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Nanotechnologies for the sustainable valorization of biowastes

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This contribution aims to highlight the role of nanotechnologies for the design of high-performance nanomaterials and nanodevices using biowastes as feedstocks. Some recent advances for environmental and energy-related applications will be discussed from residual biomass of both vegetable and animal origin.

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The vision of circular economy is literally bursting worldwide, and it is imposing a radical change of mindset transversal to all production chains from large processing companies to medium/small manufacturers and distributors of goods and services but even more generally to all segments of modern society including media, communications, culture, education, politics, and so on. Indeed, the lifestyle of billions of consumers is rapidly reshaping aimed to support a more sustainable growth through an informed choice on everyday needs such as food, clothes, cleaning products, electronics, travels, types of commute, energy supply, and so on.

The management of wastes, particularly those of biodegradable origin (biowastes, BWs) certainly play a crucial role in the sustainability scenario. This issue is becoming more and more stringent at the current rate of growth of world population, with estimates and perspective on wastes reporting increasingly distressing numbers, for example, a cumulative quantity of 250 million tons of mismanaged plastic waste entering the marine environment by 2025 [1], a footprint of 0.74 kg/person/day from the release of household waste in the major world cities [2], a global generation of 20 million ton/y of discards from fish processing [3,4]. Moreover, contrary to common belief, it is also emerging that waste generation is rather independent from social factors including education, occupation, income of the family, number of family members, and so on of different socioeconomic groups populating urban areas [5], thereby suggesting that the circular economy model will be all the more effective if the differentiation and recycle of wastes will be practiced by every individual, regardless of his/her position. BWs, in particular, are an extraordinary source of chemical richness whose valorization is not only feasible and crucial to preserve life on our planet but also drives to create business, new technologies, livelihoods, and jobs.

The present article aims to discuss recent model cases highlighting applications of nanotechnologies to promote the upgrading of BWs into high-added-value nanomaterials. The concept of sustainable nanotechnologies will be here referred to the development of areas pertinent to green and blue growth, that is, the harvesting of nanostructures and nanodevices from renewable feedstocks [6,7].

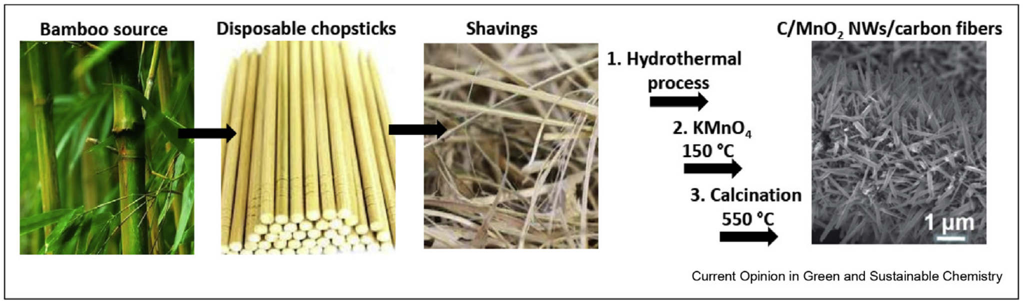
Nanocarbons, hybrids, and nanocomposites are excellent materials for their versatility and potential use in the fabrication of a variety of devices, from sensors in medicine to supercapacitor electrodes for electrocatalysis and energy storing, bioelectronic platforms, enhanced supports for precious metal–based catalysts, and so on [8–10]. Thanks to their high C-content, biodegradable wastes are an increasingly popular source for the preparation of such nanosized architectures [11].

A smart strategy to improve the performance of Li-ion batteries was proposed starting from disposable bamboo chopsticks which represent abundant wastes amounting to millions of cubic meters of timber from bamboo trees every year [12]. A hydrothermal treatment (delignification@150 °C) in an alkaline solution (KOH 3M) was first carried out to convert recycled chopsticks into cotton-like cellulose fibers. These were then mixed with aqueous $KMnO_4$ (0.04 M) and heated (150 °C). After cooling and water evaporation, the solid residue was calcined at 550 °C to afford a three-dimensional functionalized core–shell hybrid material comprised of α-type MnO_2 nanowires immobilized on a robust shell (3–5 µm) of a carbon fiber and intimately coated with a uniform carbon layer of few nanometer thickness (Figure 1, C/MnO_2 NWs/carbon fibers) [13].

