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Communication

Sodium-Cutting: A New Top-Down Approach to Cut Open Nanostructures on Nonplanar Surfaces in Large Scale

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We report a new, low-cost and simple top-down approach, “sodium-cutting”, to cut and open nanostructures deposited on a nonplanar surface in large scale. The feasibility of sodium-cutting was demonstrated with the successfully cutting open of ~100% carbon nanospheres into nanobowls in large scale from Sn@C nanospheres for the first time.

New methods to further tailor nanomaterials in large scale are highly desirable but challenging to develop. Materials at nanoscale have been attracting much attention for their numerous applications, ranging from health care, electronics, energy, environment and engineering.¹⁻⁵ They are promising to achieve paradigm shifts in many fields, such as catalysis,⁶ drug delivery,⁷ energy storage,⁸⁻¹⁰ solar cells,^{11,12} absorption,¹³ photonics,¹⁴ chemical sensors,¹⁵ and reactors in confined space at nanoscale.¹⁶ The ability to rationally design and facilyly tailor nanomaterials will enable the wide adoption of nanomaterials in many applications achieving tremendous positive impacts. Generally, there are two categories of methods to prepare nanomaterials, namely, bottom-up and top-down. The former method seeks to have molecules structured into more complex aggregates at nanoscale (e.g., self-assembly), and the later method uses external forces to create nanostructures from bulk materials. In particular, conventional top-down approaches, such as photolithography and scanning beam lithography, are widely employed in electronics industries to make nanostructures. However, those top-down approaches still have a few issues, namely, high costs, sophisticated facilities needed, restrictions to only limited materials. Another noticeable issue is inability to operate on nonplanar or curved surfaces at large scale.¹⁷ Additionally, conventional top-down approaches generally are not effective to cut a large number of nanostructures that are randomly distributed on given nonplanar substrates. For example, conventional top-down approaches are not suitable to shorten carbon nanotubes (CNTs) in large scale to open tubes and make CNTs more dispersible (e.g., to utilize the spaces in CNTs for drug delivery or energy storage). Instead, mechanical and oxidative cutting approaches, such as ball milling, high-speed agitation, ultrasonic treatment, cryogenic crushing, thermal oxidation, acid oxidation and ozonolysis are employed.¹⁸⁻³¹ Those methods are generally not compatible with the electronics industries in handling nanomaterials attached on substrates. Novel top-down approaches for cutting nanostructures are always

highly interesting but challenging to develop, given the diversity of nanostructures in terms of compositions and morphologies. Again, taking carbon for example, based on the best of our knowledge, no research has been done to cut and open carbon nanospheres in large scale.³²⁻³⁴ The methods used for shortening and thinning carbon nanotubes may not be effective in cutting hollow carbon nanospheres into carbon bowls.

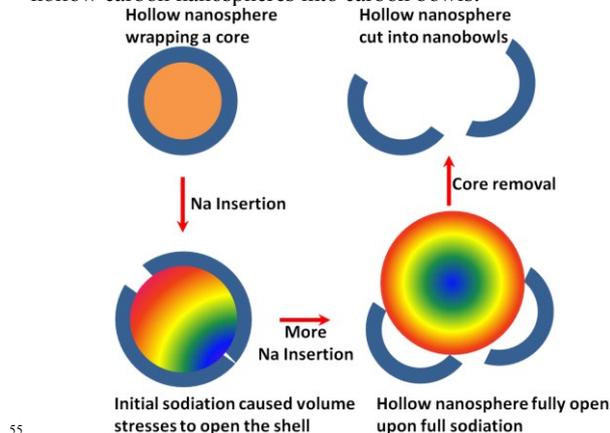


Figure 1. Schematic to illustrate the idea of top-down “sodium-cutting” approach to open a hollow nanosphere. **Note** that here spheres are used as the illustrative geometry but the principle should also be applied to other geometries such as tubes, cones, cubes, pyramids and polyhedrons.

Herein, we report a new, low-cost and simple top-down approach, *sodium-cutting*, to cut and open nanostructures deposited on nonplanar surface in large scale. We created the name “sodium-cutting” to reflect the unique nature of this top-down approach where electrochemical insertion of sodium ions is used to expand the volume of core part housing sodium ions to open the shell encapsulating the core by volumetric strains. We borrowed the term “top-down” to reflect that breaking one nanosphere into two-halves is a change from large to small. The idea is based on the understanding that the electrochemical insertion of sodium ions into sodium active cores can cause significant volumetric expansions to the cores. By controlling the degree of sodiation and direction of sodium insertion, one can control the open of shells which is less active or inactive in electrochemical insertion of sodium. The difference in volumetric strains between the core and shell parts could be achieved by selection of materials with different degree of sodiation or different sodiation induced

strains. There are a number of materials (e.g., Pb, Ge, Sn, C, P, metal/metal oxides, alloys) known to be electrochemically active toward sodium ions,³⁵⁻⁴⁴ and also a number of materials are known to be inactive (e.g., Si, C-graphite), providing a big pool of materials to select from. The overall idea is illustrated in Figure 1

