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Agitation induced loading of sulfur into carbon CMK-3 nanotubes: efficient scavenging of noble metals from aqueous solution†

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Solid sulfur was completely infiltrated into the channels of mesoporous carbon nanorods in an aqueous medium at room temperature by simple but vigorous stirring. The C–S nanocomposite exhibits ultra-fast Pt sorption, even in extremely dilute solutions.

It is economically and ecologically important to recover platinum group metals (PGM) from dilute effluents¹ which include leached electronics or catalyst wastes, fission product solutions from nuclear reactors,² and geothermal brines.³ Recently, there has been a concern that Pt based catalysts in polymer electrolyte membrane fuel cells (PEMFC) suffer dissolution during operation, particularly at high power output. This forms dilute Pt effluents, which potentially generates negative impact. Sorbents which can rapidly capture otherwise lost Pt from dilute solutions are highly desirable.⁴ Extensive efforts have been devoted to chitosan based materials⁵ that exhibit sorption mainly through an ion exchange mechanism, which is only effective for metal complex anions. It also takes hours or days to achieve full sorption due to the nature of the ion exchange process, which limits their applications.^{5,6}

It is well known that sulfur exhibits strong affinity for heavy metals through a soft acid–base interaction.^{7,8} Sulfur impregnated activated carbon (SIAC), prepared by vaporizing sulfur onto activated carbons, is used as a mercury sorbent.⁹ However, bulk SIAC exhibits very poor efficiency for the capture of Pt ions from dilute solutions, owing to poor porosity. Ordered mesoporous carbons (OMC)¹⁰ such as CMK-3,¹¹ in contrast, display various valuable characteristics, such as tunable pore structure/size and surface chemistry. These can be employed to prepare efficient nanostructured sorbents.^{12–14} We have reported a melt-diffusion method that fills the channels of bulk OMCs with sulfur by capillary action, while maintaining the structural order.¹⁵ These materials span C–S arrays above 1 μm in diameter, and show excellent properties as cathodes in Li–S batteries. But to achieve ready uptake of metal ions, the accessibility of the channels must be maintained, and wettability of the sorbent in aqueous solution is required. Herein, we report the preparation of nanorod CMK-3/S (nano-CMK-3/S) that meets these challenges, and its application as a Pt sorbent in highly dilute solutions. The material is formed by a unique preparation method that coats the inner surface with a thin layer of sulfur that maintains the channel porosity, and accessibility of the sulfur sites.

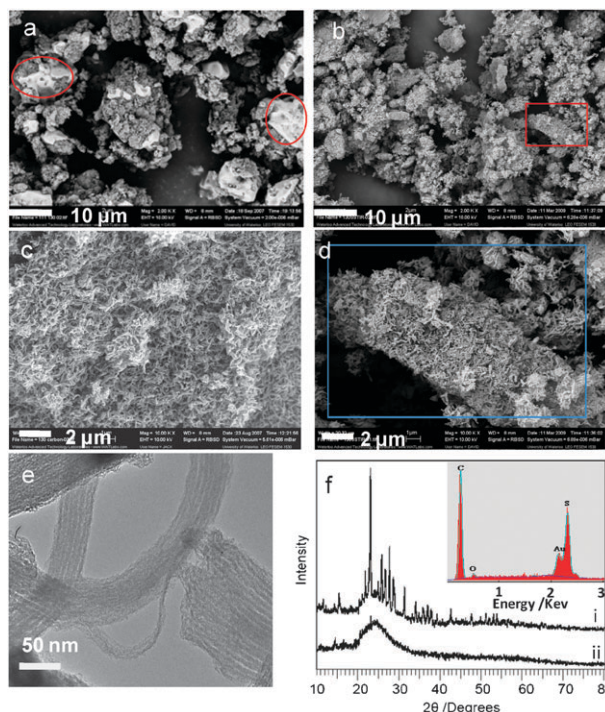


Fig. 1 SEM images of (a) nano-CMK-3/S prepared by melt-diffusion, (b) nano-CMK-3/S prepared by agitation–friction, (c) nano-CMK-3, (d) image expansion corresponding to the area outlined by the red square in (b), (e) TEM image of nano-CMK-3, (f) XRD patterns of (i) a simple mixture of nano-CMK-3 and sulfur, (ii) nano-CMK-3/S prepared by agitation–friction. Inset: corresponding EDX spectrum of inset area outlined by the blue square in (d).

