Supplementary Data for

Characteristics of electroless copper-deposited activated carbon fibers for antibacterial action and adsorption-desorption of volatile organic compounds

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S.1. Electroless copper deposition onto ACFs

For stable deposition of fine metal particles on the ACFs, we employed a pretreatment method, which was proposed by Ang et al. (1999) [1,2] and Xu et al. (2004) [3] for their studies of coating carbon nanotubes with metal. The nanotubes were activated in one bath (single-step process), while conventional activation processes consist of two-steps where two separate colloidal solutions are used. In our study, we applied a single-step process to catalytically activate the ACFs to introduce active sites on the ACFs’ surfaces for electroless copper deposition. After the ACFs’ surfaces were sensitized with Sn⁴⁺ ions (Sn⁴⁺ sensitization), the Sn⁴⁺ ions were oxidized to Sn⁶⁺ and the Pd²⁺ ions were simultaneously reduced into metallic Pd (Pd activation) which adhered to the ACFs’ surface in the form of fine Pd particles. After the Pd activation step, Cu²⁺ ions were introduced and then reduced into metallic Cu on the Pd particles formerly deposited on the ACFs. The metallic Pd sites worked effectively for depositing copper because of the galvanic displacement of the metallic Pd by Cu [4].

Since the bond strength of the copper particles was very sensitive to contaminants on the surface of the fibers, the ACFs were thoroughly degreased by immersing the ACFs into a diluted solution of degreasing agent (50mL of CC829, Yooil Material Technology, Korea, mixed with 950mL of DI water) at 327K for 10min. After the degreased ACFs were washed three times with DI water, the palladium and tin species were introduced onto the degreased ACFs by immersing the degreased ACFs in a mixed Pd-Sn colloidal solution (30mL of CATA1064, Yooil Material
Technology, Korea, diluted with 970mL of 1M nitric acid) at 318K for 6min. The catalytically activated ACFs were then immersed in an acceleration solution bath (50mL of ACCEL95, Yooil Material Technology, Korea, diluted with 950mL of DI water) for 7min at 298K and they were next washed with DI water three times. The acidic accelerator was used to preferentially dissolve the protective layer (mainly the Sn layer), to expose a greater surface area of the catalytic Pd nuclei. Copper was deposited at the catalytic sites when the catalytically activated and accelerated ACFs were immersed in an electroless deposition bath, resulting in ACFs with copper deposited particles. The deposition bath (1L) was made using a copper sulfate dominant solution (120mL of EC1051A, Yooil Material Technology, Korea, diluted with 380mL of DI water) and a formaldehyde dominant solution (110mL of EC1051B, Yooil Material Technology, Korea, diluted with 390mL of DI water) at 298K for various treatment times ranging from 0 to 30min.
S.2. Experimental setup for VOCs adsorption-desorption

![Experimental setup diagram]

Fig. S1. Schematic diagram of the experimental set-up.

ACFs have a larger micropore volume and a more uniform micropore size distribution than granular activated carbons (GACs), and thus, they are considered to have a larger adsorption capacity and greater rates of adsorption [5-10] than GACs. ACFs have recently been considered to be a promising adsorbent for controlling volatile organic compounds (VOCs). However, most of the studies conducted on the adsorption of VOCs by ACFs have pertained to equilibrium conditions, with the primary objective being the development of an appropriate isotherm. Only a few studies on the adsorption of VOCs by ACFs have been conducted for dynamic conditions [11].

The experimental setup shown in Fig. S1 consisted of BTX apparatus (Spectra Gases, model VOCs) and carrier gas supply section, test duct section, and VOCs detection section. The cylindrical test duct made of duralumin had a volume of 1,963cm$^3$ (5cm (D)×100cm (L)). The duct temperature was maintained at 296K ± 1K. The face velocity was 0.5m/sec, which belonged to a practical range
of 0.25-0.50m/sec [12]. SS sampling ports and Teflon tubings were used to connect the duct with the analytical instruments. Every prepared ACFs sample was initially dried under vacuum at 393K overnight and then it was fixed on a filter holder in the test duct. Two stainless steel (SS) meshes were used at both ends of each sample (50mm in diameter and 2mm in depth) to support the sample. Acquired from a compressed gas cylinder, the benzene, toluene, and xylene (BTX) gases with a mixing ratio of 0.47:0.45:0.09 were used as the reactant gas at a concentration of 981.6ppmv, using air as the balance gas according to National Institute of Standards and Technology (NIST) standards. Clean compressed air from a dry clean air supply system carried the BTX gas stream to the test duct. The flow rates of the BTX gas stream and the clean air stream were 0.1-100mL/min and 0.1-100L/min respectively, and they were controlled by two mass flow controllers (Tylan, US). BTX gas in air at room temperature was delivered to the test duct and then it was mixed with clean air resulting in a BTX concentration of 1ppmv at the inlet of the duct.
S.3. Stability of copper particles coated on ACFs

