Materials & Coatings

Detection of Carbon Monoxide Using Polymer-Composite Films With a Porphyrin-Functionalized Polypyrrole

This technique can be used in home safety applications, first-responder safety, fire detection, and fire cleanup.

NASA's Jet Propulsion Laboratory, Pasadena, California

Post-fire air constituents that are of interest to NASA include CO and some acid gases (HCl and HCN). CO is an important analyte to be able to sense in human habitats since it is a marker for both pre-fire detection and post-fire cleanup.

The need exists for a sensor that can be incorporated into an existing sensing array architecture. The CO sensor needs to be a low-power chemiresistor that operates at room temperature; the sensor fabrication techniques must be compatible with ceramic substrates. Early work on the JPL ElectronicNose indicated that some of the existing polymer-carbon black sensors might be suitable. In addition, the CO sensor based on polypyrrole functionalized with iron porphyrin was demonstrated to be a promising sensor that could meet the requirements.

First, pyrrole was polymerized in a ferric chloride/iron porphyrin solution in methanol. The iron porphyrin is 5, 10, 15, 20-tetraphenyl-21H, 23H-porphine iron (III) chloride. This creates a polypyrrole that is functionalized with the porphyrin. After synthesis, the polymer is dried in an oven. Sensors were made from the functionalized polypyrrole by binding it with a small amount of polyethylene oxide (600 MW). This composite made films that were too resistive to be measured in the device.

Subsequently, carbon black was added to the composite to bring the sensing film resistivity within a measurable range. A suspension was created in methanol using the functionalized polypyrrole (90% by weight), polyethylene oxide (600,000 MW, 5% by weight), and carbon black (5% by weight). The sensing films were then deposited, like the polymer-carbon black sensors. After deposition, the substrates were dried in a vacuum oven for four hours at 60 °C. These sensors showed good response to CO at concentrations over 100 ppm.

While the sensor is based on a functionalized pyrrole, the actual composite is more robust and flexible. A polymer binder was added to help keep the sensor material from delaminating from the electrodes, and carbon was added to improve the conductivity of the material.

This work was done by Margie L. Homer, Margaret A. Ryan, Shiao-Ping S. Yen, Liana M. Lara, Abhijit V. Shevade, and Adam Kisor of Caltech for NASA's Jet Propulsion Laboratory. For more information, contact iaoffice@jpl.nasa.gov. NPO-47640

Enhanced-Adhesion Multiwalled Carbon Nanotubes on Titanium Substrates for Stray Light Control

Commercial applications include telescopes, binoculars, night vision goggles, and other optical devices that benefit from stray light suppression.

Goddard Space Flight Center, Greenbelt, Maryland

Carbon nanotubes previously grown on silicon have extremely low reflectance, making them a good candidate for stray light suppression. Silicon, however, is not a good structural material for stray light components such as tubes, stops, and baffles. Titanium is a good structural material and can tolerate the 700 °C nanotube growth process.

The ability to grow carbon nanotubes on a titanium substrate that are ten times blacker than the current NASA state-of-the-art paints in the visible to near infrared spectra has been achieved. This innovation will allow significant improvement of stray light performance in scientific instruments or any other optical system. This innovation is a refinement of the utilization of multiwalled carbon nanotubes for stray light suppression in spaceflight instruments. The innovation is a process to make the surface darker and improve the adhesion to the substrate, improving robustness for spaceflight use.

Bright objects such as clouds or ice scatter light off of instrument structures and components and make it difficult to see dim objects in Earth observations. A darker material to suppress this stray light has multiple benefits to these observations, including enabling scientific observations not currently possible, increasing observational efficiencies in high-contrast scenes, and simplifying instruments and lowering their cost by utilizing fewer stray light components and achieving equivalent performance.

The prior art was to use commercially available black paint, which resulted in approximately 4% of the light being reflected (hemispherical reflectance or total integrated scatter, or TIS). Use of multiwalled carbon nanotubes on titanium components such as baffles, entrance aperture, tubes, and stops, can decrease this scattered light by a factor of ten per bounce over the 200-nm to 2,500-nm wavelength range. This can improve system stray light performance by orders of magnitude.

The purpose of the innovation is to provide an enhanced stray light control capability by making a blacker surface treatment for typical stray light control components. Since baffles, stops, and tubes used in scientific observations often undergo loads such as vibration, it was critical to develop this surface treatment on structural materials. The innovation is to optimize the carbon nanotube growth for titanium, which is a strong, lightweight structural material suitable for spaceflight use.

The titanium substrate carbon nanotubes are more robust than those grown on silicon and allow for easier utilization. They are darker than current surface treatments over larger angles and larger wavelength range. The primary advantage of titanium substrate is that it is a good structural material, and not as brittle as silicon.

