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FINAL REPORT

"SUPERSONIC BARE METAL CLUSTER BEAMS"

Principal Investigator: Richard E. Smalley

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Recipient Organization: William Marsh
Rice University
P.O. Box 2692
Houston, TX 77252-2692

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Bare metal clusters. A major portion of the project involved elucidating the relation between reactivity and the electronic structure of transition-metal (TM) clusters of 2-200 atoms, which required the construction and continuous development of two principal apparati: the Fourier Transform-Ion Cylotron Resonance (FT-ICR) apparatus, and Ultraviolet Photoelectron Spectroscopy (UPS). Together, these machines have enabled the most detailed probing of the structure and chemical reactivity of TM clusters. In combination with calculations, UPS experiments have advanced understanding of TM cluster electronic structure, while the FT-ICR technique, with the direct injection from a supersonic cluster ion source, has allowed further characterization of structure and chemical reactivity, particularly chemisorption on TM cluster surfaces. Clusters of all the transition metals were included in these studies, with the principal focus on Fe, Co, Cu, Ag, Au, Pt, Sc, Y, La, Nb, V, Ta, Rh, Ni, and Ir. Fundamental aspects in chemisorption, reactivity, and heterogeneous catalysis have also become better understood as a result of these experiments for important classes of systems such as H_2, CO, and CO_2 adsorbed onto clusters of many of the metals listed above. In particular, a correlation was found between reactivity of H_2 with Fe, Co, and Ni clusters and differences between the cluster IP and EA. This was explained microscopically as resulting from a chemisorption barrier whose height is given by the excitation energy from the frontier orbital to the lowest unoccupied d-orbital. This is a general model that is likely to apply to any closed-shell species interacting with metal clusters.

Bare metal clusters in carbon cages. As recounted in a previous technical report, the DOE's role in the initial discovery of fullerenes at Rice was central, and from the start investigations were made into metal atoms trapped in the fullerenes cage. More recently, we have discovered that 2-4 atoms of La, Y, or Sc can be produced by laser vaporization of composite

graphite/metal-oxide disks. This work was largely motivated by the prospects of using such endohedral TM metals for their catalytic activity without the well-known difficulties of effective support media and lack of control over particle size. Thus, while it will certainly be important to discover ways to efficiently scale up production (e.g., the solar generation method explored with DOE support), our efforts have concentrated more on characterization, purification, and manipulation of doped fullerenes.

Carbon nanotubes and continuous carbon fibers. For the past two years, much of the group's effort has involved the production, purification, and characterization of carbon nanotubes, novel objects holding a wealth of promise for materials applications. While pursuing the controlled growth of continuous individual nanotubes from seed crystals, several noteworthy advances have been achieved as offshoots. First, by microscopic analysis of nanotubes grown in the arc struck between two carbon electrodes, we were able to construct the first detailed model of nanotube formation as well as the source of defects in this principal production method. Also in the course of experiments aimed at controlled growth, we came to investigate the field-emission behavior of nanotubes. Our studies have led us to a model in which the electron-emitting structure is not simply the nanotube tip, but rather a single chain of carbon atoms, an atomic wire, unraveled from the tip, forming possibly the sharpest, strongest possible field-emitter. Furthermore, since the energy and angular distributions of emitted electrons are likely to be far narrower than those of any existing field-emission tips, these objects may prove to be of tremendous practical import.

Concurrent with this work, a remarkable discovery was made during laser-vaporization production runs of metalofullerenes. We found, during control experiments in which no metal was mixed into the graphite target rod, an abundance of nanotubes deposited on the cold copper collector at the end of the heated quartz flow tube. This discovery, under circumstances in which no extrinsic factors (e.g., a metal particle, electric field, hydrogen atoms) were present to help keep the nanotube tip open, led to a growth model in which the growing open end of the nanotube is stabilized against closure by an *intrinsic* factor: carbon adatoms "spot-welded" in positions between adjacent layers. Indeed, these spot-welds are likely to be important for multiwalled nanotube growth under *any* circumstances. We have demonstrated, however, that spot-welds cannot by themselves be sufficiently stabilizing to keep the tip open indefinitely. Our field-emission experiments on single mounted nanotubes confirmed the hypothesis, previously postulated by grantee, that the electric field of the arc is necessary to hold the tip open. Soon thereafter, single-walled nanotubes were synthesized by laser-vaporization by utilizing the catalytic properties of transition metals mixed into the graphite target. This work has likewise led to a firmer understanding of single-walled nanotube growth, and may be of practical significance for their bulk production.

The following list of papers acknowledging support from this grant, have either appeared in print or have been submitted for publication since the 1994 report:

"Field Emission and Growth of Fullerene Nanotubes," A. G. Rinzler, J. H. Hafner, P. Nikolaev, D. T. Colbert and R. E. Smalley, MRS proceedings, vol 359, pp. 61-68 (December 1994). conference paper removed and cycled separately

"Growth and Sintering of Fullerene Nanotubes," D. T. Colbert, J. Zhang, S. M. McClure, P. Nikolaev, Z. Chen, J. H. Hafner, D. W. Owens, P. G. Kotula, C. B. Carter, J. H. Weaver, A. G. Rinzler and R. E. Smalley, *Science*, Vol 266, 1218-1222 (11/18/94). reprint removed

"Electric Effects in Nanotube Growth," D. Colbert and R. E. Smalley, *Carbon,* Vol. 33, No. 7, pp. 921-924 (1995). reprint removed

"Self-Assembly of Tubular Fullerenes," T. Guo, P. Nikolaev, A. Rinzler, D. Tomanek, D. Colbert and R. E. Smalley, *Journal of Phys. Chem.* Vol. 99, 10694-10697 (July 6, 1995). reprint removed

"From Fullerenes to Nanotubes," J. Hafner, A. Thess, P. Nikolaev, A. Rinzler, D. T. Colbert and R. E. Smalley, Proceedings of NATO Advanced Research Workshop on "The Chemical Physics of Fullerenes 10 (and 5) Years Later," Varenna, Italy, In Press (June 1995) reprint removed

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