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Synthesis and characterization of solid, hollow, core-shell and worm-like carbon nanostructures for applications in organic photovoltaic devices and chemical sensors

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Abstract

The synthesis of carbon spheres (solid and hollow) for application in organic photovoltaics and chemical sensors is a means of using inexpensive and readily processable carbons to eliminate global warming and to monitor harmful gases. The synthesis conditions used to make solid carbon spheres can also be used to tailor their structural, paramagnetic and thermal properties. More so, the ability to tailor the morphology, surface, structural and electronic properties of the hollow carbon spheres by a templating method is an added advantage to their applicability in electronic devices.

Solid carbon spheres were synthesized by a vertically oriented chemical vapor deposition (CVD) reactor using acetylene as a carbon source and argon or hydrogen as the carrier gas. The flow rates of the acetylene or carrier gases determined the particle sizes of the carbon spheres. Annealing of carbon spheres in hydrogen resulted in an increase in thermal stability, fewer defects and narrower paramagnetic signals relative to the carbon spheres annealed in argon gas. In contrast, carbon spheres annealed in argon exhibited an increase in the number of defects, a decrease in thermal stability and broader paramagnetic signals. Doped carbon spheres portrayed an increase in I_D/I_G ratios, a decrease in thermal stability and stronger paramagnetic signals due to the presence of defects induced by nitrogen. The N doped carbon spheres synthesized in H_2 comprised of 48% pyridinic-N, 22% pyrrolic-N and 24% quaternary -N while the N doped spheres obtained in the presence of Ar had 17% pyridinic-N, 20% pyrrolic-N and 49% quaternary-N. The presence of a higher percentage of pyridinic-N confirms the presence of more edge defects in carbon spheres synthesized under H_2 gas corroborating with the stronger paramagnetic signal observed from the ESR spectra. Consequently, a higher N/C ratio was exhibited in the N doped CSs obtained in the presence of H_2 (4.96) than in the presence of Ar (3.68). This could be attributed to the presence of edge defects in carbon spheres synthesized in the presence of H_2 gas. The induction of edge defects in carbon spheres in the presence of H_2 gas without the aid of a metal catalyst opens a platform for regulating surface and catalytic reactions using H_2 gas.

Pristine and mesoporous SiO_2 spheres were synthesized using a modified Stober method. Carbonization of the pristine SiO_2, pristine SiO_2@PVP, mesoporous SiO_2 and mesoporous SiO_2@PVP spheres was carried out using a bubbling method with toluene as the carbon source and argon as the carrier gas in a CVD reactor for 1 h. Upon SiO_2 removal, hollow

carbon nanostructures of varying morphologies were obtained. The polyvinylpyrrolidone (PVP) adsorption time, PVP concentration, SiO_2 mesoporosity, SiO_2 particle size dispersion, and carbonization time played a role in the formation of unique hollow carbon nanostructures; complete HCSs, broken HCSs, deformed HCSs, edge connected, open ended, wormlike and bubble-like HCSs. The mesoporous broken HCSs and open ended HCSs portrayed a hierarchical structure with a bimodal pore size distribution. The surface area properties of these materials and the ease of control of the carbon morphology gives an insight into the application of these materials as dye adsorbents. The effect of the size dispersion of Au@SiO_2 sphere templates for the synthesis of hollow carbon structures was evaluated using a CVD nanocasting method. The diameter of the template, the presence of the gold nanoparticles and the amount of PVP determined the size, thickness and shape of the synthesized carbon nanostructures. Carbonization (and SiO_2 removal) of Au@polydispersed silica spheres for 1 h gave a graphene-like HCS layer while longer times (2-4 h) gave nanotube like (or worm like) HCSs. These results highlight the potential use of Au@carbon core shell structures for the generation of few layered graphene-like unusual nanostructures. As a proof of concept, the wormlike carbon structures were incorporated in organic solar cells and found to give a measurable photovoltaic response.

The incorporation of Au nanospheres and nanorods in a hole transport layer (PEDOT:PSS) of a solar cell device increased the current density and the photo-conversion efficiency of the device due to the local surface plasmon resonance and enhanced light scattering effects of gold. However, high series resistance and leakage currents were obtained due to barrier centres created by uneven dispersion of Au nanaorods within the polymer matrix. The performance of bulk heterojunction organic photovoltaic cells based on poly(3-hexyl-thiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) processed from chlorobenzene solution can be enhanced by solution heat treatment of the blend. The morphology of films spin coated from the heat treated blend solution reveals a more favourable diffusion of PCBM into the P3HT matrix than heating of the individual solutions separately. The films obtained from heat treated P3HT and PCBM solutions had a more homogeneous dispersion and enhanced light absorption than those obtained from solutions heat treated separately. There was a significant improvement in the performance for devices made from a solution heat treated blends relative to the non-treated blend; a

maximum power conversion efficiency of 3.5% and a fill factor up to 43% was achieved under Air Mass 1.5 at 100 mW/cm^2 illumination.

This study also reports on the sensing characteristics of ammonia in humid environment by hollow carbon spheres, hollow carbon spheres-polyvinylpyrrolidone composite and annealed hollow carbon spheres, at 20°C and 40°C. For device fabrication, a surfactant assisted method was used to homogeneously disperse the hollow carbon spheres, allowing their deposition onto an interdigitated electrode by casting. An enhanced response and recovery time of the devices was observed at the higher working temperature. Annealing of the hollow carbon spheres resulted in a tremendous decrease in the humidity dependent ammonia sensing due to a decrease in the number of the oxygenated groups and defects in their structure. The presence of hydroxyl groups on the pristine hollow carbon sphere surface resulted in an enhanced proton conductivity. However, the ammonia sensitivity at high relative humidity in the pristine hollow carbon spheres is negligible due to the inhibition of ammonia adsorption sites by the high concentration of water molecules. The sensor response was investigated by varying both ammonia concentration and relative humidity, determining the topology of the response as a function of these two variables, and applying a tristimulus analysis in an attempt to determine the ammonia concentration independently of the relative humidity. This study demonstrates the critical role played by humidity and surface chemistry in the ammonia sensing properties of hollow carbon spheres. The studies reveal the day to day application of ammonia sensors, with temperature and humidity playing a critical role in the carbon based sensor response and recovery of the materials. These carbon based sensors that simultaneously measure ammonia and relative humidity could be applied in agricultural industries to monitor ammonia concentration in soils, fishponds and in food industries to monitor meat spoilage.