CMK-3 nanorods were synthesized by the nanocasting method¹⁶ using nano-SBA-15 as a hard template, as we have previously reported.¹⁷ These carbon nanorods only span 6 to 10 mesoporous channels (Fig. 1c and e), and hence span an array of about 0.1 μm in diameter. To infiltrate sulfur into nano-CMK-3, the melt-diffusion method used for the bulk was first attempted.¹⁵ A mixture of CMK-3 nanorods (nano-CMK-3) and sulfur were ground together and heated to 155 $^{\circ}\text{C}$. As shown in Fig. 1a, the resultant C–S sample (C/S 1 : 1 in weight) does not display the same complete encapsulation of sulfur within the nano-CMK-3 channels that is exhibited by bulk CMK-3. We believe this results from the much weaker capillary force within these nanosized structures (nanoscaffolds), which is also evident in its N_2 adsorption and desorption isotherms (Fig. S1b, ESI†). Nano-CMK-3 does not exhibit the typical Type IV profiles of other mesoporous solids, and exhibits a very small hysteresis loop.

To accomplish sulfur impregnation, we developed an unusual method that relies on frictional forces, and the hydrophobic

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1 attraction of the components. Typically, a mixture of elemental
sulfur and mesoporous carbon (C/S 1 : 1 in weight) was
dispersed into de-ionized water, and vigorously stirred for 24 h.
The collision/friction with carbon forces sulfur into the carbon
nanoscaffolds. This approach is completely different from
5 any conventional impregnation which requires the molecular
mobility of guest phases (liquids^{18,19} or vapour^{20,21}).

The nano-CMK-3/S composite exhibits a strong sulfur signal
in its EDX spectrum (Fig. 1f inset), and a morphology (Fig. 1b
and d) identical to empty nano-CMK-3 (Fig. 1c). This is in sharp
contrast to the nanocomposite prepared by the melt-diffusion
method that shows bulk sulfur masses indicating incomplete
impregnation. The intense peaks in the XRD pattern (Fig. 1f i
and ii) assigned to sulfur in the nano-C-S mixture completely
15 vanish after the agitation–friction process. The C–S mixture also
exhibits a large decrease of its surface area from 543 to
137 m² g⁻¹, and decrease of the specific pore volume from
0.63 to 0.31 cm³ g⁻¹, respectively. Taken together, this
demonstrates that the nano-CMK-3 channels are infiltrated with
20 sulfur at a 50 wt% loading (as confirmed by TGA).

The mechanism takes place by a mechanical/chemical process,
which is schematically illustrated in Fig. S2.† Since sulfur is a soft
material bound together by weak van der Waals forces, with a
hardness of only ~2 (on the Mohs scale),²² the S₈ molecules can
25 be easily dislodged from the bulk by friction provided by the
hard carbon nanoscaffolds. Upon vigorous stirring in aqueous
solution, the soft sulfur particles and carbon nanorods are
provided with high kinetic collisional energy. Thus the sulfur
mass is forced in between the gaps in parallel carbon nanofibers
30 on the sides of the carbon nanoscaffolds, as schematically shown
in Fig. S2b.† The sulfur masses formed between the carbon
nanofibers are presumably pushed deeper into the interior
structure by the force of the incoming sulfur. The process ceases
when all of the sulfur is incorporated into the carbon nanoscaf-
35 folds as schematically shown in Fig. S2c (ESI†) and as experi-
mentally observed in Fig. 1b and d.

The solid–solid “wetting” or adhesion is due to the hydro-
phobicity of both sulfur and carbon, a prerequisite. This can be
understood by the fact that in an aqueous medium, the interfacial
tension γ_{cw} at carbon–water and γ_{sw} at sulfur–water is larger than
40 γ_c and γ_s (in air), respectively. Thus the surface energy of the
system will decrease if both carbon and sulfur reduce their
contact area with water, which favours infiltration.²³ This
is provided by frictional force. However, sulfur cannot be
45 incorporated into *siliceous* SBA-15 nanorods of exactly the same
dimensions. From a kinetic point of view, the energy imparted to
the system must be sufficient to overcome the cohesive energy of
molecular sulfur, which is the activation energy (E_a).

