

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231242057>

Carboxylate-Rich Carbonaceous Materials via One-Step Hydrothermal Carbonization of Glucose in the Presence of Acrylic Acid

ARTICLE *in* CHEMISTRY OF MATERIALS · JANUARY 2009

Impact Factor: 8.35 · DOI: 10.1021/cm802141h

CITATIONS

173

READS

322

4 AUTHORS, INCLUDING:



Rezan Demir-Cakan

Gebze Technical University

27 PUBLICATIONS 1,612 CITATIONS

SEE PROFILE



Maria-Magdalena Titirici

Queen Mary, University of London

134 PUBLICATIONS 7,022 CITATIONS

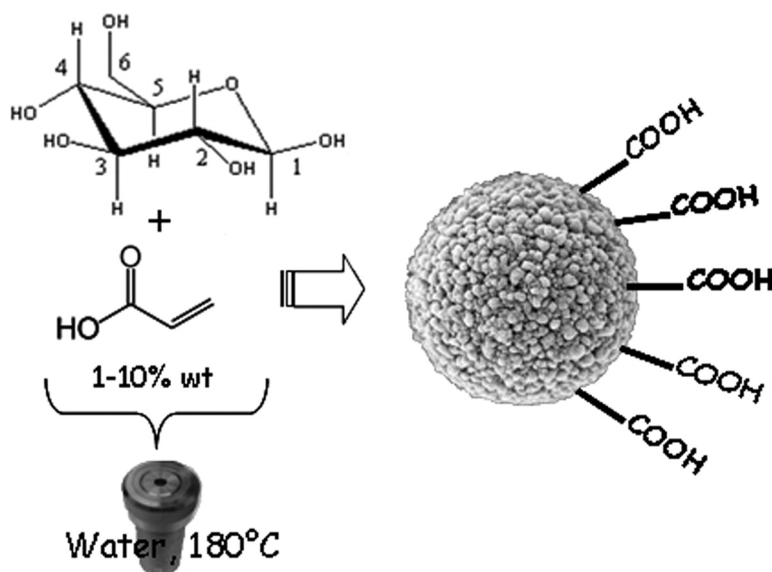
SEE PROFILE

Carboxylate-Rich Carbonaceous Materials via One-Step Hydrothermal Carbonization of Glucose in the Presence of Acrylic Acid

Rezan Demir-Cakan, Niki Baccile, Markus Antonietti, and Maria-Magdalena Titirici

Chem. Mater., **2009**, 21 (3), 484-490 • DOI: 10.1021/cm802141h • Publication Date (Web): 09 January 2009

Downloaded from <http://pubs.acs.org> on February 4, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Carboxylate-Rich Carbonaceous Materials via One-Step Hydrothermal Carbonization of Glucose in the Presence of Acrylic Acid

Rezan Demir-Cakan, Niki Baccile, Markus Antonietti, and Maria-Magdalena Titirici*

Max-Planck Institute for Colloids, MPI campus, Am Muehlenberg, 1 D-14476, Golm, Potsdam, Germany

Received August 5, 2008. Revised Manuscript Received November 19, 2008

The present study concerns the one-step aqueous route production of carbonaceous materials loaded with carboxylic groups using hydrothermal carbonization of glucose in the presence of acrylic acid. This method provides a “green” solvent and surfactant free access to hydrophilic functionalized carbons with very good water dispersivity. The resulting materials were characterized using various methods including, FT-IR, Zeta Potential, N₂ adsorption, Raman Spectroscopy, SEM, TGA, and ¹³C solid-state NMR. Among other possible applications of these types of materials, here, we discuss their use as adsorbents for heavy metals removal from aqueous solutions

Introduction

Functional carbonaceous materials with controllable size and shape have been an appealing topic in recent years because of their wide variety of applications, which include adsorbents, catalysts,¹ electrode materials,² stationary phases in liquid chromatography,³ and others. However, the production of such materials usually requires very harsh conditions and has several drawbacks. For instance, standard methods for the manufacture of activated carbons require high temperatures (>800 °C) for carbonization in the first step, followed by physical or chemical activation to transform carbon materials into activated carbon.

A related class of sorbents are ion exchange resins, made by suspension polymerization under more sustainable conditions. The synthesis of polymers via heterophase polymerization of organic monomers is a standard technology and accounts for 14% of the total value gained with polymers.⁴ The resulting latex particles are used in paints, coatings, and glues, but are also beneficial in material science applications, such as reinforcing plastics or concrete. The properties of the resulting polymers and the price, however, are fixed by the available monomers, which in addition have to suit the demands of emulsions polymerization, i.e., just a very restricted set of polymers can be made.

Here, we report a procedure in which organic monomers can be partially replaced by the controlled dehydration products of carbohydrates, which can be then copolymerised or can undergo cycloaddition reaction with functional comonomers to give a new type of hybrid between carbon

and polymer latex. These latexes consist mainly of renewable raw materials, having a low cost base and expanding heterophase polymerization processes to carbonaceous materials. This present synthetic strategy can be extended to various compositions of different water soluble organic monomers yielding materials that combine the surface properties of the polymers with the structural, mechanical, thermal, and electric properties of the carbon framework.

In carbon research, the hydrothermal carbonization of glucose and other carbohydrates is a well-known process to produce monodisperse carbon spheres featuring a hydrophilic surface.^{5–7} A simplified reaction mechanism for the formation of the carbon spheres involves the dehydration of the carbohydrate into a furan-like molecule (furfural aldehyde and/or 5-(hydroxymethyl)-2-furaldehyde) as the first step and subsequent polymerization and carbonization as a second step. However, the use of pure carbohydrates without any functional organic comonomers or processing aids of emulsion polymerization is not the target of the present work, but to be regarded as the starting knowledge.

