Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary information

Melamine adsorption on carbon materials: Impact of carbon texture and surface chemistry

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1. Melamine speciation in solution

Equilibrium constant values for the three main dissociation reactions were reported by Sal'nikov et al. [1] (Eqs. S1 to S3) were used to construct the speciation diagram shown in Fig. S1 with the HySS speciation software.[2] Both activity coefficient effects and the formation of dimers or even higher clusters were not included in the speciation calculation.[3] Based on these results, at pH >7, the predominant species in solution is the unprotonated M, while at pHs values between 2 and 6, the monoprotonated melamine ion (MH^+) is the main species.

$$MH^+ (aq) \Leftrightarrow M (aq) + H^+ (aq) \qquad K_{a1} = 10^{-5.11} \qquad (S1)$$

$$MH_2^{2+}\ (aq) \Leftrightarrow MH^{+}\ (aq) + H^{+}\ (aq) \quad K_{a2} = 10^{-1.79} \tag{S2}$$

$$MH_3^{3+}\ (aq) \Leftrightarrow M_2^{2+}\ (aq) + H^{+}\ (aq) \quad K_{a3} = 10^{-2.37} \tag{S3}$$

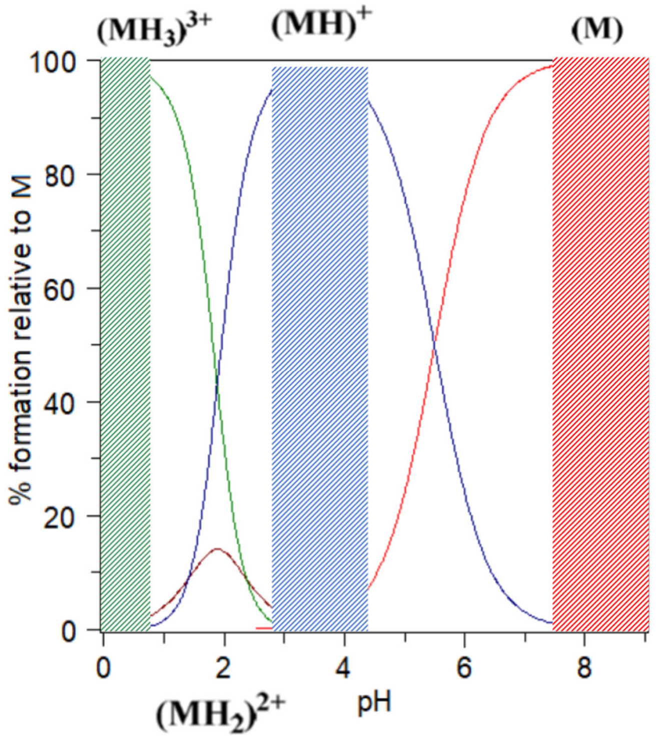


Figure S1: Speciation diagram of the melamine monomers. Diagram developed based on K values reported by Sal'nikov et al.[1]

2. Carbon Characterization (Supplementary Information)

2.1. Powder-X-ray diffraction (XRD)

Typical XRD for AC, MC, and VC are summarized in Fig. S2. Both AC and MC show a similar diffraction patterns, with broad peaks at 24° and 42° relating to the 002, and the 100 (and 101) planes of graphite, and characteristic of carbon materials.[4] A small, broad peak in the 75-95° range characteristic of the 110 plane of carbon materials is also present in the MC sample, while the two sharper peaks at 77° and 81° in AC and MC assigned to the aluminum sample holder. Similar bands are present in the case of VC, corresponding to the 002, 100 or 101 and 110 planes of graphite, but the peaks are better defined, indicating a more graphitic structure. The diffractogram for VC is also similar to other reported spectra.