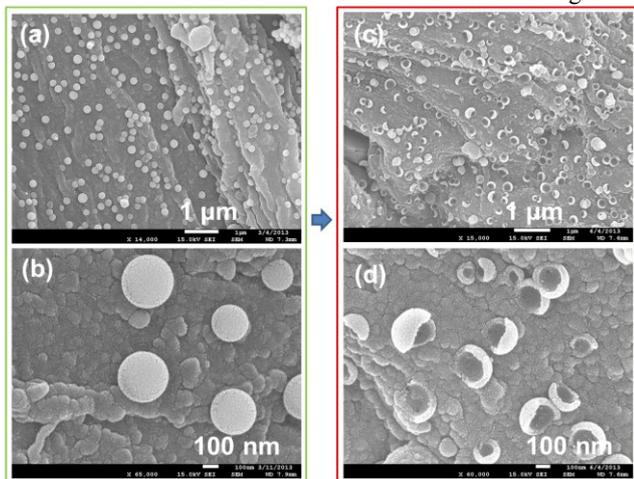


Figure 2. FESEM images: (a) low-magnification overall view and even distribution of and (b) high-magnification view of carbon nanospheres encapsulating metallic tin deposited on nonplanar surface of carbonized paper fibers obtained by CVD; (c) low-magnification overall view and nearly 100% cutting of and (d) high-magnification zoom-in view of carbon nanobowls obtained by “sodium-cutting”.

To demonstrate the feasibility of this top-down approach and idea, we tried to open hollow carbon nanospheres on nonplanar surface in large scale by “sodium-cutting”. We identified graphitized hollow carbon nanosphere to be cut and metallic tin as the core to provide the volumetric strains and stresses required to open carbon shell. The selection of carbon shell was based on our understanding that graphitized carbon can be intercalated with insignificant amount of sodium ions, typically less than 5 mA h g⁻¹.⁴⁵⁻⁴⁸ The selection of tin core was based on our understanding that tin is highly active to electrochemically alloy with sodium, with theoretical sodium-storage capacity of 847 mA h g⁻¹ (or Na₁₅Sn₄) and the insertion can induce a volumetric expansion as high as 420%.⁴⁹ This Sn@C couple with significant contrast toward insertion of sodium ions provides an ideal model to test our idea of “sodium-cutting”.

The Sn@C core-shell nanospheres were fabricated on in-situ carbonized paper as the substrate. There were two steps involved: (1) The SnO₂ nanoparticles were prepared by hydrolysis of SnCl₄ under hydrothermal conditions and then deposited on pieces of filter papers; (2) *in situ* chemical vapor deposition (CVD) process to reduce SnO₂ nanoparticles to metallic Sn by acetylene and enclose the Sn with carbon sheaths from the catalytic decomposition of acetylene. Acetylene was selected as both reduction agent and carbon source for the reduction of SnO₂ to metallic Sn and encapsulating metallic Sn with carbon sheaths under the CVD conditions.⁵⁰⁻⁵⁴ The carbon sheaths obtained by Sn assisted catalytic decomposition of acetylene are typically graphitized carbon with defects and disordered carbon at the CVD temperature of 650°C. The relative intensity of D and G bands (I_D/I_G) from Raman spectrum, corresponding to degree of disordered carbon prepared using acetylene, is in the range

between 0.85-1.3.^{54,55} This features of lack of extended graphene sheets and presence of defects in the carbon sheaths could facilitate the transport of sodium ions through shells to cores.

The as prepared Sn@C core-shell nanoparticles decorated on carbonized papers at different magnifications are showing in Figure 2a-b. The Sn@C core-shell nanoparticles are evenly distributed on the nonplanar surface of filter paper fibers. Their sizes are about 300-500 nm and are firmly attached on the carbonized paper fibers. During the EM sample preparation, no noticeable amount of attached Sn@C core-shell nanospheres were peeled off the surface indicating interaction between the Sn@C core-shell nanoparticles and the carbonized surface are strong enough to preserve the particles. The mechanical robustness could be ascribed to the C-C bonds formed between carbon deposited on the surface of carbonized paper fibers and the carbon sheaths wrapping the Sn particles. The carbon could be deposited at the interface from locally catalytically decomposed acetylene which can enhance the integration between the particle and the nonplanar surface.