In this strategy, the main precursor is a cheap water soluble carbohydrate (e.g., glucose), whereas the organic monomer is required in very small amounts in order to provide the functionality. This method offers a facile, cheap, and general route toward the production of carbonaceous materials with a variety of functionalities, which will depend on the employed organic monomer.

The present study concerns the production of carbon microspheres rich in carboxylic acid groups using hydrothermal carbonization of glucose in the presence of acrylic acid. This is therefore, to the best of our knowledge, the first time when carbohydrates via their decomposition products are employed as a monomer base for functional

* Corresponding author. E-mail: magdalena.titirici@mpikg.mpg.de. Fax: 49 331 567 9502.

(1) Makowski, P.; Demir-Cakan, R.; Antonietti, M.; Goettmann, F.; Titirici, M. M. *Chem. Commun.* **2008**, 999.
(2) Hu, Y. S.; Demir-Cakan, R.; Titirici, M. M.; Müller, J. O.; Schlögl, R.; Antonietti, M.; Maier, J. *Angew. Chem., Int. Ed.* **2008**, 47, 9.
(3) Knox, J. H.; Kaur, B. J. *Chromatograph* **1986**, 352, 3.
(4) Distler (e.d) D. *Wässrige Polymerdispersionen: Synthese, Eigenschaften, Anwendungen*; Wiley-VCH: Weinheim, Germany, 1999.

(5) Wang, Q.; Li, H.; Chen, L. Q.; Huang, X. J. *Carbon* **2001**, 39, 2211.
(6) Titirici, M. M.; Thomas, A.; Antonietti, M. *Adv. Funct. Mater.* **2007**, 17, 1010.
(7) Cui, X.; Antonietti, M.; Yu, S.-H. *Small* **2006**, 2, 6–756.

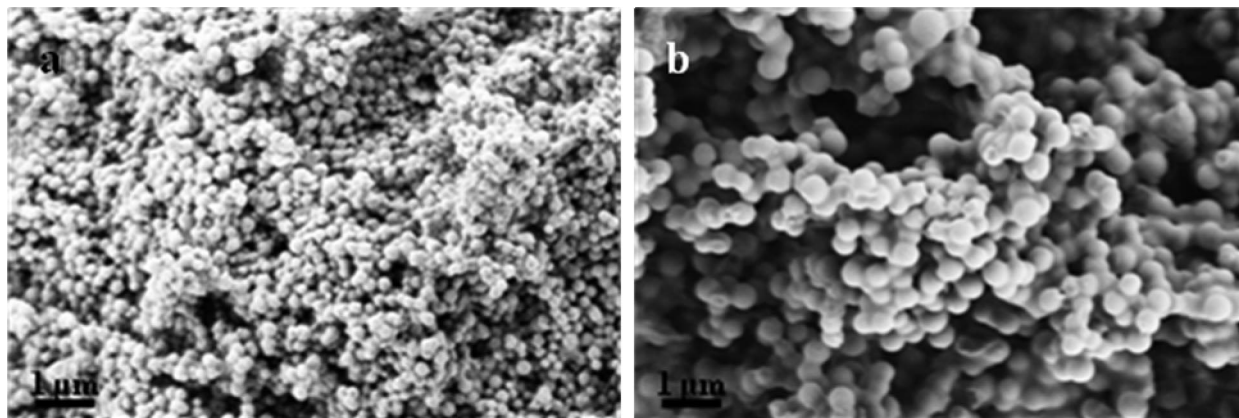


Figure 1. SEM micrographs of dehydrated glucose dispersions after (a) 5 and (b) 8 h.