Before investigating the effect of copper deposition time on the adsorption and desorption of VOCs, the prepared samples’ resistance to air flow was checked by measuring the amount of copper aerosol particles detached from each sample by using an ultrafine condensation particle counter (UCPC, TSI 3025A). The sample was exposed to injected particle-free air at a face velocity of 0.5m/sec. Fig. S2 shows that the concentration of aerosol particles varied with time for all samples. The sample deposited with Cu-30 released the highest amount of particles; however, the concentration became negligible after 100sec. After the stability of copper particles deposited on the ACFs samples was checked, experiments on the adsorption and desorption of VOCs were conducted.

![Fig. S2. Particle detachment characteristics during air flow (@ 0.5m/s of air velocity).](image-url)
**S.4. Amounts and effective diffusivities of adsorbed and desorbed VOCs**

The amounts of adsorbed and desorbed VOCs by the ACFs samples were calculated by using the following equation:

\[
m (\text{mg of VOCs} / \text{g of ACFs}) = m_f \int_0^t f (C_i - C_e) Q dt
\]

where \( m \) is the ratio between the mass of the adsorbed VOCs (or the desorbed VOCs) and the mass of the pristine ACFs sample \( m_f \), \( t \) (min) is the VOCs adsorption time (or VOCs desorption time when the BTX gas supply is stopped), \( f \) is the unit conversion factor (ppm to mg/m\(^3\)), \( C_i \) is the influent VOCs concentration (ppmv), \( C_e \) is the effluent concentration (ppmv), and \( Q \) is the air flow rate (L/min).

The combined diffusivity inside the pores was defined as the harmonic average of Knudsen and molecular diffusivities \([11,13-15]\) and is given by

\[
\frac{1}{D} = \frac{1}{D_k} + \frac{1}{D_m}
\]

where, \( D_m \) is the molecular diffusivity. The Knudsen diffusivity is given by

\[
D_k = \frac{2 \times r_e \left( \frac{8RT}{\pi M} \right)^{\frac{1}{2}}} {3} = 97 \times R_{pore} \left( \frac{T}{M} \right)^{\frac{1}{2}}
\]

where, \( R_{pore} \) = pore radius in m, \( M \) = molecular weight in g/mol, \( T \) = temperature in K, \( D_k \) = Knudsen diffusivity in cm\(^2\)/sec.

Finally, the effective diffusivity inside the pores is determined by using the formula

\[
D_e = \frac{\alpha D}{\tau}
\]

where, \( \alpha \) = intrafiber void fraction, \( \tau \) = tortuosity factor.
Fig. S3. VOCs adsorption and desorption amounts of the pristine and the copper-deposited ACFs.
Fig. S4. Effective diffusivities of VOCs adsorption and desorption of the pristine and the copper-deposited ACFs.
Figs. S3 and S4 show the amounts and effective diffusivities of VOCs adsorption and desorption that were calculated by using equation (1) and equations (2)-(4), respectively. The amounts of Cu-00 after 400 min were 40 mg-BTX/g-ACFs and 35 mg-BTX/g-ACFs for adsorption and desorption tests, respectively. Moreover, the ranges of effective diffusivity for Cu-00 during 400 min were approximately $7.3-7.7 \times 10^{-5}$ cm$^2$/sec and $4.6-7.6 \times 10^{-5}$ cm$^2$/sec for adsorption and desorption tests, respectively. These amounts and effective diffusivities were higher than those of the other samples due to the higher specific surface area (or pore volume).
S.5. SEM results

(a) Cu-00

(b) Cu-Ac

(c) Cu-10

(d) Cu-20

(e) Cu-30

Fig. S5. SEM micrographs of the pristine, catalytically activated and the copper-deposited ACFs.
Fig. S5 (a-e) shows the FESEM micrographs of the prepared ACFs samples. Cu-10, Cu-20, and Cu-30 represent the copper-deposited ACFs at deposition times of 10, 20, and 30min, respectively, while Cu-00 and Cu-Ac represent the pristine ACFs and the catalytically activated ACFs, respectively. As the deposition time increased, there were more particles on the surface of the fiber and the particles grew larger. Particles having a “snowflake” shape or aggregates of 50nm-1µm are displayed in Fig. S5 (c)-(e).
S.6. EDX results

