1634
doi:10.1017/S1431927618008656

Microsc. Microanal. 24 (Suppl 1), 2018

An Eco Friendly Mechanochemical Alternative Route for Exfoliated Graphite preparation

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Exfoliated graphites (EG) are interesting materials for a variety of functional applications. Few decades ago, they attracted attention as promising sorbents for liquids such as heavy oils [1]. The chemical exfoliation of graphite, involves an oxidation process using strong acids and others oxidants. This process has received wide attention because of its scalability and low production cost [2]. Unfortunately, after the reaction, the byproducts and washing solutions contain harmful concentrations of acids and others oxidizing agents that are a threat to the environment [3].

The present study deals with an eco friendly route based on a solid phase exfoliation of natural graphite using a mechanochemical procedure based on high-energy ball milling while avoiding the use of the above mentioned chemicals. As raw material we use natural graphite (Gr) flakes and sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$), citric acid and vinegar were used as exfoliating reagents. Pure Gr, Na_2CO_3-Gr and $CaCO_3$-Gr equimolar mixtures were milled in a SPEX ball-mill for 8 hours. Then the milled powders were subjected to a lixiviation process refluxing them on an aqueous solution of citric acid (8% by wt.) or vinegar (8% by vol.). The suspensions were filtered, washed and dried at 80°C for 4 hours. The remaining byproducts are composed of an aqueous solution of citric acid, vinegar, sodium citrate and calcium acetate. All the above compounds are eco friendly with no toxicity; in fact, they are commonly used in the food industry as food additives. Thus, the environmental concerns related with their correct disposal can be considered as null.

The micrographs of the Fig 1 show the general morphology of the EG particles. We can notice that the original graphite structure is strongly modified because of the impacts of the highly energized balls during the milling process. This is an important signal of defoliation mainly related with a comminution and layers sliding effects.

The Fig. 2 shows the adsorption–desorption isotherm curves of four types of graphite samples. The noticeable increase in surface area (SA) is a result of the milling and the addition of the exfoliating agent. In the summary table, it is evident that the SA of raw material is increased by milling from 4 to 68 units. But using the described mechanochemical process the SA is increased to 190 and 300 m^2/g, on top of the important advantage of the elimination of dangerous chemicals manipulation.

References

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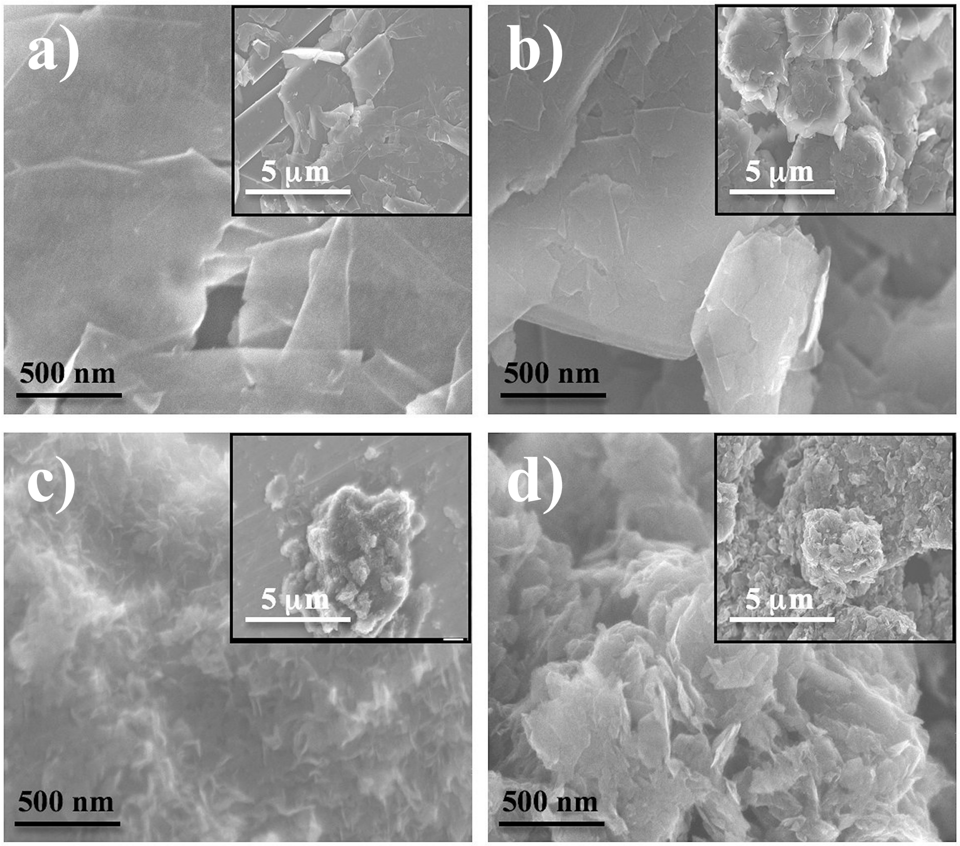
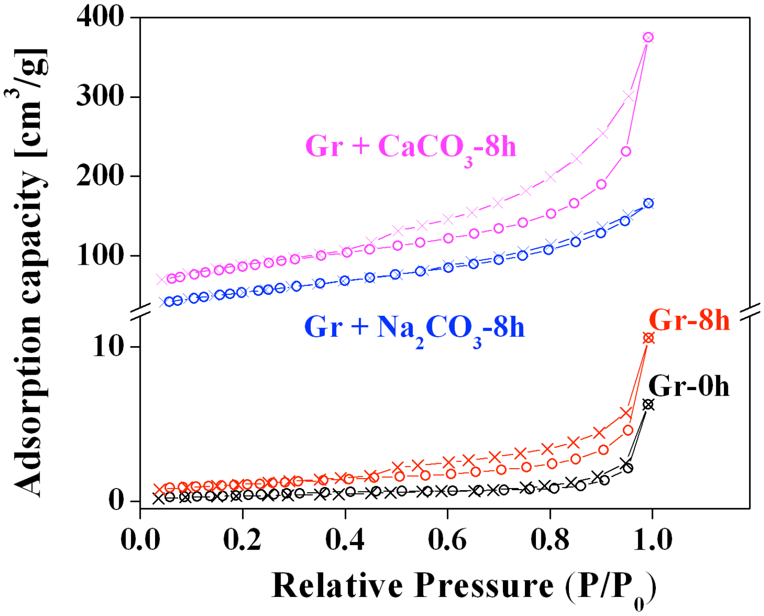


Figure 1. SEM micrographs of: (a) raw material (b) pure milled material, (c) milled graphite + Na_2CO_3 and (d) milled graphite + $CaCO_3$.



Sample	Milling Time (hours)	SA (m^2g^{-1})
Pure Gr	0	3.8
	8	67.6
Gr + Na_2CO_3		190.4
Gr + $CaCO_3$		300.2

Figure 2. Adsorption-desorption isotherms of samples and summary chart with their surface area values.

https://doi.org/10.1017/S1431927618008656