Notably, the hybrid material proved to be an excellent anode for Li-ion batteries with a reversible capacity as high as 710 mA h g^{-1} effectively maintained without decay for up to 300 cycles.

Although under a microscope for its devastating consequence on tropical forests, the production of palm oil is still growing at an impressive rate with current amounts

Figure 1



Procedure for the preparation of a C/MnO_2 NWs/carbon fiber hybrid material from disposable chopsticks. Right: scanning electron microscopy (SEM) image of the hybrid solid, adapted from the study by Jiang et al [13].

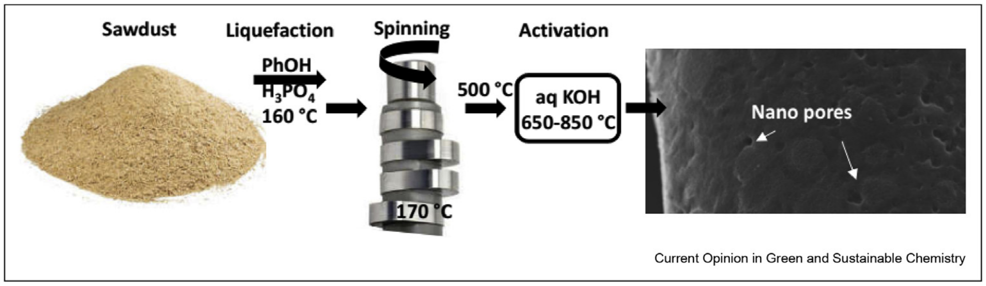
of ca 60 Mtonnes/y and estimates of 240 Mtonnes/y by 2050 [14]. This industry cogenerates biomass wastes including fruit fibers, palm shells, mill effluents, trunks, and fronds in amounts exceeding 9 times than those of produced oil, meaning for major manufactures as Malaysia and Indonesia, a total of ca 280 Mtonnes/y [15,16]. An interesting approach to valorize such residues was designed starting from oil palm leaves whose pyrolytic treatment in a tube furnace at 700°C under nitrogen afforded porous carbon nanoparticles with average size of 20–40 nm compatible for electrochemical applications to facilitate ion diffusion [17]. Indeed, these (nano)materials proved suitable precursors for superior supercapacitor electrodes as they showed a specific capacitance value of 368 F/g at 0.06 A/g in 5 M KOH, high stability (96% over 1700 cycles), and energy density of 13 Wh/kg.

With a global production of groundnut totaling 38.6 million tons and a cultivation worldwide covering about 22.2 million hectares, groundnut shells accounting for approximately 20% of the dried peanut pod by weight represent another inexpensive and largely abundant BW [18–20]. Controlled pyrolysis at 550–950 °C under inert atmosphere was the technique used also for the treatment of this residue to fabricate nanocarbons comprising spherical shaped particles with a diameter of 40–70 nm [21]. This material proved photoluminescent active in the visible region at 532, 628, and 652 nm and exhibited antibacterial activity against gram-positive and gram-negative pathogens such as *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia Coli*, *Chromobacterium violaceum*.

In the effort of designing sustainable protocols for the preparation of high-performance materials, the use of sawdust as a cheap residue of the wood refining industries was recently explored to obtain activated carbon fibers (ACFs) for supercapacitors [22]. After pulverization of sawdust, a mixture of wood flour, phenol, and phosphoric acid was liquefied at 160 °C and then placed into a spinning machine to produce fibers which were finally cured in a solution of H_2CO/HCl. ACFs were obtained by further heating at 500 C for carbonization, followed by treatment with aqueous KOH 5–30 wt% in a special activation chamber at 650–850 °C under N_2 (Figure 2).

