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CHARACTERIZATION OF GRAPHENE LAYERS OBTAINED FROM RICE HUSK

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Abstract

Graphene layer were obtained from a four-step approach starting from rice husk. The chemical-physical characterization of the samples indicates the presence of a mixture of graphene layers and amorphous carbon. A higher amount of activation agent (1:5) seems to increase the relative amount of graphene component while the number of layers resulted unaffected. A further treatment with H₂O₂ (performed on the AC(1/4) sample) seems to unaffected the graphene content and their overall quality.

Introduction

Graphene is a single-atom thick sheet of sp² hybridized carbon atoms arranged in a honeycomb lattice structure with outstanding properties. It has been used for multifunctional applications, from energy, environment to health [1]. Graphene can be synthesized by numerous chemical or mechanical techniques [2], but new methods to produce graphene via unconventional and inexpensive precursors are also emerging. Bottom-up and top-down strategies for the production of graphene from organic molecules, carbon black and coal have been recently proposed. Renewable and sustainable resources as biomasses are also sensible entrants for graphene precursor [2]. In this framework the first attempts to produce graphene related materials from rice husk (RH) have been recently proposed by [3,4]. The RH husk is the outer covering of rice kernels and it represents one of the most widely available agricultural wastes in many rice producing countries. Utilization of RH directly for manufacturing and synthesizing value-added materials is a feasible strategy to mitigate the disposal problem and reduce the cost of waste treatment [5,6]. In this work, graphene layers are synthesized from RH through a top-down approach and their morphological and chemico-physical properties have been evaluated.

Experimental section

Synthesis. The carbonaceous materials containing graphene layers were obtained from rice husk (RH) through a top-down approach following a four-step strategy: pre-carbonization, desilication, activation and exfoliation. Firstly, the RH was washed several times with distilled water to remove impurities, and then dried at 383 K for 1 hour. After that the RH was pre-carbonized for 45 minutes in a rotating reactor under argon atmosphere at a temperature between 523-573 K at 5 cm³/min gas flow rate. The resulting pre-carbonized material (CRH) was desilicated by treating 60 g of CRH with 3 liters of 1M NaOH solution at 353 K for 3 hours. The suspension was decanted to

remove the surfactant containing sodium silicate and washed up to a neutral pH, and dried in oven (2 h, 383K). The desilicated sample was mixed with crushed KOH by using two carbon to KOH ratios (1:4, 1:5). The mixtures were compacted in an iron crucible and annealed at 1123 K for 2 h in Ar atmosphere. After the activation treatment, the resulting samples, labeled as AC(1/4) and AC(1/5), respectively, were washed with distilled water to neutrality and dried at 373 K for 24 h. On AC(1/4) also an exfoliation process to remove amorphous carbon was carried out by treating the material with a hydrogen peroxide solution (H_2O_2 , 37% v/v) for 48 h after that it was washed and dried. The yield of the product was ~ 3% by weight.

Methods. Scanning electron microscopy was performed on powdered samples Au, Pd coated by using a field emission SEM (Nova NanoSem 450 FEI/Termofisher), at 3.00 kV in high vacuum mode, using an Everhart Thornley Detector (ETD) and Through the Lens Detector (TLD) for details micrographs and elemental microanalysis (EDX) at 15.00 kV. The carbon, hydrogen and nitrogen contents of the samples were measured 628 LECO elemental analyzer according to the ASTM E870 procedure. Infrared spectroscopy (FTIR) analysis of the materials was performed on solid sample dispersions prepared by mixing and grinding the powdered materials (0.5-0.8 wt.%) with KBr. Pellets were obtained upon compression at 10 Ton for 10 minutes. FTIR spectra in the $3400 - 400 \text{ cm}^{-1}$ range were acquired in transmittance mode using a Nicolet 5700 spectrophotometer. The conductivity of the pellets was measured in a four-contact geometry (low currents recorded through a Keithley picoammeter model 6485). The Raman spectroscopy was performed on a confocal Raman microscope (Jasco, NRS- 3100). The 514 nm line of a water cooled Ar⁺ laser, 4 mW at the sample, was injected into an integrated Olympus microscope and focused to a spot diameter of approximately 2 μm by a 100 \times objective. A holographic notch filter was used to reject the excitation laser line. Raman scattering was collected by a Peltier-cooled 1024 \times 128 pixel CCD photon detector (Andor DU401BVI). Raman measurements were at least triplicated for scope of reproducibility. Cyclohexane was used for calibration.

Results and Discussion

The carbonization at 1123 K coupled with chemical activation induces, as expected, the increase of carbon content (from ~55 wt.% of CRH up to ~75 wt.% in AC(1/4)) and a reduction of hydrogen content (Figure 1a). This feature was highlighted also by infrared spectroscopy (Figure 1b). CRH infrared spectrum is characterized by different signals ascribable to various functional groups: around 3000 cm^{-1} , the low-intense bands are due to the stretching vibrations of aliphatic and aromatic C-H bonds while in the medium-frequency range (1700 and 1000 cm^{-1}) a broad combination of peaks generated by the overlapping of carbon skeleton adsorption bands (C=O, C=C, C-C, C-H- C-O stretching and bending modes) was found [7]. AC(1/4) and AC(1/5) spectra are characterized by the typical broad shape of large condensed aromatic carbon networks. Only the peak due to C=C stretching modes and the overlapped peaks between 900 and 1500 cm^{-1} due to skeleton vibrations are detected. The dc conductivities (\square) of the solid sample dispersions prepared for FTIR measurements (0.5-0.8 wt.% in KBr) were: $\square\text{CRH} = 14 \pm 3 \text{ nS/m}$, $\square\text{AC}(1/4) = 80 \pm 10 \text{ nS/m}$ and

\square AC(1/5) = 60 ± 10 nS/m. The dc conductivity trend confirms that the a more extended conductive moiety in the AC samples was established.