This work was done by John Hagopian, Stephanie Getty, and Manuel Quijada of Goddard Space Flight Center. Further information is contained in a TSP (see page 1).
GSC-16247-1

Three-Dimensional Porous Particles Composed of Curved, Two-Dimensional, Nano-Sized Layers for Li-Ion Batteries

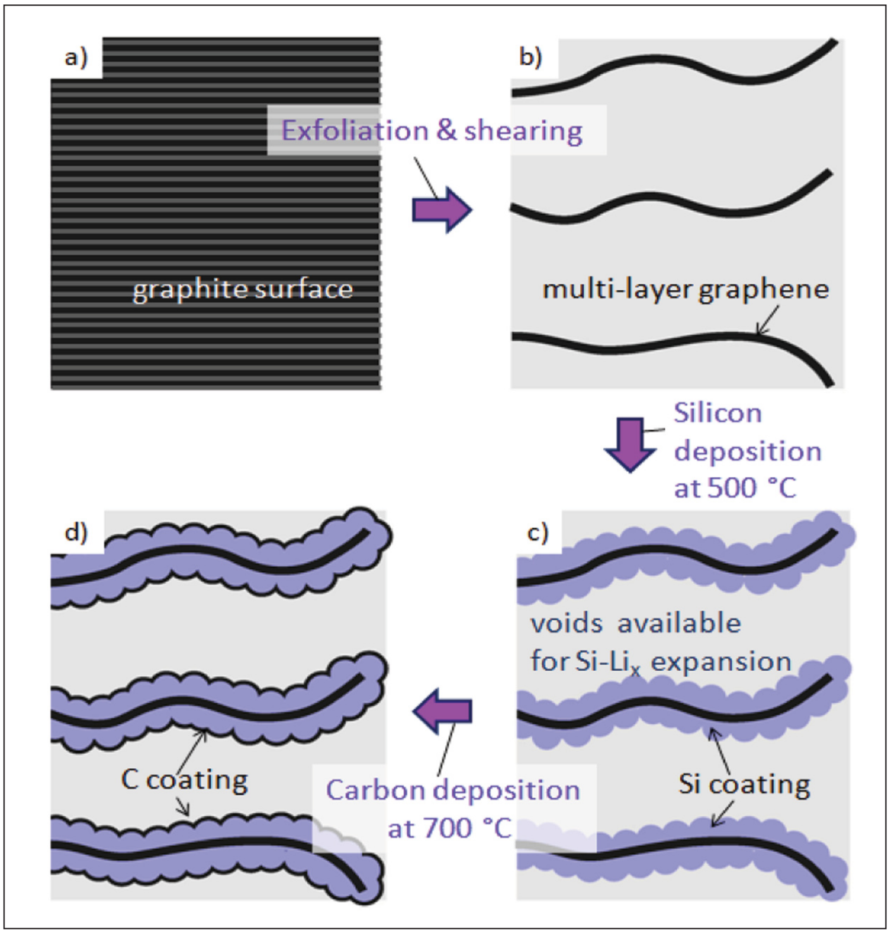
A new method and materials were developed for preparing high-performance Si-based anodes for secondary Li-ion batteries.

John H. Glenn Research Center, Cleveland, Ohio

Building on previous knowledge acquired through research on thin-film batteries, three-dimensional (3D) porous macroscopic particles consisting of curved two-dimensional (2D) nanostructures of Si may bring unique advantages for Si anode technology. Prior work on thin Si films showed that during Li insertion, large-area Si films mostly accommodate the volume changes via variation in thickness. Therefore, the changes in the external surface area can fundamentally be minimized and thus, formation of a stable, solid electrolyte interphase (SEI) should be easier to achieve. In contrast, Si nanoparticles expand uniformly in all dimensions and thus, their outer surface area (where SEI forms) changes dramatically during insertion/extraction of Si. The low elasticity of the SEI makes it difficult to achieve the long-term stability under cycling load. Further, thin Si films have lower surface area (for the same mass), in comparison to Si nanoparticles, and better potential for achieving low irreversible capacity losses on the first and subsequent cycles.

Thin Si films coated on porous 3D particles composed of curved 2D graphene sheets have been synthesized utilizing techniques that allow for tunable properties. Since graphene exhibits specific surface area up to 100 times higher than carbon black or graphite, the deposition of the same mass of Si on graphene is much faster in comparison — a factor which is important for practical applications. In addition, the distance between graphene layers is tunable and variation in the thickness of the deposited Si film is feasible. Both of these characteristics allow for optimization of the energy and power characteristics. Thicker films will allow higher capacity, but slower rate capabilities. Thinner films will allow more rapid charging, or higher power performance.

In this innovation, uniform deposition of Si and C layers on high-surface-area graphene produced granules with specific surface area (SSA) of ≈ 5 m^2g^{-1}. The over 100 times reduction in SSA of the initial graphene material is important for high Coulombic efficiencies on the first and subsequent cycles. Here, the low surface area of the composite resulted in an average Coulombic effi-



A schematic of **C-Si-Graphene Composite Formation**: (a) natural graphite is transformed to (b) graphene, and then (c) coated by Si nanoparticles and (d) a thin C layer.