FLUORINE-ETCHED NANOSTRUCTURES FOR ENERGY STORAGE APPLICATIONS

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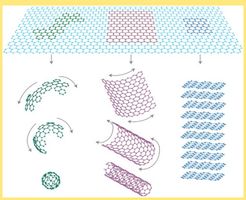
Abstract

Graphene has been the focus of much current research, due to its interesting electrical and structural properties for electronics applications. Here we show that fluorine can be introduced during graphene growth on stainless steel (SS) substrates to simultaneously create useful nanostructures, using the chemical vapor deposition (CVD) technique. These structures are geometrically optimal for reversible ion intercalation, where the graphene acts as an electrode and the SS is a current collector. Direct growth of graphene on electrode materials makes this process very scalable and cost-effective for developing thin-film energy storage devices.

Introduction



Since the two-dimensional carbon structure, known as graphene, was discovered in 2004, it has been a very promising material for various applications such as solar cells, sensors, transistors, inert coatings, etc..

Figure 1: Changing the configuration of the honeycomb lattice illustrates graphene's ability to form buckyballs, carbon nanotubes, and Graphite

Graphene can be a useful battery electrode due to its superior electrical conductivity, high surface area and a broad electrochemical window.

Originally, exfoliated graphene coated on to conducting electrodes resulted in poor adhesion and electrical contact. Chemical vapor deposition (CVD) allows graphene to be grown directly on substrates.

Experimental Methods

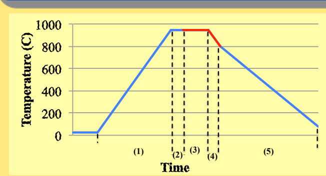


Figure 2: Schematic of optimized growth process, (1) Ar/H_2 30 minute heating cycle. (2) Annealing time and 2 minute Ar flush. (3) 10 minute exposure to organic compound and fluorine etch. (4) 2 Cs^{-1} cooling rate while exposed to organic compound. (5) C diffusion under gradual cooling.

1. Create SS discs with constant diameter for coin-cells
2. Etch nanostructures on to the substrate using fluorine-based organic vapors
3. Allow carbon diffusion of carbon as SS cools to produce graphene
4. Analyze under scanning electron microscope (SEM) and Raman Spectroscope
5. Load sample in device and obtain charge/discharge profile

Results

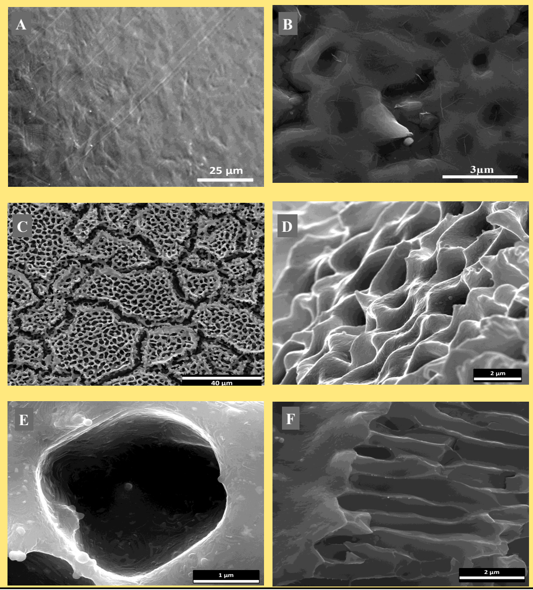


Figure 3: Broad SEM images of SS (A) before CVD growth, (B) after growth with organic vapor, and (C) after growth with fluorinated organic vapor. (D) Image of the surface of fluorinated sample from an angle. (E) View of single pore blanketed in graphene. (F) Inside view of broken substrate to reveal cylindrical structure of pores.

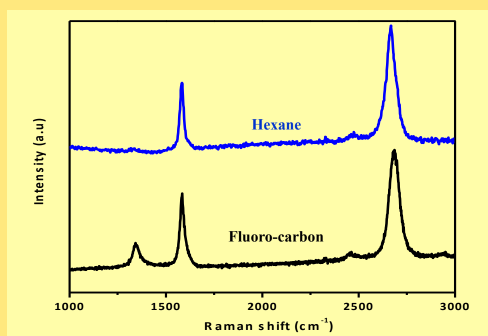


Figure 4: Raman spectra of the graphene grown directly on stainless steel using hexane and a fluorinated organic compound

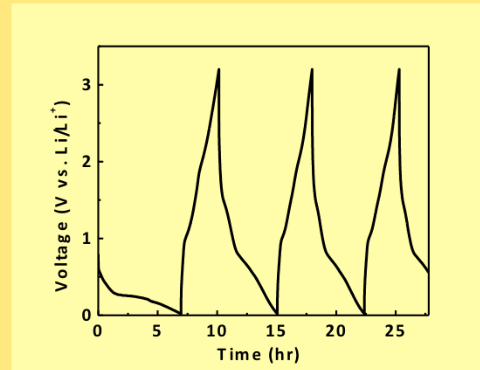


Figure 5: Charge-discharge voltage profile of cycles between 3.2 V and 0.02 V vs Li/Li+ at a current rate of 8μA/cm^2 in an electrolyte of $LiPF_6$ in mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)

Summary

- **Scalable method for growth of graphene layers and useful nanostructures on SS substrates with CVD**
- **Good electrochemical properties and stability over Li-ion charge/ discharge cycles makes this a promising step towards better electrode materials**

Future Work

- Further optimize the growth parameters
- More systematic battery testing on a variety of SS samples
- Growth on similar metallic substrates (copper, nickel, etc.)
- Optimization of growth to create new controlled structures
- Alternative precursors with fluorine or chlorine

References

[1] X. Li, *et al.*, *Science* **2009**, *324*, 1312; K.S. Kim, *et al.*, *Nature* **2009**, *457*, 706.
[2] A.C. Ferrari *et al.*, *Phys. Rev. Lett.* **2006**, *97.* ; D. Wang *et al.*, *ACS Nano* **2009**, *3,* 907.
[3] H. Gullapalli, *et al.*, *Small* **2011**, *7, No. 12, 1697-1700*
[4] A.L.M. Reddy, *et al.*, *ACS Nano* **2010**, *4* (11), 6337–6342

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