(a) Cu-00

(b) Cu-Ac

(c) Cu-10

(d) Cu-20

(e) Cu-30

Fig. S6. EDX profiles of the pristine, catalytically activated and the copper-deposited ACFs.
Chemical analysis was performed via energy dispersive X-ray spectroscopy (EDX, JED-2300, JEOL, Japan). The EDX results of Fig. S6 show that any sample contained carbon, copper, and a small amount of oxygen. The observed oxygen may have originated from the commercially purchased ACFs for this study. Fig. S6 shows that while Cu-00 had no copper peak, the copper-deposited ACFs samples had some peaks of CuKa, CuLa, etc., which indicated the presence of copper on the ACFs samples. Cu-Ac contained a minute amount of tin, which might have been originated from the Pd-Sn activation process. Even though palladium was not detected in the EDX results, from the ICP analyse, the concentration of palladium particles was found to be about 350ppm, which was below the EDX detection limit (refer to Main text).
S.7. BET results

To understand the effect of excessive amount of copper on VOCs adsorption and desorption, we measured the textural properties of the copper-deposited ACFs. Fig. S7 shows that the major uptake occurred at a relatively low pressure (P/P_o<0.1) and reached a plateau at P/P_o ≈ 0.3. The data implies that all of the ACFs samples had microporous characteristics (type I isotherm) according to the IUPAC classification [16]. The adsorption amount was the highest for Cu-00. However, it decreased as the amount of copper increased. Fig. S8 shows that the pore size distributions of all the samples were concentrated for pore diameters smaller than 30Å. The pores within porous materials are typically classified as either micropores (<20 Å), mesopores (20-500 Å), or macropores (>500 Å), in accordance with IUPAC classification [16]. Fig. S8 shows a fairly homogeneous microporous size distribution. The decrease of pore volumes with an increase in the amount of copper is due to copper particles obstructing the pore wall. Detailed results on the textural properties of the samples are summarized in Table S1. The total specific surface areas, micropore specific surface areas, average pore diameters, total volumes and micropore volumes decreased with increasing deposition time. The adsorption characteristics observed on the copper-deposited ACFs samples are indicative of reduced adsorption due to the possible loss of active sites for adsorption. Therefore, the amount of copper must be controlled for the determination of optimal VOCs adsorption. From these results, it was concluded that both the fluid-to-fiber mass transfer resistance and/or intraparticle (pore) resistance controlled the adsorption (or desorption) of VOCs.
on the ACFs, and all the dynamics were solely determined by the adsorption (or desorption) rates.

Fig. S7. Adsorption isotherms of N\textsubscript{2} at 77.4K of the pristine and the copper-deposited ACFs.
Fig. S8. Pore size distributions of the pristine and the copper-deposited ACFs.

Table S1 Textural properties of copper-deposited ACFs

<table>
<thead>
<tr>
<th>Sample</th>
<th>TSSA (m²/g)</th>
<th>MSSA (m²/g)</th>
<th>TPV (cm³/g)</th>
<th>MPV (cm³/g)</th>
<th>APD (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-00</td>
<td>1,598</td>
<td>1583</td>
<td>0.91</td>
<td>0.86</td>
<td>17.7</td>
</tr>
<tr>
<td>Cu-10</td>
<td>931</td>
<td>929</td>
<td>0.69</td>
<td>0.65</td>
<td>16.9</td>
</tr>
<tr>
<td>Cu-20</td>
<td>865</td>
<td>860</td>
<td>0.59</td>
<td>0.55</td>
<td>16.6</td>
</tr>
<tr>
<td>Cu-30</td>
<td>814</td>
<td>808</td>
<td>0.53</td>
<td>0.50</td>
<td>16.0</td>
</tr>
</tbody>
</table>

* TSSA: Total specific surface area
* MSSA: Micropore specific surface area
* TPV: Total pore volume
* MPV: Micropore volume
* APD: Average pore diameter
The nitrogen adsorption isotherms of an ACFs sample were measured using a porosimeter (ASAP 2010, Micromeritics Ins. Corp., US) at 77.4K in a relative pressure ranging from $10^{-6}$ to 1. High purity (99.9999%) nitrogen was used. All the samples were out-gassed at 573K for two hours before each measurement. The specific surface area was determined by a BET equation. The total pore volume, which was estimated on the basis of the N$_2$ volume adsorbed at a relative saturation pressure (~0.996), actually corresponded to the total amount of N$_2$ adsorbed. The pore size distribution was determined by the method of BJH (Barrett, Joyner, and Halenda), which uses the area of the pore walls, and it employs the Kelvin equation to determine the correlation between the relative pressure of N$_2$ in equilibrium and the porous solid with the size of the pores where the capillary condensation takes place.
References