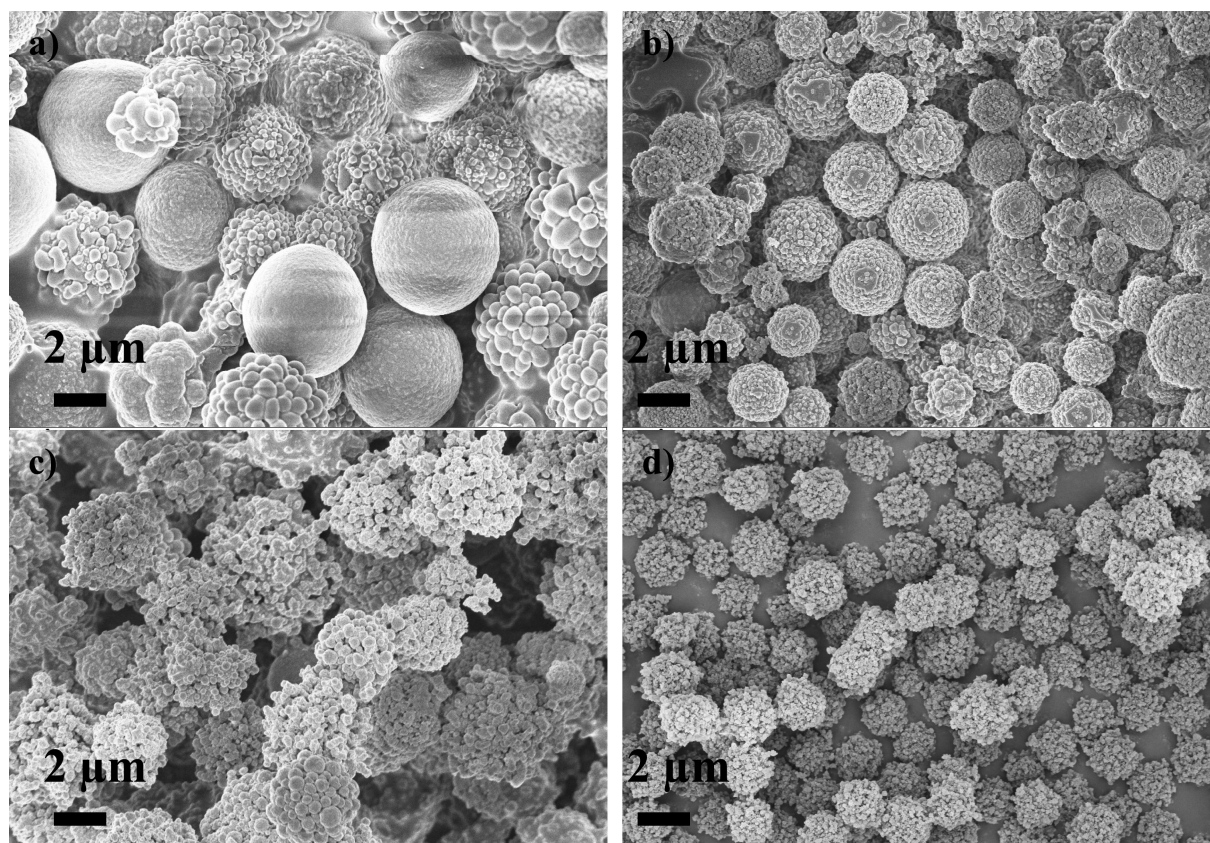


Figure 2. SEM micrographs of (a) 1AcA-C, (b) 2AcA-C, (c) 5AcA-C, (d) 10AcA-C.

copolymer dispersions. The resulting carboxylate-rich materials can have a broad spectrum of applications in fields such as catalysis, adsorption, chromatography, electrochemistry, or other industrial processes. Furthermore, the resulting carboxy groups can be used for further functionalization aiming at different applications.

In this contribution, the carboxylate rich carbonaceous materials were used as sorbents for the heavy metals removal from aqueous solutions. It is a known fact that water pollution caused by heavy metals is a serious worldwide environmental problem with a significant impact on human health and the environment.⁸ Chromium, nickel, cadmium, and lead are classified as heavy metals and are commonly associated with

water pollution. Among them, cadmium and lead are the most toxic elements to human beings and are often present in high concentration in liquid industrial waste.^{9,10} The concentration of any individual heavy metal in drinking water must be in the low microgram per liter range. For instance, according to the World Health Organization guidelines, the permissible concentrations of cadmium and lead are 0.003 and 0.01 mg/L, respectively.¹¹ Adsorption is the most widely used method to remove heavy metals because of its simplicity and low cost. Carbonaceous adsorbents may offer certain advantages

(8) Deng, S.; Ting, Y. P. *Langmuir* **2005**, *21*, 5940.

(9) Lao, C.; Zelendon, Z.; Gamisans, X.; Sole, M. *Sep. Purif. Technol.* **2005**, *45*, 79.

(10) Benhima, H.; Chiban, M.; Sinan, F.; Seta, P.; Persin, M. *Colloids Surf., B* **2008**, *61*, 10.

(11) Pedro, F., Jr.; Nyer, E. K.; *The Water Encyclopedia: Hydrologic Data and Internet Resources*; CRC Press: Boca Raton, FL, 2006.

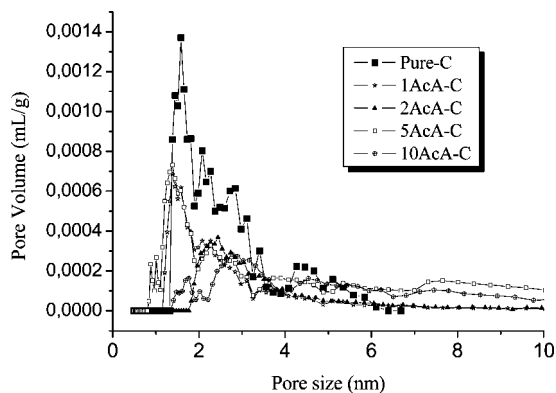


Figure 3. DFT pore analysis of the resulting materials.

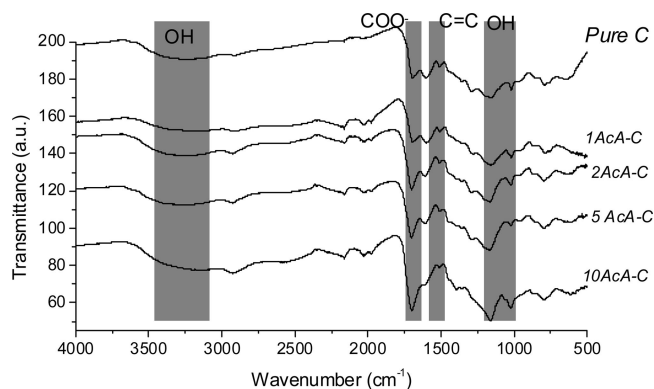


Figure 4. FT-IR spectra of the carbonaceous materials.

in this respect because of their rigid porous structure; high chemical, thermal, and ionizing radiation stability; and distinctive sorptive behavior in the solution of electrolytes.^{12,13}

Experimental Section

Materials and Apparatus. All chemicals used in this study were analytical grade. D-Glucose monohydrate was purchased from ABCR GmbH (Karlsruhe, Germany). Acrylic acid monomer was supplied from Acros. Lead(II) chloride (99.999%, metal basis) is purchased from Alfa Aesar and cadmium(II) chloride (99.99%, metal basis) from Sigma Aldrich.