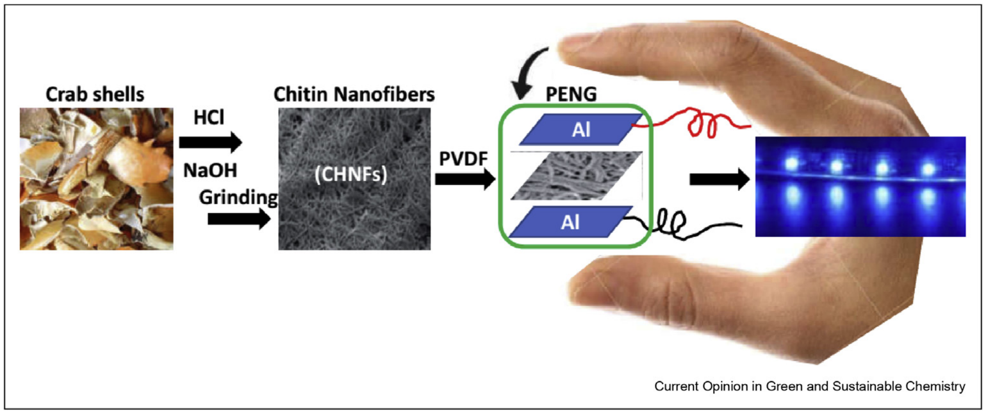
When activated above 800 °C, the surface of ACFs was etched by the development of porosity due to the formation of metallic potassium intercalated onto the carbon hexagonal structure of graphite in the samples (Eq. (1)).

Figure 2



Protocol for the fabrication of activated carbon fibers from sawdust. Right: scanning electron microscopy (SEM) image of the sample activated at 850 °C, highlighting the presence of nanopores, adapted from the study by Yallappa et al [21].

Figure 3



Assembly of a piezoelectric nanogenerator (PENG) using chitin nanofibers as a doping agent of poly(vinylidene fluoride) (PVDF).

$$6KOH + 2C \rightarrow 2K_2CO_3 + 2K + 3H_2 \quad (1)$$

Particularly, ultramicropores were obtained with a distribution around 0.8 and 1.1 nm (SEM image, Figure 2, right). The as-prepared fiber (ACF1) was assembled to a supercapacitor which exhibited an outstanding electrochemical performance with a specific capacitance of 225 F g^{-1} at a current density of 0.5 A g^{-1} and 94.2% capacity preserved after 10000 charge–discharge cycles at 3 A g^{-1}.

Another impressive source of BWs is generated by the fish processing and aquaculture industry from which excellent biopolymers can be obtained. A representative example is chitin extracted from crustacean wastes as shells of shrimp, crab, lobster, prawn, and krill, whose total annual production is estimated at 2.8×10^7 and 1.3×10^9 tonnes from freshwater and marine ecosystems, respectively [23,24]. Among applications of chitin for waste water treatment, purification processes, food additivities, packaging, controlled agrochemical release, pulp and paper treatment, cosmetics, tissue engineering wound healing, and so on [25–28], an increasing number of articles describe its use for the fabrication of advanced nanomaterials. One such case has recently reported the use of chitin nanofibers (ChNFs) to engineer a piezoelectric nanogenerator [29]. Crab shells were initially subjected to both chemical (acid–base) and mechanical (grinding) treatments to generate uniform ChNFs of 10–20 nm. These were then mixed with poly(vinylidene fluoride) (5 wt%) to produce a thin film (2.4 × 1.8 cm, 47 μm thickness) which was covered on both sides with aluminum foils as electrodes and encapsulated on polydimethylsiloxane. ChNFs acting as dopants of poly(vinylidene fluoride) were able to maximize the piezoelectricity of the device up to 35.56 pC N^{-1}. Under human finger impulses of 27.5 N at 6 Hz, the piezoelectric nanogenerator charged a 2.2 mF capacitor to 3.6 V within only 20 s and illuminated a series of 22 blue light emitting diode (LEDs), thereby demonstrating its suitability for energy harvesting in biomedical applications (*in vivo* blood flow and heart beats), or from body movements, moving cars, sea waves, and so on (Figure 3)

Conclusions

BWs may concur to the sustainable design of carbon-based and hybrid nanomaterials exhibiting outstanding properties for uses in a variety of fields, spanning from biomedicine to electronics, environmental monitoring, packaging, and so on Nanotechnology-enabled applications in these areas offer potential benefits in reducing costs and toxicity, while at the same improving efficiency and reliability. In this context, green nanotechnologies not merely facilitate the implementation of innovative technological solutions but they contribute in determining an overall positive feedback in the life cycle assessment of complex engineered nanomaterials.