We also attempted to infiltrate bulk CMK-3 with sulfur (to a
target of C/S 1 : 1 in weight) using the agitation–friction
approach. The SEM image and corresponding sulfur EDX
map (Fig. 2a and b) show that infiltration took place although
the depth of sulfur penetration cannot be determined from a 2D
50 map. This is also suggested by the SEM image of the particle
surface (Fig. 2c) that shows the expected surface ordering of the
sulfur and carbon rods, indicating that the infiltrated sulfur is
pushed into the mesoporous structure rather than lying on the
surface. The imbibition in bulk CMK-3 is incomplete, however,
55 as shown by the presence of large sulfur masses in the SEM

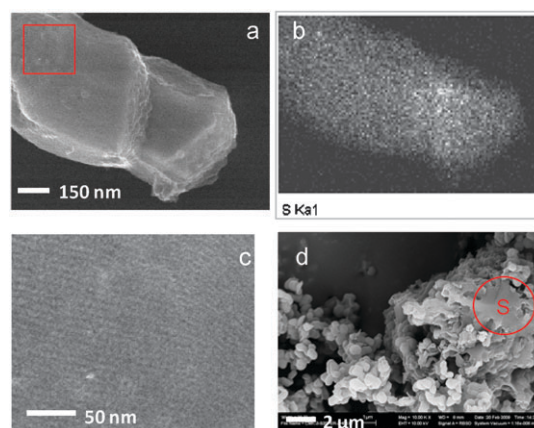


Fig. 2 SEM images and sulfur map of bulk CMK-3/S composite prepared by agitation–friction (a) high resolution image, (b) corresponding EDX sulfur map to (a), (c) enlarged image corresponding to the area outlined by the red square in (a), (d) low resolution image.

(Fig. 2d). Note that nano-CMK-3 (diameter 80 nm and pore volume 1.1 cc g⁻¹) has 43.9% of its pore volume within a depth of 10 nm, which is enough to accommodate an equivalent mass of sulfur (assuming infiltrated sulfur has a density of 2.07 g cc⁻¹). However, bulk CMK-3 (1 μm in diameter and pore volume 2.06 cc g⁻¹) has only 4% of its pore volume within a depth of 10 nm. To accommodate an equivalent sulfur/carbon ratio, the initial moving front has to be forced 62 nm into the bulk which leads to a higher activation energy (due to channel blockage) and less favourable kinetics, comparing to the nano-version.

For practical studies of noble metal absorption, composites comprising 10 wt% sulfur were prepared as above by the agitation–friction process. The nano-CMK-3/S composite (C/S 9 : 1 in weight) was briefly heated at 155 °C to ensure an even distribution layer of the infiltrated sulfur over the inner surface area of the nanorods. BET data (ESI†) revealed a slightly reduced pore volume for the sulfur-impregnated CMK-3 compared to bare CMK-3 itself (from 1.1 → 0.92 cm³ g⁻¹), and a shift in the pore size distribution maximum, from 3.5 nm to 3.0 nm. After treatment at 155 °C, a sharp maximum was apparent at 2.8 nm, with a broad component remaining at 3.5 nm. This is consistent with the formation of a thin sulfur layer on the carbon surface. Bulk CMK-3/S composite as a sorbent was also prepared by the melt-diffusion method for comparison.

Fig. 3 shows the platinum sorption kinetics of nano-CMK-3/S (S: 10% wt) and bulk CMK-3/S (S: 10% wt) at pH 4.0. Rapid uptake took place after the dispersion of both sorbents, particularly for the nanomaterial. Within the first minute of contact, 70% of the Pt was adsorbed in nano-CMK-3/S, and 99% within the first 10 min. This is more rapid compared to bulk CMK-3/S (94.4% in the first 10 min, and 99% after one hour).

In these tests, sorbents (10 mg, 100 mg L⁻¹) were dispersed in dilute solutions of H₂PtCl₆ (100 ml, Pt: 5 mg L⁻¹). After specific time intervals, portions of the mixture were filtered and the filtrate was analyzed. We observed that nano-CMK-3/S was initially much more readily dispersed in solution than its bulk counterpart. The external carbon surface of either material is decorated with hydroxyl or ketone functionalities from the sucrose based carbon precursor. However, nano-CMK-3/S exhibits much more external (carbon) surface area than its bulk

