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Coating of solid substrates with carbon via hydrothermal carbonization

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Abstract

Carbon coatings are synthesized on various solids via hydrothermal carbonization as a green and environmental-friendly method. The coatings can be produced on various solid substrates independent of their shape and surface properties by application of stirring during the reaction. Coatings on stainless steel felt and mesh as well as on ceramic tubes were further investigated. In their raw state, the coatings obtained have a high content of various oxygen-containing functional groups, and are somewhat lacking in surface area. However, thermal treatment creates porosity (up to 500 $m^2 g^{-1}$ specific surface area) and reduces oxygen content and density of functional groups. The heat-treated carbonaceous materials can be used as cost-efficient adsorbents in water treatment systems for adsorption of organic pollutants, with the option for regeneration through electro-thermal heating.

Keywords

Carbon coating

Hydrothermal carbonization

Water treatment

1. Introduction

Using hydrothermal carbonization (HTC) for coating/encapsulation of nano- and microstructures is a common research topic and known for many years [1]. In addition to the coating of smaller particles and fibers, the possibility to coat macroscopic substrates via HTC has received much more attention recently, mainly focused on carbon substrates [2-6]. Only a small number of publications have dealt with HTC coating of other substrates, e.g. metals and glass [7-10]: these are, to the best of our knowledge, the only ones dealing with non-carbonaceous macroscopic substrates. The use of HTC reaction products, mainly in the form of small carbon particles, in (waste)water treatment is known [11]. However, the removal of small particles from cleaned suspensions requires considerable efforts. Carbon-coated fixed substrates as adsorbents can avoid this problem. In this article we describe a broad spectrum of macroscopic substrates coated via HTC by using sucrose of commercial quality. Stirring and substrate movement during the hydrothermal reaction were applied as upgrading factors for more even and stable coatings on various substrates. The carbon coatings can be activated easily via heating and could serve as versatile additions to established (waste)water treatment installations. Combination with electrically heatable structures provides additional, more effective regeneration options.

2. Materials and methods

Sucrose (suc) solutions were prepared from deionized water and commercially available sucrose (c_{suc} = 0.0625 – 0.5 M) (Table S1). Various substrates, namely stainless steel (SS) 316L felt (Felt) (Shanghai Everspring Filtration, Pudong, China), SS 316 mesh100/mesh80 (Mesh100/Mesh80) (Alfa Aesar), ceramic tubes (Cer), copper mesh or a glass-plug, were placed together with a magnetic stir bar in a glass inlay. 11 mL of sucrose solution were added and the inlay was placed in a SS autoclave which was then sealed. The autoclave was heated in an oven to T = 180 °C for t_{oven} = 6 to 24 h while constantly stirring with the magnetic bar, and left to cool to room temperature afterwards. The raw hydrochar (rHc) coated substrates were removed from the inlay, washed three times in deionized water, ultra-sonicated and dried overnight. For activation, the carbon-coated substrates were placed in a tube furnace and heated under nitrogen flow for 1 h at 100 °C and then further to 600 °C, held for 2 h. Some of the rHc coated and heat treated (HcT) substrates were selected for characterization and further investigation (Table 1).

3. Results and discussion

A stable carbon coating on various substrates is obtained when using the HTC process combined with stirring. Although the carbon deposition on the solid surfaces already takes place without stirring, this leads to uneven coatings and lack of reproducibility. By introducing stirring to the reaction, complementary chemical and mechanical factors are combined. The preformed hydrochar (Hc) microspheres gain more kinetic energy, giving rise to dense carbon layers when they collide with the surface of solid substrates. As soon as the first layer is formed, the addition and adhesion of new and sticky carbon spheres continues through a known polymerization/polycondensation process, resulting in a structured coating that contains sphere- and cauliflower-like structures. Due to the mechanical factor, it is also possible to coat structures that are more challenging than e.g. metal-felt (Figure 1 a.), such as tubes or meshes (Figure 1). While a lack of favorable anchor groups or surface roughness on the substrate (e.g. Teflon® or glass) usually results in instable coatings, this problem can be overcome by intensifying the mechanical factor or by surface roughening. Therefore, magnetic stir bars or glassware can also be coated, even when the surface is not "coating-friendly" (Figure 1e and f). The coating surfaces can become smoother when adding substrate movements, thus intensifying the mechanical factor further. In addition to the previously mentioned advantages, stirring during the HTC process enables simpler up-scaling of experiments.