Upon reversible insertion and extraction of sodium ions into and from the Sn@C core-shell nanospheres, we could cut open nearly 100% carbon nanospheres (Figure 2c-d). The low-magnification overall view (Figure 2c) shows that carbon nanospheres regardless their locations on the nonplanar surface of carbonized paper fibers, from upper surfaces, the valleys, folded spaces to those in between paper fibers, were cut open. The successful opening all carbon nanospheres on nonplanar surface could be interpreted from the perspective of high strains and stresses induced by volumetric expansion upon sodium insertion into the metallic tin core or “sodium-cutting”. The insertion of sodium could cause a volumetric expansion as high as 420%, which which could induce huge radial and tangential stresses in the order of MPa to GPa.^{56,57} At the same time, the carbon sheaths with graphitized and non-graphitized carbons may hold certain amount of sodium ions upon electrochemical insertion, which may change the elastic properties of the carbon sheaths and make them brittle. It is known that high strain could make carbon nanotubes brittle.⁵⁶ However, in contrast to carbon nanotubes, there are lack of studies regarding the fractures and stresses involving carbon nanospheres. Our results here will provide rich experimental evidences for fracture mechanics regarding cutting open carbon nanospheres by volumetric expansion.

Close examination (Figure 2d) shows that the carbon nanospheres were cut by different percentages of removal of carbon sheath: there are nanospheres with more than half carbon sheaths remained, and also those with less than a quarter carbon sheaths remained. The remained cut carbon sheaths formed carbon bowls with different orientation and holding volumes on the surface of the carbonization paper fibers. Those remained bowls also revealed that the carbon spheres were partially embedded on the surface, which could explain the robust attachment discussed previously. The sharp cutting edges indicate that the carbon nanospheres were brittle with fracture propagation in line-manner in each carbon nanospheres. The different percentages of carbon sheath removal could be attributed to different fracture propagation starting points on the nanospheres upon the insertion of sodium ions into tin cores. The defects on the carbon nanospheres may not be evenly distributed, and the weak points

could be those starting locations for the fracture propagation. On the other hand, the volumetric expansion of metallic tin during the process of alloying with sodium may not be in evenly distributed symmetric radial directions, although those encapsulated metallic Sn core are spherical inside carbon nanospheres before cutting. In another word, the stresses applied on the carbon nanospheres are not symmetric in radial directions which also contributed to shaping the resulted carbon bowls. The asymmetric volumetric expansion of metallic Sn core was directly observed (Figure S1 in Supporting Information (SI)). The expanded Sn core separated the two carbon bowls apart when it grew into elongated shape to cut open the carbon nanosphere. The asymmetric volumetric expansion in Sn upon reversible insertion of sodium ions was also observed by Wang et al. during in situ TEM observation of pure tin nanoparticles.⁴⁹ The asymmetric volumetric expansion of spherical tin cores suggests that the insertion of sodium ions into tin may not be symmetric inward radially. This result confirms that the sodium alloying with tin core which expanded asymmetrically was the source of volumetric strains to cut open the carbon nanospheres.

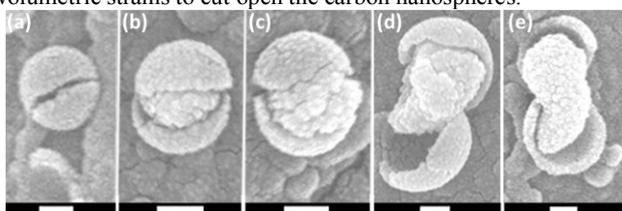


Figure 3. Selected carbon nanospheres with different degree of opening upon different volumetric strains applied on them when sodium alloys with tin at different degree (Na_xSn , $0 < x < 3.75$). Each white scale bar is 100 nm.

Figure 3 of a few selected carbon nanospheres with different degree of opening vividly illustrates the different volumetric strains applied on carbon nanospheres when different amount of sodium alloys with tin (Na_xSn , $0 < x < 3.75$). Upon the insertion of sodium ions, the following components, such as NaSn_5 , NaSn_2 , NaSn , Na_9Sn_4 , $\text{Na}_{15}\text{Sn}_4$, could be formed depending on the degree of charge.^{43,49} The volumetric expansion for NaSn_2 , Na_9Sn_4 , $\text{Na}_{15}\text{Sn}_4$ generated during the insertion of sodium ions was estimated to be 56%, 252%, 420%, respectively.⁴⁹ With core volumetric expansion, the volumetric strain (23% estimated based on the crack size and diameter of the nanosphere in Figure 3a) could generate significant stresses to break the encapsulating carbon nanosphere forming a circular crack (Figure 3a). The Young's modulus E was estimated to be in the range between 270-950 GPa for multiwall carbon nanotubes.⁵⁸ Although there is lack of information regarding the strain-stress relationship in carbon nanospheres, the circular crack observed here suggests that a huge stress in the range of 60-200 GPa might have been generated and applied on the carbon nanosphere. When the amount of sodium ions were continuously inserted electrochemically into the tin core, the crack propagated to open big with continue volumetric expansion of the core. Eventually, the significantly elongated core could separate apart the two nano bowls (Figure 3e). Upon washing, the other half of the carbon nanosphere and the tin core without any attachment to the surface of carbon fiber could be removed, with only one portion of the carbon nanosphere, or carbon bowl, left on the surface.