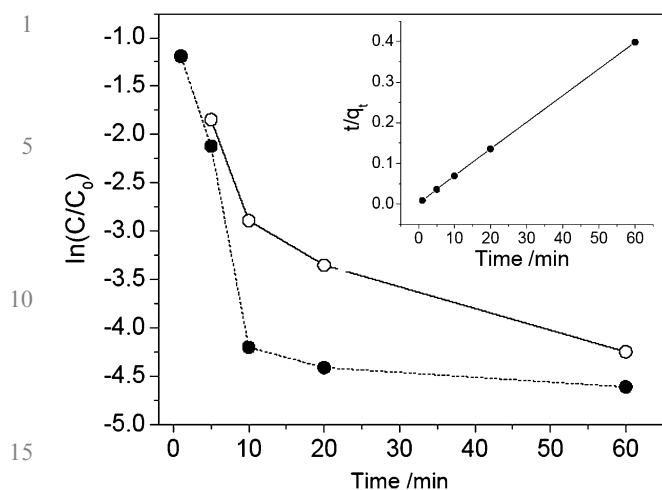


Fig. 3 Plots of $\ln(C/C_0)$ versus t , for Pt sorption kinetics, nano-CMK-3/S (solid black dots) and bulk CMK-3/S (hollow circles), inset: pseudo-second order model fit of Pt sorption on nano-CMK-3/S.

Table 1 Measurement conditions and parameters calculated from the pseudo-second-order model. Sorbent dosage: 10 mg L^{-1} ; stirring speed: 300 rpm , $C_0 = 5 \text{ mg L}^{-1}$; q is units of (mg metal/g) . k is the rate constant $(\text{g mg}^{-1} \text{ min}^{-1})$, and the value q_t (mg g^{-1}) is the amount of solute captured by a sorbent at any time t . The sorption capacity q_e and $q_{e,\text{exp}}$ (mg g^{-1}) are the theoretical and experimental amounts of solute absorbed at equilibrium, respectively

Sample	q_e	$k/\text{g mg}^{-1} \text{ min}^{-1}$	$q_{e,\text{exp}}$
CMK-3/S	149	8.2×10^{-3}	145
Nano-CMK-3/S	151	2.0×10^{-2}	154

counterpart and higher curvature, which renders it more wettable. This is a prominent advantage of nano-CMK-3/S.

Sorption controlled by chemical interactions typically fits a pseudo-2nd order kinetics model.^{24,25} A plot of t/q_t vs. t (Fig. 3 inset) confirms that sorption (for both bulk and nano-CMK-3/S) fits the pseudo-second-order kinetic model very well ($R^2 = 1.0$). The rate constant for nano-CMK-3/S calculated from the intercept is over two times that of its bulk counterpart, as shown in Table 1. The better wetting properties facilitate interaction of the material with the hydrated Pt^{4+} from aqueous solution, and absorption—a rate-limiting process—is enhanced.

More importantly, although a lower sorbent dosage (0.1 g L^{-1}) and a lower initial platinum concentration (5 mg L^{-1}) were employed, the rate constant exhibited by nano-CMK-3/S is three times higher than the widely used chitosan sorbents ($k = 7.4 \times 10^{-3}$) which also follow pseudo-second-order sorption kinetics.^{5b} Note that both the pseudo-first-order model and the intraparticle diffusion model²⁶ do not fit our sorption data as they fail to yield straight lines from their linearized model equations. Neither the nano or bulk system is diffusion limited.

This can be further quantified through the use of a mass-weighted partition coefficient (K_d), which represents the distribution of noble metal in the absorbent vs. the solution ($K_d = [(C_0 - C_f)/C_f] \times V/M$; C_0 and C_f represent the initial and final concentrations of solute, V is the volume of solution and M is the mass of sorbent). This measure of a sorbent material's affinity for the metal yields a K_d of 900 000 for nano-CMK-3/S. K_d values of 100 000 are considered excellent, and values as high as 200 000 have been reported for Hg

absorption on heteroaromatic-functionalized mesoporous carbon.¹⁴ However, Pt and Hg adsorption are not strictly comparable.

In summary, nano-CMK-3 rods were imbibed with solid sulfur by vigorously stirring an aqueous mixture at room temperature. The facile infiltration can be explained by a combination of chemical and mechanical schemes, and is an unusual example of a porous solid which can be infiltrated by another solid phase at room temperature. This synthetic strategy may be applied to prepare other nanostructured materials by using soft materials as the fillers. Owing to its high rate constant for metal uptake, nano-CMK-3/S shows excellent properties for recovery of a wide range of noble or toxic metals that have a strong affinity for sulfur (such as Pd, Ru, Au, Hg and Cd) from dilute effluents of PEFCs or other sources.

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