prepared 750 °C ((A) and (C)) and 900 °C ((B) and (D)).

This aerogel material possesses a unique continuous interconnected 3D structuring circumventing many of the “plumbing” problems associated with more ordered (templated) mesoporous solids (Fig. 2). The nitrogen rich protein additive is incorporated into the carbogel structure, providing an inexpensive route to heteroatom carbon doping.

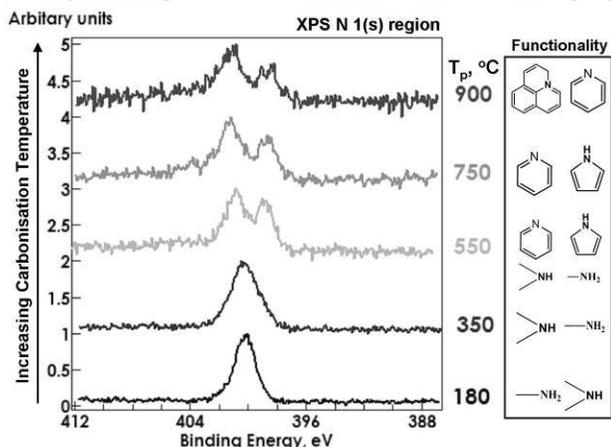


Figure 3: XPS analysis of the N 1(s) photoelectron envelope for Glu/Alb-derived carbon aerogels prepared at increasing carbonisation temperature (T_p).

Carbonisation temperature provides a control vector over surface chemistry, surface basicity (e.g. N chemical state; Fig. 3) and by implication surface polarity; other features deemed necessary to optimise material for a given application. More

specifically, low temperature aerogel, presenting 1° amine have potential as CO₂ sorbents, whilst more condensed systems may be applicable in electrochemical applications.

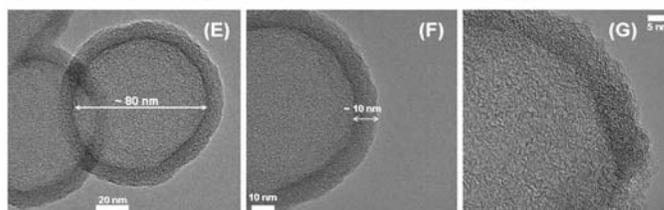


Fig. 4: HR-TEM images of Glu-derived hollow spheres prepared via latex templating.

Hollow carbonaceous nanospheres (HS) have been prepared using monodisperse polystyrene latex nanoparticles templates (e.g. diameter $\sim 100 \text{ nm}$). The latex nanoparticles are coated with hydrothermal carbon and are removed in a thermolysis step above 500 °C. HS size is determined by template size, shell thickness by sugar concentration, whilst functionality and order are directed by carbonization temperature. HS materials possess large surface areas ($S_{\text{BET}} > 360 \text{ m}^2\text{g}^{-1}$) and pore volumes ($> 0.6 \text{ cm}^3\text{g}^{-1}$), and residual surface functionality is available for chemical modification (e.g. introduction of stimuli responsive polymers), making these materials suitable for a wide range of applications (e.g. insulation, encapsulation, delivery *etc.*).

Conclusions

Our research provides the basis for the development of a range of highly useful carbon materials, the properties of which are tunable in terms of texture, morphology and chemical properties. The materials presented are directly applicable in a variety of high value end applications including heterogeneous (base) catalysis, electrochemistry / energy storage and CO₂ sequestration. Notably these advanced sustainable materials are prepared directly from carbohydrate-based biomass in a green, inexpensive and non-resource intensive manner; appropriate for tomorrow’s porous carbon technology.

Acknowledgment: The authors thank to Prof. K. Tauer (MPIKG, Germany) for providing the polystyrene latex nanoparticles. Dr. N. Yoshizawa (AIST, Japan) is thanked for acquiring HR-TEM images.

References

- [1] (a) R. J. White, V. Budarin, R. Luque, J. H. Clark, D. J. Macquarrie, *Chemical Society Reviews*, **2009**, 38, 3401; (b) M. M. Titirici, M. Antonietti, *Chemical Society Reviews*, **2010**, 39, 103
- [2] B. Hu, K. Wang, L. H. Wu, S. H. Yu, M. Antonietti, M. M. Titirici, *Advanced Materials*, **2010**, 22, 813
- [3] M. M. Titirici, M. Antonietti, N. Baccile, *Green Chemistry*, **2008**, 11, 1204
- [4] R. J. White, M. Antonietti, M. M. Titirici, *Journal of Materials Chemistry*, **2009**, 19, 8645
- [5] R. J. White, N. Yoshizawa, M. Antonietti, M. M. Titirici, *Advanced Materials*, **2010**, submitted
- [6] R. J. White, K. Tauer, M. Antonietti, M. M. Titirici, *Advanced Materials*, **2010**, submitted
- [7] K. Tauer, H. Müller, *Colloids and Polymer Science*, **2003**, 281, 52