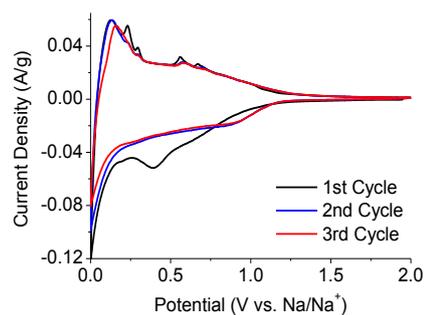


Figure 4. The CV profiles of carbon nanospheres encapsulating metallic tin deposited on nonplanar surface of carbonized paper fibers under reversible sodium insertion/extraction cycles. Scan rate of 0.05 mV/s, between the voltage window of 0 and 2 V.

We used cyclic voltammograms (CV) analysis to prove the electrochemically assisted sodium alloying with tin forming Na_xSn (Figure 4). In the first cathodic scan, the broad dominant reduction peak between 0.5 and 0.35 V could be attributed to the insertion of sodium ions forming NaSn_5 and NaSn , and the barely visible peaks between 0.2 and 0.1 V could indicate the formation of Na_9Sn_4 and $\text{Na}_{15}\text{Sn}_4$.⁴³ In the first anodic scan, multiple oxidation peaks at around 0.23, 0.30, 0.55 and 0.67 V could be assigned to the desodiation of $\text{Na}_{15}\text{Sn}_4$, Na_9Sn_4 , NaSn , and NaSn_5 , respectively.⁴³ The CV analysis clearly evidenced the formation of Na_xSn , which could generate significant volumetric strains. In the 2nd and 3rd CV scans, the intensively those peaks observed in 1st scan were reduced, which could be attributed to the detachment and peeling off of those expanded and exposed tin cores without carbon encapsulation.



Figure 5. Illustration to show the idea of "sodium-lithography" on nonplanar surface. Note: the pattern is for illustration and other patterns could be achieved as well, and the patterns could be on either side or both sides of the curved surface in principle.

We believe that our method of "sodium-cutting" could eventually add another dimension to the widely used lithography technologies by offering the possibility to tailor nanostructures on nonplanar surfaces. The basic idea of "sodium-lithography" is illustrated in Figure 5. For example, two materials (G and R) with G (green) is inert or significantly less active and R (red) is active toward electrochemical sodium insertion are selected. One can properly deposit R with a unique pattern onto the nonplanar substrate followed by covering the pattern with a thin layer of G (Step 1 in Figure 5). The sodium-cutting will selectively tailor the layer G by using the volumetric strains generated during the electrochemical insertion of sodium ions into R (Step 2). If the volumetric expansion could be controlled to be asymmetric or even with certain directions, one may guide the opening lines of sodium-cutting at nanoscale. For the integration of sodium-lithography into the electronics industry where semiconductor silicon is widely used, the good news is that silicon is not active in electrochemical alloying with sodium.⁵⁹ Therefore, it will be possible to tailor silicon (for example, $\text{Sn}@\text{Si}$ nanostructures on nonplanar surfaces) into various patterns using our technique of

sodium lithography. The preliminary results of Sn@C nanospheres on nonplanar surface of paper fibers discussed in the communication could be considered one special case of “sodium-lithography”, where carbon (G) encapsulated tin nanoparticles (R) on nonplanar surface of fiber substrate were cut open (interpreted in Figure S2 in SI).

Conclusions

In summary, we discussed the idea of “sodium-cutting” via electrochemical insertion of sodium ions into two materials with different degree of sodiation and sodiation induced strains and stresses to cut open nanomaterials in large scale. The feasibility was demonstrated with the successfully cutting open of ~100% carbon nanospheres into nanobowls in large scale from Sn@C nanospheres deposited on nonplanar surface of carbonized paper fibers for the first time. This technique could eventually enable the development of sodium lithography for the manipulating nanoscale patterns on nonplanar surfaces.

Notes and references

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† Electronic Supplementary Information (ESI) available: EM and Sn mapping; illustration; reactions. See DOI: 10.1039/b000000x/

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