Mechano-chemical activation of biochar using N-doping

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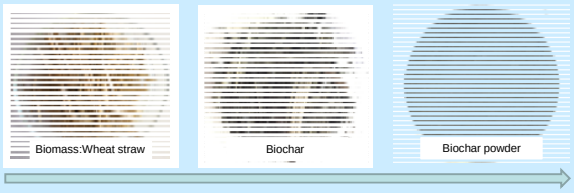
Biochar

➢ Biochar is a novel carbon-rich material produced through the pyrolysis of biomass such as wood, shell, husks, or crop residues[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[2].

➢ The production of biochar is low cost and environmental friendly.
A two-step process is usually pursued for the preparation of the electrode materials of biochar supercapacitor[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.

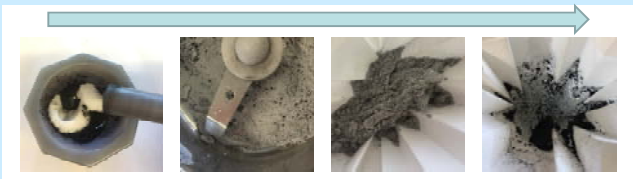
➢ Graphene is a two-dimensial one-atom-thick carbon material composed of sp^2 hybridized carbon atoms[4] exhibiting excellent electrical, mechanical and thermal properties which has been widely used in many fields, such as electronics, sensor, batteries, supercapacitors and many more.

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_2O
- 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 pretreated with NaCl and pyrolysed at 600°C

  M2 800 + Urea : was pretreated with deionised water, pyrolysed at 800°C and doped with nitrogen



Analysis Method

a) Raman Spectroscopy
b) Stereomicroscope
c) Scanning electron microscope (SEM)

References

1. Mdoe J, Mkayula L (2002) Preparation and characterization of activated carbons from rice husks and shells of palm fruits. Tanzan J Sci 28:131–142
2. Zhang, L.L.; Zhao, X.S. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* 2009, *38*, 2520–2531
3. Dobele G, Dizhbite T, Gil M, Volperts A, Centeno T (2012) Production of nanoporous carbons from wood processing wastes and their use in supercapacitors and CO2 capture. Biomass Bioenergy 46:145–154
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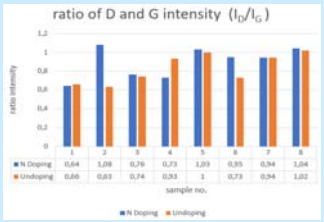
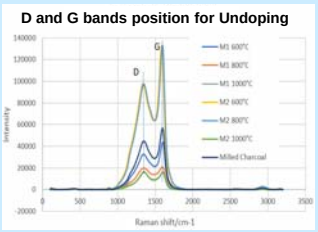
Result and discussions

❖ Raman Spectroscopy

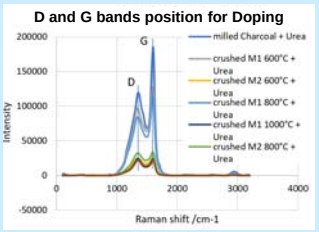
No	Sample with Doping	Sample without Doping
1	Milled charcoal + Urea	Milled charcoal
2	crushed charcoal + Urea	crushed charcoal
3	M1 600 + Urea	M1 600
4	M 1 800 + Urea	M 1 800
5	M 1 1000 + Urea	M 1 1000
6	M 2 600 + Urea	M 2 600
7	M 2 800 + Urea	M 2 800
8	M 2 1000 + Urea	M 2 1000



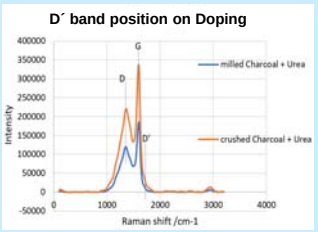
- Intensity ratio of D band to G band in sample no.2 with doping is very high compared to without doping.
- It indicates significantly increased defects and might be due to crushing induced grain size reduction and heteroatom doping.
- Intensity ratio is generally increased by doping.



- D band is caused by disordered structure of graphene. The presence of disorder in sp2-hybridized carbon systems results in resonance Raman spectra . The value of D band is about 1340 cm^{-1}.
- The G-mode is at about 1597 cm^{-1}.
- G-band arises from the stretching of the C-C bond in graphitic materials, and is common to all sp2 carbon systems.

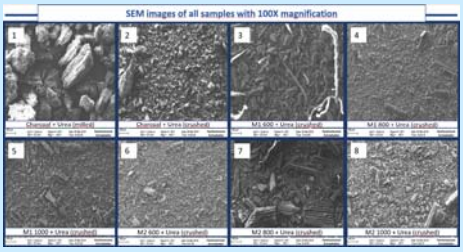


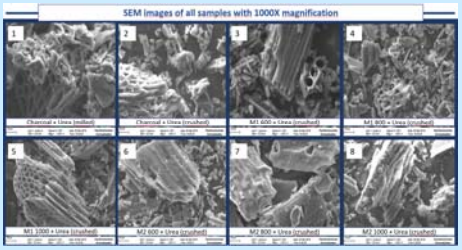
- All of samples are crushed with mortar and pestle.
- D band is 1343 cm^{-1}.
- G band is 1597 cm^{-1}.
- Clearly shows higher D and G bands intensity.



- a D` band appears as the shoulder on the G bands around 1700 cm^{-1}.
- Usually is the characteristic of few layered graphene.
- Also related to disorder due to defects introduced by defects or heteroatoms,which further could confirm the doping of N element.

❖ SEM





- Both milling and crushing introduce significant reduction on the particle size.
- Generally, there is inhomogenity of particle size.
- Wheat straw has relative strong honeycomb-like structure which is not easy to break.
- On picture no. 7with 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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