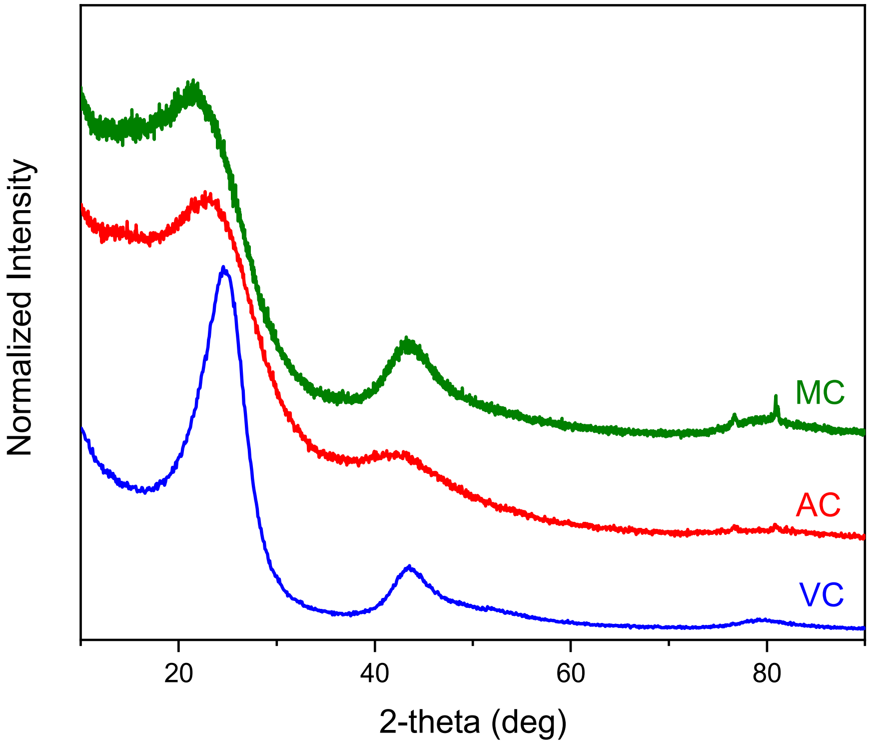


Figure S2: XRD for AC, MC, and VC

2.2. FTIR spectra analysis

The quality of the FTIR spectra made a rigorous analysis and comparison between materials impossible because of the high absorption of carbon in the IR region. As an example, Fig. S3 shows typical FTIR spectra for the two commercial carbon materials (AC and VC). Though determination of several common functional groups was possible, the extreme baseline correction required for this analysis precludes quantitative analysis.

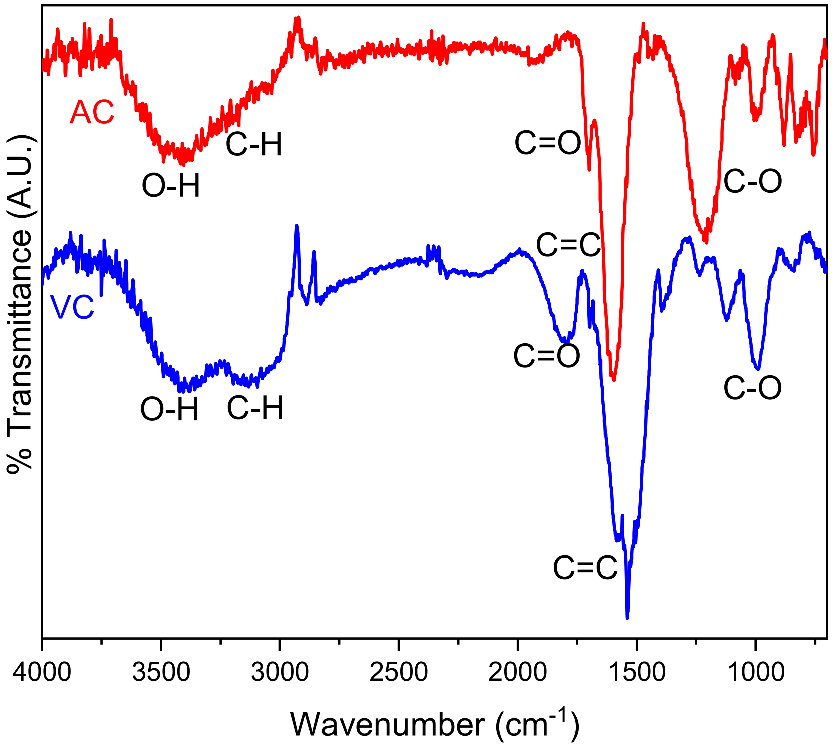


Figure S3: FTIR spectra of AC and VC, with select funtional groups labeled.