Structural characterizations were carried out with several apparatus. The particle size and morphology was visualized using a Gemini scanning electronic microscope (SEM). The pore size distribution of carbon materials were determined by using NLDFT model of the both nitrogen adsorption and desorption isotherms at 77 K by means of a QUADROSORB SI, equipped with automated surface area and pore size analyzer. Before analyzing the samples, they were degassed at 150 °C 16 h using a masterprep degasser. FT-IR spectra were recorded using a Varian 600 FT-IR Spectrometer. Raman spectra were recorded on a Alpha300 (Witec) spectrometer. Thermogravimetric analysis was carried out using a NETZSCH TG 209 at a heating rate of 10 K/min under N₂. Zeta potential values of the carbon suspensions were recorded using Zeta Sizer 3000 HS, Malvern Instruments, as a function of pH. ¹H and ¹³C solid-state magic angle spinning (MAS) NMR experiments have been acquired on Bruker Avance 300 MHz (7 T) spectrometer using the 4 mm zirconia rotors as sample holders spinning at MAS rate $\nu_{\text{MAS}} = 14$ kHz. The chemical shift reference was tetramethylsilane

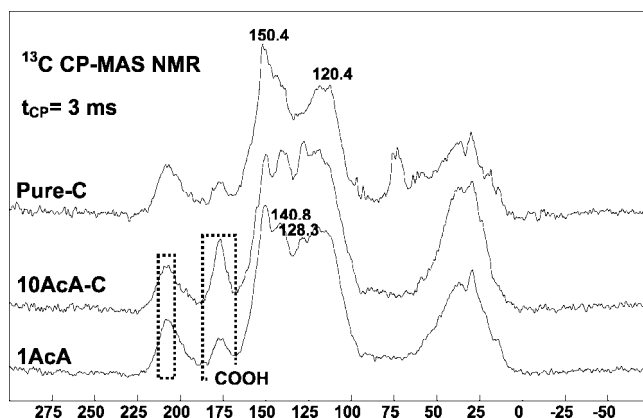


Figure 5. ¹³C solid-state NMR of the carbonaceous materials.

Table 1. Metal Uptake Capacity of the Carbonaceous Materials

adsorbent	Pb uptake (mg/g)	Cd uptake (mg/g)
pure-C	60.8	6.5
1AcA-C	61.1	4.2
2AcA-C	77.7	11.0
5AcA-C	293.2	51.3
10AcA-C	351.4	88.8

(TMS; $\delta = 0$). Proton-to-carbon CP MAS was used to enhance carbon sensitivity; recycle delay for all CP experiments is 3 s and TPPM decoupling is applied during signal acquisition. Cross-polarization transfers were performed under adiabatic tangential ramps to enhance the signal with respect to other known methods and CP time $t_{\text{CP}} = 3$ ms was found to be a good compromise¹⁴ in order to have a good overview on all carbon species. The number of transients is 1200 for all other carbon samples. Gas chromatography (GC) was coupled to mass spectroscopy (MS) to separate and identify the main molecular species by mean of the NIST database included in the spectrometer software package. The instrument used is an Agilent Technologies (GC = 6890N; MS = 5975) apparatus. An inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determinate the metal concentration in solution by Varian Inc.-Vista MPX Simultaneous ICP-OES with the wavelength of 217 000 nm for Pb and 214 439 nm for Cd.

Synthesis of Carbonaceous Materials. To obtain carbonaceous materials with a high degree of functionality, we have added acrylic acid monomer to the reaction mixture with different ratios; 1, 2, 5, and 10 wt % with respect to glucose concentration. The reaction mixture was then sealed into the Teflon inlet in an autoclave and hydrothermally treated at 190 °C for 16 h. Then, the obtain materials are washed several times by water and put into an oven at 80 °C under a vacuum overnight.

Adsorption Studies. One thousand mg/L stock solutions of the lead and cadmium metal ions were prepared in deionized water from Millipore-Q water system, which were further diluted to the required concentrations before use.

One-tenth of a gram of adsorbent was placed into 100 mL solutions with initial concentrations of Pb from 10 to 1000 mg/L and Cd from 10 to 200 mg/L, respectively. Adsorption experiments were carried out at room temperature. The initial and final pH values of the solution were adjusted with 0.1 N HCl and NaOH solution and kept at 6.0 ± 0.1 . The pH value was equilibrated every 24 h and reached equilibrium after 72 h, then suspensions were filtered through 0.45- μm membrane filters. The filtrates were immediately

(12) Li, Y. H.; Wang, S.; Luan, Z.; Ding, J.; Xu, C.; Wu, D. *Carbon* **2003**, 41, 1057.

(13) Strelko, V., Jr.; Malik, D. J. *J. Colloid Interface Sci.* **2002**, 250, 213.

(14) Baccile, N.; Laurent, G.; Babonneau, F.; Titirici, M. M.; Antonietti, M. *Carbon* **2008**, submitted.