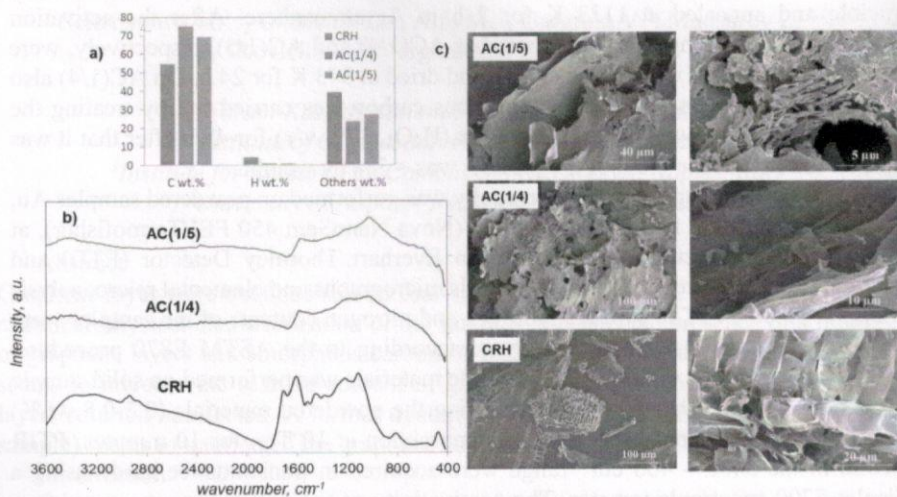


Figure 1. Elemental analysis (a), FTIR (b) and SEM imaging (c) of CRH, AC(1/4) and AC(1/5) samples

SEM images of CRH, AC(1/4) and AC(1/5) are reported in Figures 1c at different magnifications. The CRH is a highly porous material with a large internal surface area although any significantly changes in its morphology, compared to the raw rice husk (data not shown) are detected. The AC(1/4) and AC(1/5) exhibit a layered structure with a crumpled-silk-veil-wave fashion and folded regions. Overall, after activation the samples morphology appears more defined and ordered (Fig. 1c, right): the annealed graphene sheets stack into a layer-by-layer structure throughout the transverse section, extending continuously along the longitudinal direction. However, microvoids are generated between graphene sheets during thermal annealing, resulting in a higher porosity.

CRH exhibits Raman features related to only amorphous carbon (D and G bands) no trace of G' band, namely a band (also called 2D) around 2700 cm^{-1} typical of non-amorphous sp^2 carbon structures (data not shown). Raman spectra of AC(1/5) and AC(1/4) in Figure 2 clearly indicate a mixture of amorphous and graphene components. A significant spatial heterogeneity is detected, but two major components can be isolated: amorphous carbon (with D and G bands around 1352 and 1594 cm^{-1}) and graphene (with detectable D, G and G' bands).

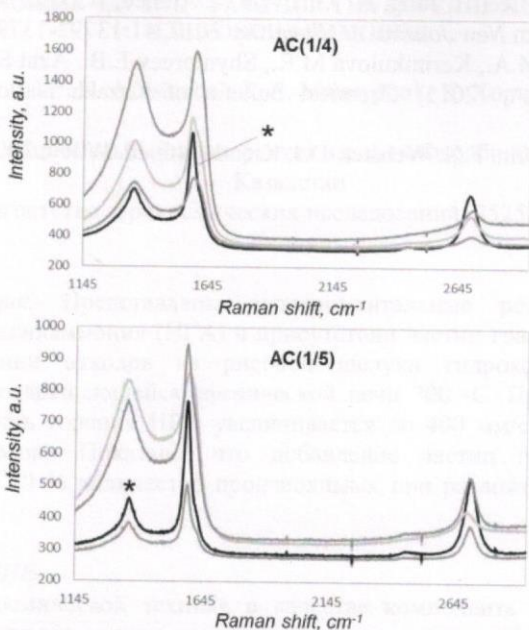


Figure 2. Raman spectra of AC(1/4) and AC(1/5) samples.

We analyzed the ratio $I_G/I_{G'}$ only for those spots where amorphous C was considered negligible (marked with * in Fig. 2). For both samples AC(1/5) and AC(1/4), the ratio $I_G/I_{G'}$ is close to 1.56 ± 0.10 , suggesting a multilayered structure. By comparing sample AC(1/5) and AC(1/4) in the limited sampling we have performed, it can be assessed that the activation ratio 1:5 provides a higher graphene content than 1:4.

Conclusions

The carbonization/activation treatment of RH leads to the formation of a mixture of graphene layers and amorphous carbon. The higher amount of activation agent (1:5) seems to increase the relative amount of graphene component while the number of layers resulted unaffected. The treatment with H_2O_2 (performed on the AC(1/4) sample) seems to be unaffected the graphene content and their overall quality.

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