2.3. Surface Functional Groups Analysis

XPS

XPS was intended to get a more accurate description of the surface functional groups on the three carbon samples, taking advantage of the excellent agreement between studies on the assignment of the peaks in the C 1s and O 1s bands.[5] The oxygen content based on the XPS data for the three carbon samples were: 13 atom% for AC, 5 atom% for MC, and 2 atom% for VC. The identification of surface functional groups on carbon was achieved by analysis of the C 1s peak, because the oxygen in esters, carboxylic acids, and anhydrides have both single and double bonds, and these groups contribute to more than one signal in the deconvoluted O 1s spectra.[5]

Typical XPS spectra for the C1s binding energy region for AC, VC, and MC are summarized in Fig. S4.

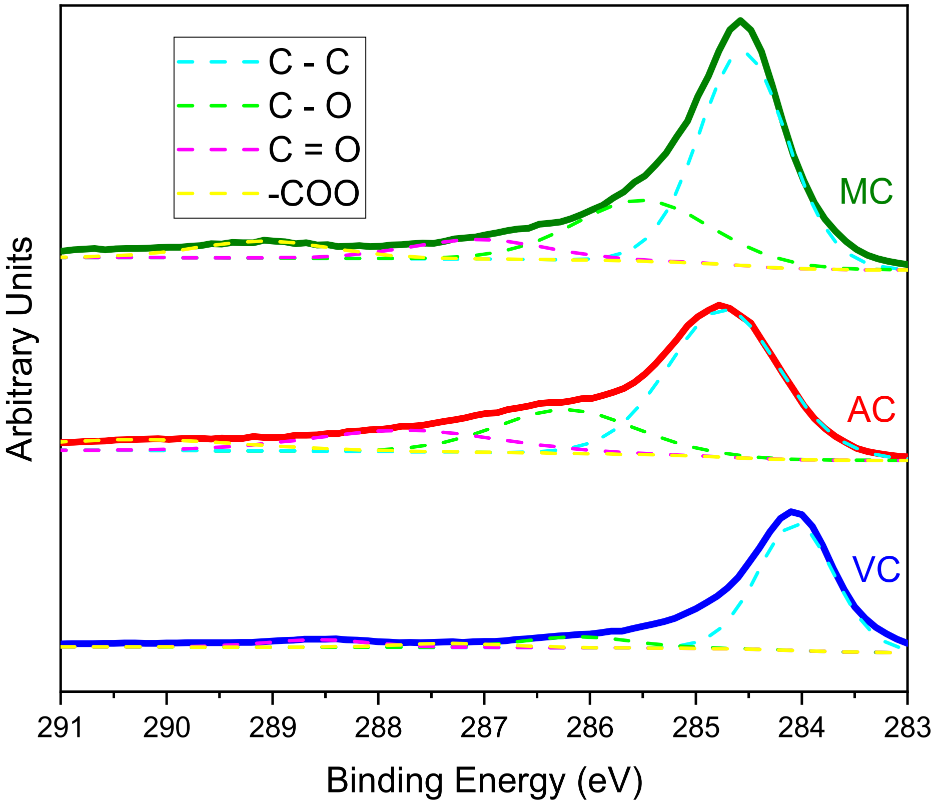
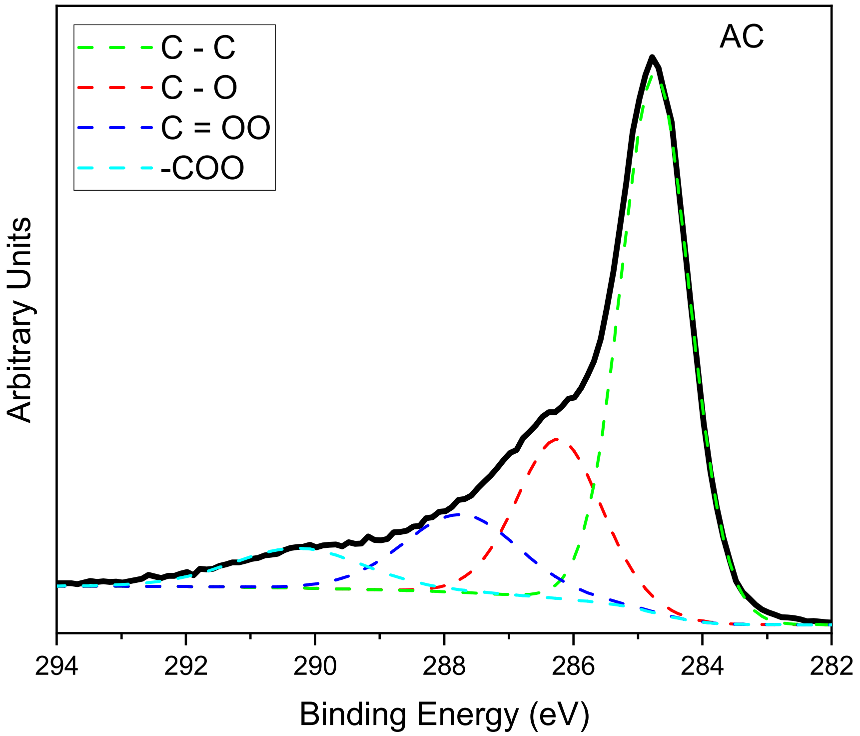
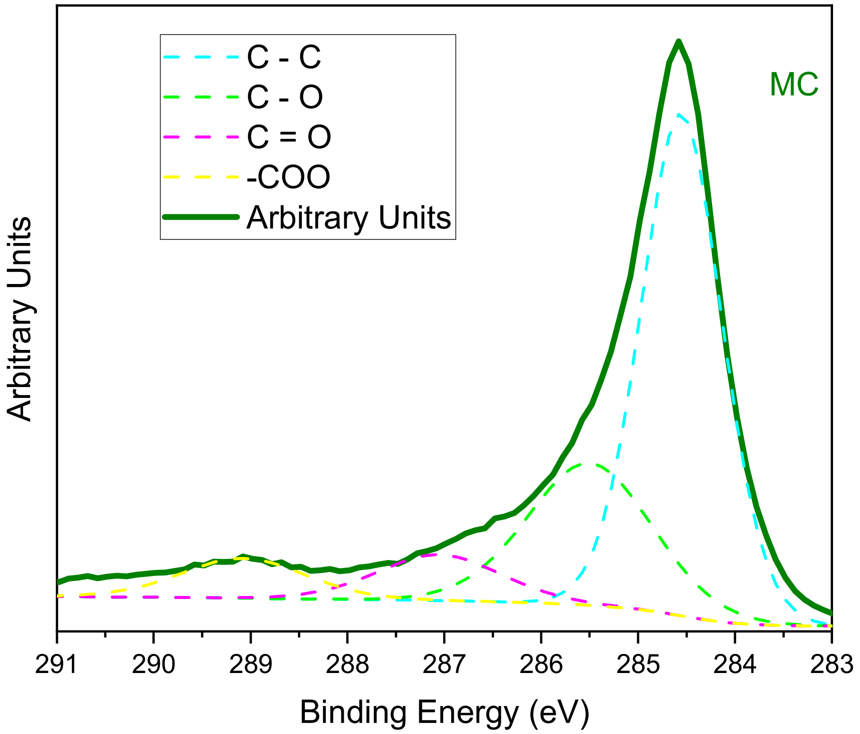