Table 2. Comparison of Pb²⁺ and Cd²⁺ Adsorption Capacities of Different Adsorbents

adsorbent	Pb ²⁺ (mg/g)	Cd ²⁺ (mg/g)	conditions	refs
10AcA-C	351.4	88.8	pH 6; room temperature	our data
leonardite (low-rank coal)	250.7	50.6	pH 5.4–5.6; room temperature	9
HNO ₃ oxidized carbon nanotube	97.08	10.86	pH 5; room temperature	21
algae	331.52	134.88	pH 5; room temperature	26
Amberlite IR-120 synthetic sulfonated resin	19.6	201.1	pH 4–8; room temperature	27
carbon aerogel	~ 35.0	~ 15.0	pH 4.5; 37 °C	28

determined by ICP-OES. The amounts of metal ions adsorbed on functional carbonaceous materials were calculated by subtracting the equilibrium solution concentration from the initial ion contents.

Results

Synthesis and Structural Characterization. To obtain carbonaceous materials with a high degree of carboxylic groups, acrylic acid has been added as a comonomer to the reaction mixture. Different ratios (1, 2, 5, and 10 wt %) with respect to the total glucose concentration have been employed. Glucose is used as carbon source and its concentration in water is 10 w/v %, and hence the maximal acrylic acid concentration in water is 10 w/v % overall. The reaction mixtures were then sealed into glass vials inserted inside PTFE inlets in autoclaves and hydrothermally treated at 190 °C for 16 h. The resulting carbonaceous samples were labeled according to the acrylic acid monomer (quoted as AcA) concentration added into the reaction mixture. For instance, 1AcA-C, 2AcA-C, 5AcA-C, 10AcA-C, respectively, accounting for 1, 2, 5, and 10 wt % acrylic acid (AcA) used in the reaction media and “C” refers to the carbonaceous material. The carbon material obtained from 10% pure glucose solution without any monomer is called Pure-C.

The SEM images of dehydrated glucose dispersions prior to final carbonization (stopped after 5 and 8 h hydrothermal treatment) show that the resulting particles grow in size with increasing reaction time with a diameter of ca. 250 and 500 nm, respectively, as depicted in Figure 1. This indicates that the early dehydration products are constituted by a weakly water soluble oily phase which can be used as a major monomer source for the emulsion polymerization processes. According to GC-MS analysis (see Figure S1 in the Supporting Information), the composition at this stage of reaction is formed of nondecomposed glucose, 5-(hydroxymethyl)-2-furaldehyde (HMF), the well-known decomposed product of glucose^{15,16} and other side products like dihydroxyacetone, formic acid, acetic acid, and furfural.^{17,18} HMF most probably reacts via a polymerization-condensation-dehydration cascade to form the final carbonaceous scaffold, which contains the furan unit as the main repeating motif constituting the carbon scaffold, as was shown by advanced ¹³C solid-state NMR studies.¹⁴

Figure 2 shows the morphologies of the materials prepared in the presence of acrylic acid. It is known that upon hydrothermal carbonization of glucose, micrometer sized, microporous carbon spheres with smooth surfaces are obtained.^{5,6} In the present case, addition of acrylic acid induces a change in the particle morphology, that is, the surface of the particles is no longer smooth and the microspheres indicate that they are formed out of small aggregated particles (~250 nm). Acrylic acid appears to stabilize the first formed small droplets depicted in Figure 1, thus preventing them from further growth, as might occur in the pure glucose case. Later on in the process, the primary polymerized particles assemble into micrometer-sized “raspberry”-like structures.

This effect is more pronounced the more acrylic acid is added into the system. Upon addition of only 1 wt % monomer, some of the spheres possess this morphology, whereas the others appear smooth like in the case of Pure-C. In this case, the amount of acrylic acid was probably not sufficient in order to be incorporated in all intermediary particles formed during the hydrothermal carbonization, e.g., lately formed particles may be depleted in acrylic acid and progress via the classical hydrothermal carbonization route.¹⁹ The 2AcA-C material shows monodisperse micrometer-sized

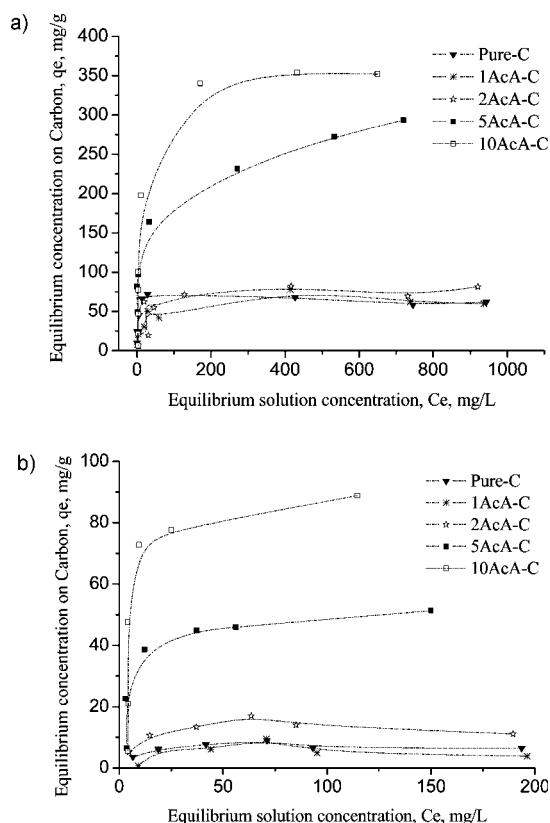


Figure 6. (a) Pb(II) and (b) Cd(II) adsorption isotherms on the obtained carbonaceous materials.