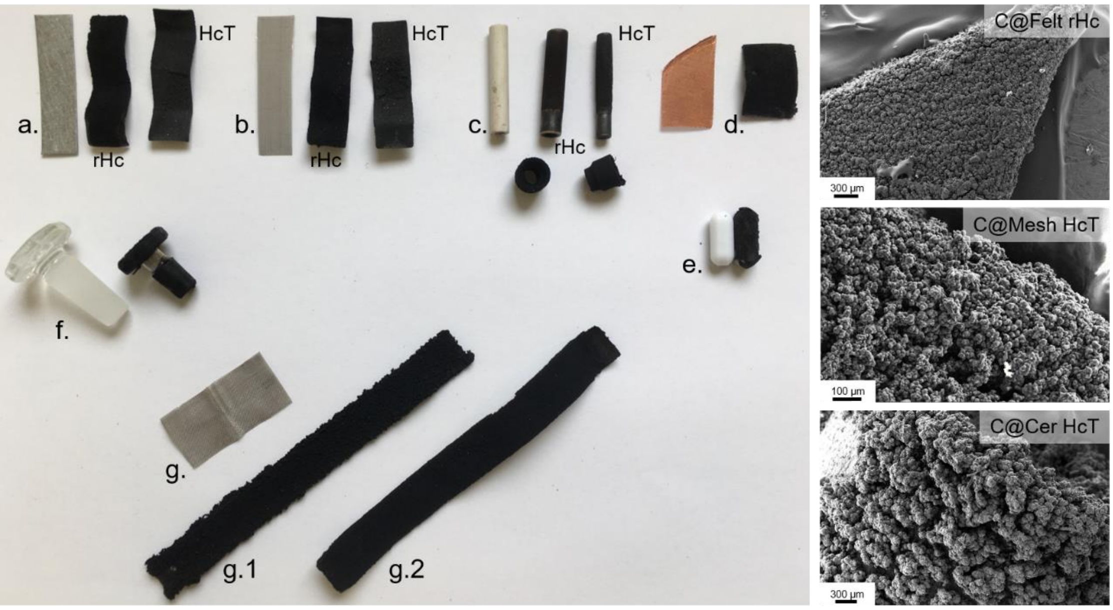

Figure 1. Pictures of uncoated vs. coated substrates (rHc and HcT), namely a. SS316L felt, b. SS316 mesh100, c. ceramic, d. copper mesh, e. Teflon® stir bar, f. glass-plug, g. SS316 mesh80 (g.1 without and g.2 with additional movement) together with exemplary SEM pictures.

Masses of coating per surface area (m_c/A) and related coating thicknesses vary with the educt concentration c_{suc} and the treatment time t_{oven}, whereby the dependencies are rather complex. For each substrate, there is an optimum combination of t_{oven} and c_{suc} for obtaining a large m_c/A and a high stability with acceptable reaction times (Table S2).

Table 1. Summary of coating properties of further investigated substrates.

Sample	t_{oven} [h]	c_{suc} [M]	m_c/A [mg cm^{-2}]		S_{BET} b)	O-content [wt-%] c)	
			rHc	HcT	[m^2 g^{-1}]	rHc	HcT
C@Felt18 a)	18	0.25	15.5 ± 1.1	8.7 ± 0.5	470	8.4	3.5
C@Felt24	24	0.25	16.0 ± 0.9	8.6 ± 0.7	508	8.6	2.5

C@Mesh[a)]	18	0.25	13.9 ± 2.7	6.4 ± 0.4	432	9.0	3.1
C@Cer18	18	0.50	23.4 ± 4.1	11.6 ± 2.3	470	8.9	3.0
C@Cer24[a)]	24	0.25	5.3 ± 0.7	2.2 ± 0.4	455	8.9	3.0

[a)] with additional substrate movement; [b)] for HcT, referred to the weight of carbon [c)] oxygen content calculated from released CO and CO_2 in TPDec experiments

The stability of the coatings was tested by ultra-sonication for 10 min in an ultrasonic bath. Only small losses of coating mass were observed, about 4 % rHc and up to 6 % for HcT (Figure S1).