Figure S4: C1s XPS spectra and deconvolution for: AC, VC and MC (top to bottom).


C - C
C - O
C = OO
-COO
AC
Arbitrary Units
294
292
290
288
286
284
282
Binding Energy (eV)


C - C
C - O
C = O
-COO
Arbitrary Units
MC
Arbitrary Units
291
290
289
288
287
286
285
284
283
Binding Energy (eV)

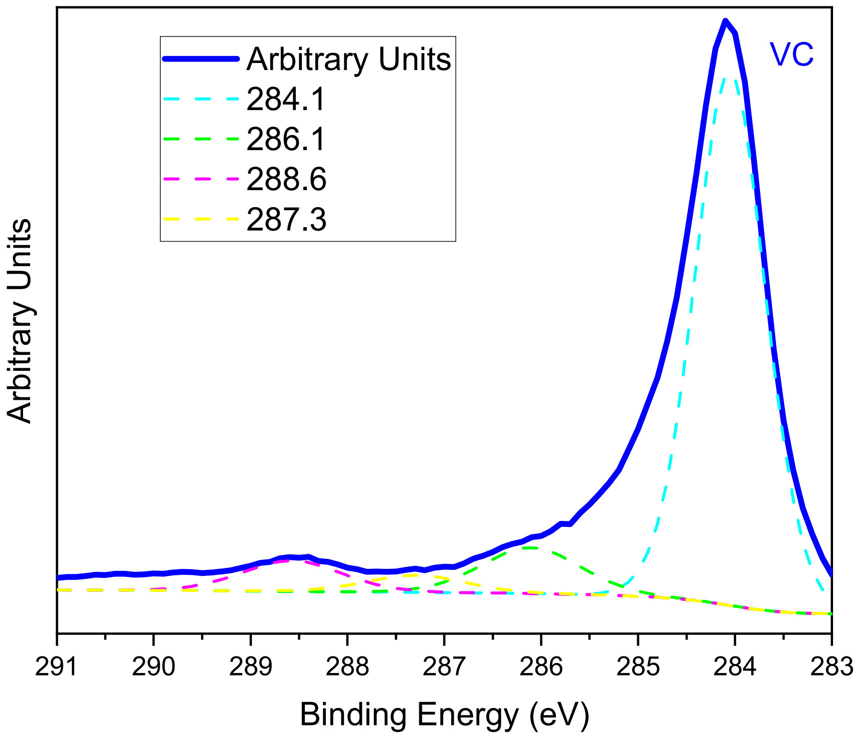


Figure S4: C1s XPS spectra and deconvolution for: AC, VC and MC (top to bottom).

The XPS binding energy obtained by deconvolution of the C 1s peak are summarized in Table S1 along with reference values from other carbon materials. For instance, for oxidized CNTs, Kundu et al.[5] reported the following bands for: carbon in graphite (284.5 eV), carbon singly bound to oxygen in phenols and ethers such as C-O (286.1 eV), carbon doubly bound to oxygen in ketones and quinones (C=O at 287.5 eV), and carbon bound to two oxygens in carboxyls, carboxylic anhydrides and esters (-COO at 288.7 eV). Similar values were found by Terzyk et al.[6] for activated carbons.

Table S1: XPS binding energy (BE) for oxygen functional groups on AC (C1s peak) and comparison with other studies

Functional Group	This work BE (eV)	Kundu et al.[5] BE (eV)	Terzyk et al.[6] BE (eV)
C	284.1 - 284.8	284.5	284.2 – 284.9
C-O	285.5 - 286.1	286.1	285.4 – 286.3
C=O	287.1 – 287.3	287.5	287.2 – 287.9
COO	288.6 - 290.3	288.7	288.7 – 290.8

Boehm Titration

For the titration, 1.5 g of carbon was left to equilibrate with 50 mL of each 0.05 M $NaHCO_3$, 0.05 M Na_2CO_3 and 0.05 M NaOH for 24 hours. These base solutions were standardized with KHP, and NaOH used to standardize 0.05 M HCl solution. After equilibration, the carbon was removed from solution by filtration, and the solution bubbled with inert gas (N_2 or Ar) for 2 hours to remove dissolved CO_2 before titration. An excess of HCl (30 mL for Na_2CO_3, 20 mL for $NaHCO_3$ and NaOH) was then added to 10 mL of each solution, and back titrated with standardized NaOH, using phenolphthalein indicator to determine endpoint, and with bubbling during titration to prevent the dissolution of CO_2. Titrations were performed in triplicate [23].

The functional groups present on the carbon surface were analyzed by Boehm titration using Eq. S4[7]

$$n_{FG\,B} = C_B \cdot V_B - \left(C_{HCl} \cdot V_{HCl} - C_{NaOH} \cdot V_{NaOH} \right) \tag{S4}$$

where $n_{FG\,B}$ represents the moles of functional groups determined with base B (NaOH, $NaHCO_3$ or Na_2CO_3), C_B the initial concentration of that base, V_B the volume of the aliquot of the base solution, C_{HCl} and V_{HCl} are the concentration and volume of the HCl solution, respectively, and C_{NaOH} and V_{NaOH} the concentration and volume of the NaOH titrant, respectively.

$NaHCO_3$ is used to quantify carboxylic groups on the carbon surface using Eq. S5.

$$n_{Carb} = n_{FG\ NaHCO3} \tag{S5}$$

while Na_2CO_3 reacts with both carboxyl and lactonic groups, making the difference between these results the concentration of lactonic groups (Eq. S6).

$$n_{Lac} = n_{FG\ Na2CO3} - n_{FG\ NaHCO3} \tag{S6}$$

NaOH reacts with carboxylic, lactonic and phenol surface functional groups, providing both the total concentration of functional groups (Eq.S7),

$$n_{FG\ Tot} = n_{FG\ NaOH} \tag{S7}$$

and the concentration of phenol groups when the Na_2CO_3 result is subtracted (Eq. S8).

$$n_{Phen} = n_{FG\ NaOH} - n_{FG\ Na2CO3} \tag{S8}$$

References

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