- (15) Ulbricht, R. J.; Northup, S. J.; Thomas, J. A. *Fundam. Appl. Toxicol.* **1984**, *4*, 843.
- (16) Antal, M. J.; Mok, W. S. L.; Richards, G. N. *Carbohydr. Res.* **1990**, *199*, 91.
- (17) Sharma, R. K.; Wooten, J. B.; Baliga, V. L.; Hajjaligol, M. R. *Fuel* **2001**, *80*, 1825.
- (18) Sharma, R. K.; Wooten, J. B.; Baliga, V. L.; Martoglio-Smith, P. A.; Hajjaligol, M. R. *J. Agric. Food Chem.* **2002**, *50*, 771.
- (19) Yuanzhu, M.; Yingliang, L.; Dingsheng, Y.; Zhang, J. *Chem. Lett.* **2005**, *34*, 846.

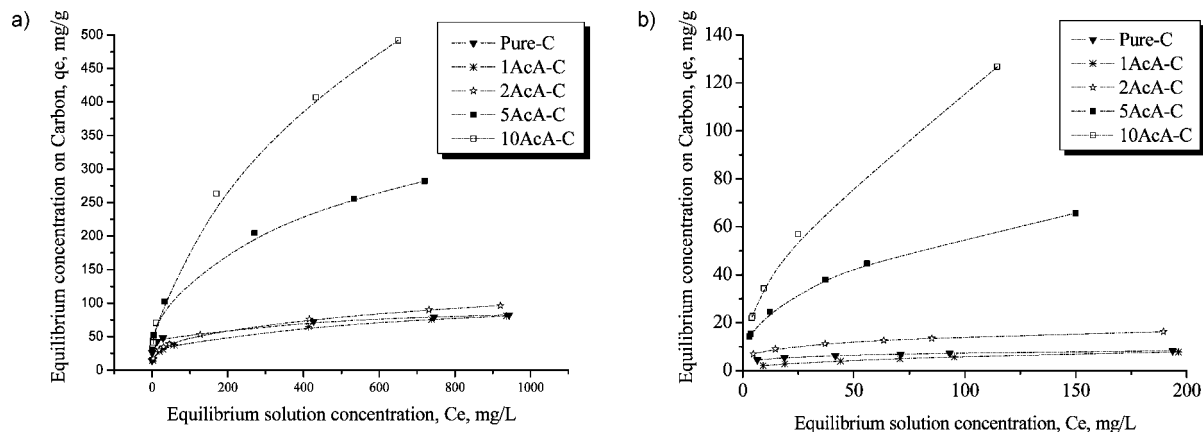


Figure 7. (a) Pb, (b) Cd Freundlich isotherm curves on the different adsorbents.

Table 3. Freundlich Isotherm Parameters of the Adsorption for Pb(II) and Cd(II) on Carbonaceous Materials

sample	Pb ²⁺			Cd ²⁺		
	<i>K</i>	<i>n</i>	<i>r</i> ²	<i>K</i>	<i>n</i>	<i>r</i> ²
pure-C	21.99	5.23	0.85	3.18	5.52	0.86
1AcA-C	12.35	3.64	0.91	1.13	2.80	0.93
2AcA-C	12.30	3.31	0.90	4.83	4.33	0.91
5AcA-C	26.48	2.68	0.93	9.22	2.55	0.91
10AcA-C	24.01	2.146	0.95	10.47	1.91	0.98

spheres formed out of a uniform arrangement of nanosized spheres. It seems that the amount of acrylic acid is in this case optimal for producing such uniform superstructures. Once the acrylic acid amount is increased up to 5 and 10%, a massive stabilization of the formed droplets occurs which can no longer assemble into perfectly spherical micrometer-sized aggregates due to steric effects.

The materials produced via this process are microporous having small micropore volumes and low surface areas (<50 m²/g), which is common for hydrothermal carbons.⁵ The pore size distributions of all the obtained materials together with the carbon obtained from hydrothermal carbonization of glucose are given in Figure 3. The Raman spectrum of the obtained materials is shown in Figure S2 in the Supporting Information. For both the pure-C and the materials prepared in the presence of acrylic acid, the spectra contain the characteristic wide D and G bands around 1360 and 1590 cm⁻¹, respectively, typical for amorphous carbons or disordered graphite. The large *I*_D/*I*_G value (0.8) indicates the low degree of graphitization of the resulting hydrothermal carbon material.¹⁹ This proves that the materials obtained via the hydrothermal carbonization of glucose in the presence of acrylic acid are amorphous like carbonaceous materials and are no different than the ones obtained from pure glucose.

Functionality. The presence of carboxylic groups on the surface was first proved using FT-IR spectroscopy. The FT-IR spectra of the pure-C and all the resulting materials are shown in Figure 4. Upon hydrothermal carbonization of glucose, carbon materials rich in functional groups such as hydroxyl, esters, ethers, carbonyl, and carboxylic groups are obtained.^{5,6} However, it is observed that the intensity of the adsorption band at 1700 cm⁻¹, corresponding to the carboxylate group, increases upon increasing the amount of acrylic acid in the sample, proving a higher degree of carboxylic groups in the modified materials. The other

adsorption bands belong to C=C double bonds (1620 cm⁻¹), C—OH stretching and OH bending vibrations (1000–1300 cm⁻¹), the latter underlining also the existence of a large number of residual hydroxyl groups coconstituting the hydrophilic surface.