In addition to the stability tests, microscopic and scanning electron microscopy (SEM) pictures were taken for a closer investigation of the surface (Figures 1, S2 and S3). There, it is clearly visible that the overall structures of the coatings are similar to those of Hc particles from sugar solutions. The generated cauliflower-like surface structure is already relatively rough, which could favor mass-transfer processes. No visible structural changes occurred during the heating procedure. In addition, Raman spectroscopy was performed in order to investigate carbon bonding in HcT (Figure S4). The spectra show the typical D- and G-bands at 1350 and 1590 cm^{-1}, with an intensity ratio $I_D/I_G \approx 0.5$ that suggests a significant fraction of graphite-like carbon [12].

The rHc coating has no measurable specific surface area (S_{BET}), while HcT has S_{BET} up to 500 $m^2\ g^{-1}$ (Table 1), which is a promising value for various applications. The N_2 adsorption-desorption isotherms are of type 1, with small hysteresis loops indicating the prevalence of micropores (Figure S5). For some applications, such as adsorption of heavy metal ions, a certain density of oxygen-containing functional groups is favorable [2, 11]. Therefore, temperature-programmed-decomposition (TPDec) measurements (Figures 2 and S6) were performed in order to investigate the various functional groups [13] and evaluate the related oxygen contents. The rHc coating has a higher oxygen content and a variety of functional groups, such as carboxylic, lactone, phenol, carbonyl and ether groups. In the course of the TPDec procedure, volatile and semi-volatile constituents were removed from the samples, thus only partially contributing to the CO_x balance. In HcT, the TPDec-based oxygen content related to functional groups decreases by more than 60 %. The most prominent remaining groups are carbonyl and phenol. Therefore, the surface of HcT should be more hydrophobic than that of rHc, which could favor the adsorption of hydrophobic contaminants.

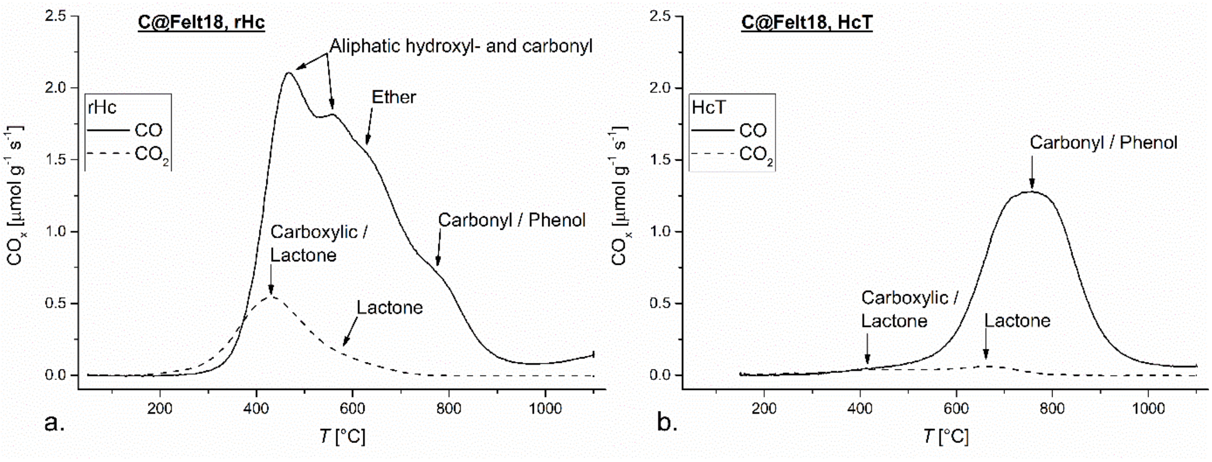

Figure 2. Results of TPDec measurements for C@Felt18 rHc (a.) and HcT (b.) (heating rate 10 K min^{-1}).