Conflict of interest statement

Nothing declared.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Lavender Law K: **Plastic waste inputs from land into the ocean**. *Science* 2015, vol. 347:768–771.
2. http://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management. [Accessed 30 January 2019].
3. Caruso G: **Fishery wastes and by-products: a resource to be valorised**. *J Fisheriessciences.com* 2016, vol. 10:12–15.

4. Guillen J, Holmes SJ, Carvalho N, Casey J, Dörner H, Gibin M, Mannini A, Vasilakopoulos P, Zanzi A: **A review of the European union landing obligation focusing on its implications for fisheries and the environment**. *Sustainability* 2018, vol. 10:900.

5. Khan D, Kumar A, Samadder SR: **Impact of socioeconomic status on municipal solid waste generation rate**. *Waste Manag* 2016, vol. 49:15–25.

6. * Shapira P, Youtie J: **The economic contributions of nanotechnology to green and sustainable growth**. In *Green processes for nanotechnology*. Edited by Basiuk V, Basiuk E, Eds, Cham: Springer; 2015.

The contribution comments on some illustrative applications and research areas involving nanotechnologies

7. Kagan CR, Fernandez LE, Gogotsi Y, Hammond PT, Hersam MC, Nel AE, Penner RM, Willson CG, Weiss PS: **Nano day: celebrating the next decade of nanoscience and nanotechnology**. *ACS Nano* 2016, vol. 10:9093–9103.

8. * Vilatela JJ, Eder D: **Nanocarbon composites and hybrids in sustainability: a review**. *ChemSusChem* 2012, vol. 5:456–478.

The review compares the developments of syntheting methods and challenges for energy applications for model nanocarbon composites and hybrid materials

9. Lv T, Liu M, Zhu D, Gan L, Chen T: **Nanocarbon-based materials for flexible all-solid-state supercapacitors**. *Adv Mater* 2018, vol. 30:1705489.

10. Govindaraj P, Fox B, Aitchison P, Hameed N: **A review on graphene polymer nanocomposites in harsh operating conditions**. *Ind Eng Chem Res* 2019, vol. 58:17106–17129.

11. * * Xu C, Nasrollahzadeh M, Selva M, Issaabadi Z, Luque R: **Waste-to-wealth: biowaste valorization into valuable bio(nano)materials**. *Chem Soc Rev* 2019, vol. 48:4791–4822.

The authors provide a detailed overview on the waste-to-wealth approach starting from biowastes.

12. Liu W, Hui C, Wang F, Wang M, Liu G. In *Bamboo - current and future prospects*. Edited by Khalil A, Ed, IntechOpen; 2018. https://doi.org/10.5772/intechopen.76485.

13. * * Jiang J, Zhu JH, Ai W, Fan ZX, Shen XN, Zou CJ, Liu JP, Zhang H, Yu T: **Evolution of disposable bamboo chopsticks into uniform carbon fibers: a smart strategy to fabricate sustainable anodes for Li-ion batteries**. *Energy Environ Sci* 2014, vol. 7:2670–2679.

Starting from disposable chopsticks, the paper describes a simple, though highly effective, method to fabricate a hybrid material based on carbon fibers and MnO_2 nanowires with excellent properties as an anode for LI-ion batteries

14. Tullis P, The guardian weekly, https://www.theguardian.com/news/2019/feb/19/palm-oil-ingredient-biscuits-shampoo-environmental (last access December 04, 2019).

