Mechano-chemical activation of biochar using N-doping

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Biochar
- Biochar is a novel carbon-rich material produced through the pyrolysis of biomass such as wood, shell, husks, or crop residues\cite{1}.
- Porous carbon materials are widely used as supercapacitor electrodes due to their high surface area, well-developed porosity, high conductivity, good physicochemical stability, and the presence of functionalities, such as oxygen and nitrogen complexes, which can introduce pseudocapacitance phenomena\cite{2}.
- The production of biochar is low cost and environmentally friendly. A two-step process is usually pursued for the preparation of the electrode materials of biochar supercapacitors\cite{3}:
  1. A carbonization of biomass into biochar (pyrolysis)
  2. A post-activation of the biochar

Simple mechanochemical N-doping of biochar
- Milling or crushing process does not only exfoliate the graphite into multi-layer graphene nanosheet, but also enables the N element to be doped onto the graphene.
- Graphene is a two-dimensional one-atom-thick carbon material composed of sp\textsuperscript{2}-hybridized carbon atoms\cite{4} exhibiting excellent electrical, mechanical and thermal properties which has been widely used in many fields, such as electronics, sensor, batteries, supercapacitors and many more.

Preparation of sample
- Biochar from wheat straw was prepared by using pyrolysis equipment at different temperatures which are 600°C, 800°C and 1000°C at university.
- There were two thermochemically pre-treatments of raw material that have been carried out before pyrolysis:
  1. With NaCl
  2. With H\textsubscript{2}O
- For doping experiment, both kind of biochar and urea were mixed at the weight ratio 1:20 and crushed using the mortar and pestle about 15 minutes for each sample and 1 sample was prepared by milling with small mill device for 15 minutes.
- The sample is labeled like following:
  M1 600 : was pre-treated with NaCl and pyrolysed at 600°C
  M2 800 + Urea : was pre-treated with deionised water, pyrolysed at 800°C and doped with nitrogen

Analysis Method
- Raman Spectroscopy
- Stereomicroscope
- Scanning electron microscope (SEM)

References
4. A.K. Geim, K.S. Novoselov, Nat. Mater. 6 (2007) 183-191

Result and discussions
- Raman Spectroscopy

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample with Doping</th>
<th>Sample without Doping</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Milled charcoal</td>
<td>Milled charcoal</td>
</tr>
<tr>
<td>2</td>
<td>Crushed charcoal</td>
<td>Crushed charcoal</td>
</tr>
<tr>
<td>3</td>
<td>M1 600 + Urea</td>
<td>M1 800</td>
</tr>
<tr>
<td>4</td>
<td>M2 800 + Urea</td>
<td>M2 800</td>
</tr>
<tr>
<td>5</td>
<td>M1 800 + Urea</td>
<td>M1 800</td>
</tr>
<tr>
<td>6</td>
<td>M2 800 + Urea</td>
<td>M2 800</td>
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<tr>
<td>7</td>
<td>M1 1000 + Urea</td>
<td>M1 1000</td>
</tr>
<tr>
<td>8</td>
<td>M2 1000 + Urea</td>
<td>M2 1000</td>
</tr>
</tbody>
</table>

- D band is caused by disordered structure of graphene. The presence of disorder in sp\textsuperscript{2}-hybridized carbon systems results in resonance Raman spectra. The value of D band is about 1340 cm\textsuperscript{-1}.
- The G-mode is at about 1597 cm\textsuperscript{-1}.
- G-band arises from the stretching of the C-C bond in graphitic materials, and is common to all sp\textsuperscript{2} carbon systems.
- A D’ band appears as the shoulder on the G bands around 1700 cm\textsuperscript{-1}.
- Both milling and crushing introduce significant reduction on the particle size.
- Generally, there is inhomogeneity of particle size.
- Wheat straw has relative strong honeycomb-like structure which is not easy to break.
- On picture no. 7 with 1000X magnification show some porosity.

Conclusions
- Biogenic carbon from wood charcoal is good material to produce graphene.
- Simple, clean, economical and scalable mechanochemical method.
- Small molecular urea, acting as both doping and assist-grinding agent.
  - low cost
  - water soluble
- Doping of nitrogen atoms to graphene is accounted for enhanced power performance of supercapacitor.
- Shows increase in surface area of particle.
- Shows porosity produced.

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