Solid-state ¹³C CP-MAS NMR was also employed to confirm the presence of carboxylic groups (Figure 5). The ¹³C spectra of acrylic acid-added carbons, shows large similarities with the one of pure carbon, which is largely discussed elsewhere.¹⁴ A large peak between 14 and 60 ppm indicates the presence of aliphatic and ether carbons, the peaks between 100 and 160 ppm result from sp²-hybridized carbons, the peak at 175 is mainly due to carboxylic acids plus a low amount of aldehydic groups, while in the 200 ppm region ketones and a small population of aldehydes resonate. When acrylic acid is added, two main changes in the spectrum occur and become more visible with increasing its amount from 1 to 10%. On the one hand, the COOH peak experiences a considerable increase in intensity, whereas on the other hand, two additional resonances at 141 and 129 ppm appear and increase with increasing amount of AcA. In good agreement with the FT-IR experiments, these experiments therefore show that a larger amount of carboxylic acid is incorporated in the carbon materials when the concentration of AcA increases (peak at 175 ppm). In addition, the NMR data seem to propose a cycloaddition mechanism between acrylic acid and hydroxymethylfurfural due to the enhancement of the 141 and 129 ppm peaks, typical for aromatic compounds. Linear polymerization of acrylic acid can be excluded, as this would largely increase the aliphatic-methylene peak in the 30 ppm region, which is not found at all.

To obtain information about the surface charge of the materials, zeta potential measurements were performed at various pH values. (see Figure S3 in the Supporting Information). The experiments were performed using variable amounts of 0.1 N NaOH (from 0 to 4.5 mL) and 0.1 N HCl (from 0.1 to 4 mL) to adjust the pH of the samples. 0.1 N NaCl solution was added to each flask to maintain a high background electrolyte concentration.

These measurements showed that all the obtained materials, the pure-C as well as the acrylic modified materials have an overall negative surface charge above pH 2. This very

low isoelectric point is indicative of a strong acid site, as they are needed for ion exchange resins.

The zeta potential values for the pure-C material are even more negative than those of acrylic-acid-modified carbons. This can be due to the fact that zeta potential is a surface technique and although most of the acidic functionalities are located at the surface for pure-C,⁵ presumably some of the carboxylic groups for the acrylic acid modified samples are also located within the carbon matrix.

Also TGA analysis (see Figure S4 in the Supporting Information) shows clear differences between the pure-C material and the acrylic acid modified ones. The pure-C material has the lowest mass loss of 50% upon further heating under N₂. The acrylic acid modified materials show systematically better decomposition into volatile fragments well beyond the acrylic acid content, which we attribute to the carboxylic groups, but also aromatization on the expense of structural network formation.

Adsorption of Heavy Metals (Cd²⁺, Pb²⁺). Among other possible applications indicated in the introductory part, the obtained functional carbonaceous materials rich in carboxylate groups are promising candidates for use as cheap, sustainable, and effective sorption materials. Even if the micropore volumes of these materials are rather low, because the functional groups are mainly located at the surface, the metal ions can easily bind to the carboxylate groups. The objective of this study is to demonstrate the efficiency of carbonaceous materials for removing heavy metals from aqueous solutions. Cd(II) and Pb(II) in aqueous media may exist in different species depending on the pH value and initial metal concentration. In the pH range between 2 and 6, cadmium and lead ions are likely to be found as free ions (Cd²⁺ > 99.9%, Pb²⁺ > 98%), in equilibrium with the solvated species.⁹ At higher pH value (>8), metal ions tend to be precipitated because of the OH⁻ ions forming complexes,²⁰ whereas at lower pH values, a low adsorption capacity can be expected due to the neutralization of the sorption sites. In this context, an “environmental” pH of 6 was chosen as the initial pH and adjusted in regular intervals to avoid complex responses of the system.

Adsorption isotherms and sorption capacities of the resulting materials for Pb and Cd removal are shown in panels a and b in Figure 6, respectively, where q_e is the amount of metal ions adsorbed on the carbon material (mg/g), C_e is the equilibrium solution concentration (mg/L). The carbon materials Pure-C and 1AcA-C samples have, expectedly, the lowest binding capacity for both cadmium and lead. The capacity increases slightly for the 2AcA-C sample (11.00 Cd (II) mg/g, 77.7 Pb(II) mg/g). A dramatic increase in adsorption capacity is observed upon further increasing the amount of acrylic acid in the samples. In both Pb²⁺ and Cd²⁺ sorption cases, 10AcA-C functional carbon has the highest metal uptake capacity.

Table 1 summarizes the cadmium and lead ion sorption results of the produced materials. In good agreement with

other reports,^{9,20,21} Pb²⁺ ions are retained more strongly than Cd²⁺ ions on all our carbon functional materials. For instance, the capacity of the 10AcA-C for lead ion is 351.4 mg/g (1.7 mmol/g) and for cadmium is 88.8 mg/g (0.79 mmol/g). This different adsorption behavior of Pb²⁺ and Cd²⁺ ions is usually explained by the metal ion properties such as ionic radius, electronegativity, and ionization potential.⁹ Because of the higher ionic potential and electronegativity, Pb(II) ions have better electrostatic interaction with the functional negative surface groups of the resulting materials. An additional contribution may arise from the smaller radii of hydrated Pb(II) ions (0.275 nm) so that ions can more easily penetrate through the carbon pore system as compared to Cd(II).¹⁰

Table 2 shows a comparison between the adsorption capacities obtained from our report and those of other adsorption studies. Results clearly suggest that values of 100–300 mg/g are indeed extraordinarily high and well beyond the capacities of synthetic ion exchange resins and other type of sorption materials. This underlines the extraordinary potential of functional hydrothermal carbon materials for ion binding and ion buffering purposes.