15. Abdullah N, Sulaiman F: *Biomass now – sustainable growth and use*. Matovic MD: Intechopen; 2013. https://doi.org/10.5772/55302.

16. Dungani R, Aditiawati P, Aprilia S, Yuniarti K, Karliati T, Suwandhi I, Sumardi I. In *Palm oil*. Edited by Waisundara V, Ed, Intech; 2018. https://doi.org/10.5772/intechopen.72350.

17. * Ali GAM, Manaf SAA, Divyashree A, Chong KF, Hegde G J: **Superior supercapacitive performance in porous nanocarbons**. *Energy Chem* 2016, vol. 25:734–739.

The pyroltic treatment of an abudant biowaste as oil palm leaves is described to design a symmetric supercapacitor with superior supercapacitance performance

18. Duc PA, Dharanipriya P, Velmurugan BK, Shanmugavadivu M: **Groundnut shell - a beneficial bio-waste**. *Biocatal Agricul Biotechnol.* 2019, vol. 20:101206.

19. International food policy research institute, https://globalfutures.cgiar.org/project-overview/, (last access December 04, 2019).

20. Torkashvand AM, Alidoust M, Khomami AM: **The reuse of peanut organic wastes as a growth medium for ornamental plants**. *Int J Recycl Org Waste Agric* 2015, vol. 4:85–94.

21. Yallappa S, Deepthi DR, Yashaswini S, Hamsanandini R, Chandraprasad M, Ashok Kumar S, Hegde G: **Natural biowaste of Groundnut shell derived nano carbons: synthesis, characterization and its in vitro antibacterial activity**. *Nano-Structures Nano-Objects* 2017, vol. 12:84–90.

22. * * Huang Y, Peng L, Liu Y, Zhao G, Chen JY, Yu G: **Biobased nano porous active carbon fibers for high-performance supercapacitors**. *ACS Appl Mater Interfaces* 2016, vol. 8: 15205–15215.

Starting from wood sawdust, Authors describe a multistep procedures comprised of lignin liquefaction, carbonization and high-temperature alkali activation to generate carbon fibers with 0.8- and 1.1 nm micropores, suitable as an electrode materials

23. Verlee A, Mincke S, Stevens CV, Polym Carbohydr: **Recent developments in antibacterial and antifungal chitosan and its derivatives**. *Carbohydr Polym* 2017, vol. 164:268–283.

24. Kaur S, Dhillon GS: **Recent trends in biological extraction of chitin from marine shell wastes: a review**. *Crit Rev Biotechnol* 2015, vol. 35:44–61.

25. * Hamed I, Ozogul F, Regenstein JM: **Industrial applications of crustacean by-products (chitin, chitosan, and chitooligosaccharides): a review**. *Trends Food Sci Technol* 2016, vol. 48: 40–50.

The paper offers an excellent overview of recent methodologies for the valorization of biopolymers extracted from crustacean shells.

26. Zargar V, Asghari M, Dashti A: **A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives, and applications**. *ChemBioEng Rev* 2015, vol. 2:204–226.

27. Anitha A, Sowmya S, Sudheesh Kumar PT, Deepthi S, Chennazhi KP, Ehrlich H, Tsurkan M, Jayakumar T: **Chitin and chitosan in selected biomedical applications**. *Prog Polym Sci* 2014, vol. 39:1644–1667.

28. Yadav M, Goswami P, Paritosh K, Kumar M, Pareek N, Vivekanand V: **Seafood waste: a source for preparation of commercially employable chitin/chitosan materials**. *Bioresour. Bioprocess.* 2019, vol. 6:8.

29. * * Hoque NA, Thakur P, Biswas P, Saikh MM, Roy S, Bagchi B, Das S, Ray PP: **Biowaste crab shell-extracted chitin nanofiber-based superior piezoelectric nanogenerator**. *J Mater Chem A* 2018, vol. 6:13848–13858.

Authors provide an inventive approach for the valorisation of chitin obtained from crab shells, by which a mixture of chitin nanofibers and an organic polymer (polyvinylidene fluoride) is incapsulated in a piezoelectric device for energy harvesting.