Adsorption experiments were performed with monochlorobenzene (MCB) and perchloroethylene (PCE). The adsorbent loading *q* as well as distribution constant K_d were determined (Figure S7). From the experimental data K_d values up to $3 \cdot 10^5$ L/kg (MCB) and $1 \cdot 10^5$ L/kg (PCE) were determined with loadings of about 25 g/kg for both, MCB and PCE. Since the regeneration of loaded Hc is an important aspect, electro-thermal heating is considered as a possible desorption/degradation method. For demonstration, the coated metal substrates were contacted and an electrical current was applied. The resulting temperatures were visualized with an IR camera (Figure 3), showing the expected temperature distributions which make them suitable candidates for thermal regeneration.

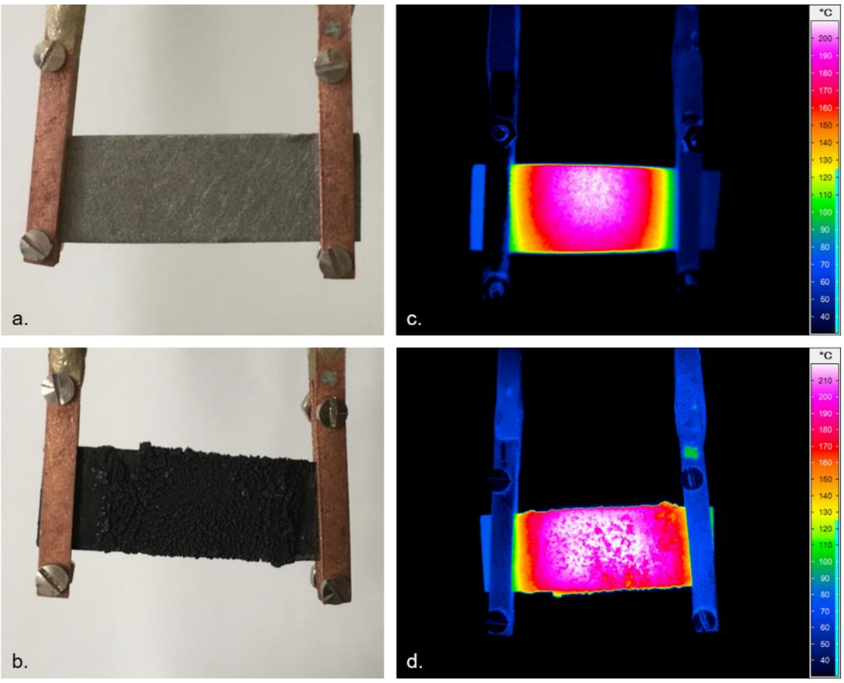

Figure 3. Setup with SS Felt (a.) and C@Felt18, HcT (b.) and IR-camera pictures of heated uncoated felt (c.) and C@Felt18, HcT (d.).

4. Conclusions

We present a simple way of carbon coating via hydrothermal carbonization that is largely independent of and very flexible with respect to the type and shape of the solid substrates used. It produces even and mechanically stable coatings. rHc coatings have a variety of oxygen-containing functional groups, whereas HcT coatings have lower oxygen contents and high surface areas, which makes them ideal candidates for adsorption of organic contaminants like monochlorobenzene or perchloroethylene that were investigated as model compounds. The HTC-coating process for various non-carbonaceous substrates could become a fruitful addition to already established methods, environmentally friendly and applicable in almost every installation. Another advantage is the variety of modifications that can be applied in order to tailor the coating for many different applications. Regeneration of spent adsorber materials can be facilitated using the potential of coated solids combined with heating.

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