The adsorption behavior of lead and cadmium ions on the pure carbon and acrylic-acid-functionalized carbons were further described by Freundlich²² and Langmuir isotherms.²³ Here, the initial metal concentrations are changed, whereas all other conditions are kept constant. A Langmuir isotherm describes a homogeneous adsorption surface meaning all the adsorption sites have equal adsorbate affinity. On the other hand, the Freundlich isotherm model assumes heterogeneity of adsorption surfaces. This is expressed by the Freundlich equation (eq 1), where K and n are the Freundlich isotherm constants.

$$q_e = KC_e^{1/n} \quad (1)$$

A fit of the data according to Freundlich (panels a and b in Figure 7) and Langmuir (data not shown) and comparing the correlation coefficients, r^2 , only the Freundlich isotherm model fit both the Pb(II) and Cd(II) ions uptake. Table 3 depicts the corresponding parameters and correlation factors. According to the correlation coefficients, the 10AcA-C sample was a better fit into Freundlich isotherm model with 0.95 and 0.98 values.

The K value indicates the adsorption capacity. n is related to the energetic heterogeneity (average energy of sites), and n values here are between 1 and 10, which represents beneficial adsorption.^{24,25} Upon hydrothermal carbonization, a decrease in n value and an increase with the K value was observed with carboxylic acid rich carbons except pure-C, probably because of the low degree of fitting the data to the

(20) Mohan, D., Jr.; Bricka, M.; Smith, F.; Yancey, B.; Mohammad, J.; Steele, P. H.; Alexandre-Franco, M. F.; Gómez-Serrano, V.; Gong, H. *J. Colloid Interface Sci.* **2007**, *310*, 57.

(21) Li, Y.-H.; Ding, J.; Luan, Z.; Dia, Z.; Zhua, Y.; Xua, C.; Wu, D.; Wei, B. *Carbon* **2003**, *41*, 2787.

(22) Freundlich, H.; Helle, W. *J. Am. Chem. Soc.* **1939**, *61*, 2.

(23) Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.

(24) Treybal, R. E. *Mass Transfer Operations*, 3rd ed.; McGraw Hill: New York, 1980; p 447.

(25) Salame, I. I.; Bandosz, T. J. *J. Colloid Interface Sci.* **2003**, *264*, 307.

(26) Yu, Q.; Matheickal, J. T.; Yin, P.; Kaewsarn, P. *Water Res.* **1999**, *33*, 1534.

(27) Demirbas, A.; Pehlivan, E.; Gode, F.; Altun, T.; Arslan, G. *J. Colloid Interface Sci.* **2005**, *282*, 20.

(28) Kadirvelu, K.; Goel, J.; Rajagopal, C. *J. Hazard. Mater.* **2008**, *153*, 502.

Freundlich isotherm. Similar observation has been reported by the group of Bandoz²⁵ with ammonium persulfate oxidized activated carbons of wood origin. Here in our approach, addition of acrylic acid monomer causes an increase in the acidic functional groups (Figure 5) and a decrease in the pore volume (Figure 3). These effects further lead the above mention trend with a decrease in heterogeneity, and increase in the adsorption capacity, meaning that 10AcA-C sample has the lowest energetic heterogeneity, resulting in strongest metal uptake.

Conclusion

Here, we described the synthesis of a new type of functional carbon microparticles by simple hydrothermal carbonization of glucose in the presence of acrylic acid monomer. The method is highly sustainable, using predominantly natural products as a carbon source and a low amount of organic monomer. Furthermore, this method offers a general platform for the production of carbonaceous materials with different functionality provided by the availability of water-soluble functional organic monomers. The final products consist mainly of an amorphous carbon framework with its high thermal and chemical stability, however with increased functionality brought in by the monomer. By solid-state NMR and other analytical techniques, it was proven that the acrylic acid is not added in a polymerization type process, but presumably undergoes cycloaddition to a more conjugated and therefore more effective binding site.

The synthesized materials proved to be feasible for use in adsorption experiments for removal of heavy metals from aqueous solutions. The adsorption capacity was as high as 351.4 mg/g for Pb(II) and 88.8 mg/g for Cd(II), which is well beyond ordinary sorption capacities and proving the efficiency of the materials to bind and buffer ions, or more specifically to remove heavy metal pollutants. The possibility of water purification achieved with carbonaceous materials produced under mild conditions and with an overall low cost base is definitely an attractive alternative, especially for less-developed areas of the world.

Beyond heavy metal adsorption as an easy-to-quantify model case, we expect, however, wider applications in a variety of fields such as catalysis, chromatography, construction chemicals, and as functional colloids.

Acknowledgment. The authors thank EnerChem/MPG for the financial support. Florence Babonneau (Laboratoire de Chimie de la Matière Condensée de Paris, CNRS/UPMC, Paris, France) and Guillaume Laurent (LCMCP, CNRS/UPMC, Paris, France) are kindly acknowledged for providing access to NMR facilities and R. Oberhänsli (Universität Potsdam, Institut für Geowissenschaften, Potsdam, Germany) for providing access to ICP-OES.

Supporting Information Available: GC-MS chromatogram, Raman spectra, zeta potential vs pH, and TGA profile. This material is available free of charge via the internet at <http://pubs.acs.org>.

CM802141H