New Nanophase Materials and Catalysts from Laser Pyrolysis

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The production of nanoscale (dia. <100 nm) particles, their consolidation under pressure into a solid, or the incorporation of these particles into a solid medium is the subject of much recent interest to solid state physicists and materials scientists. These “nanophase” materials, as well as the particles themselves, are being intensively studied for several reasons. Although they may exhibit an atomic arrangement similar to that of larger crystals (micron size), these very small particles, or “nanoparticles,” can exhibit an expanded or contracted crystal lattice. Furthermore, the atoms near the surface are expected to be displaced from their exact crystallographic positions. In some cases, the surface atoms may even be organized in an altogether different arrangement from those atoms in the particle core. The atom rearrangement is particularly important for small nanoparticles, (dia. < 5 nm) when one is reminded that a 5 nm diameter particle has ~90% of its atoms located within one atomic layer of the particle’s surface; and the physical and chemical properties of solids are very sensitive to these interatomic separations. Certain physical properties of small nanoparticles can also be affected by “quantum confinement phenomena” which occur when a particular “physical length” exceeds the particle size. So, for several reasons, exciting new properties and phenomena are expected from small nanoparticles and the so-derived “nanophase” materials. It is, therefore, of fundamental importance to understand the relationship between the nanoparticle properties and their atomic structure.

From the perspective of catalysis, highly dispersed 5 nm particles represent a high, non-porous surface area substrate (~100-200 m²/g) easily accessible to the chemical reaction. From the perspective of new composite materials, for example, formed from a mixture of nanoparticles and a conventional supporting medium (e.g., polymer), the nanoparticles can represent a high value-added ingredient, provide an unusual and desirable character to the composite. By adjusting the particle size and the wt% of the nanoparticles in the composite, the material’s physical properties can be tailored to suit a particular application, e.g., the dielectric response, optical transmission, magnetic shielding, electrical and/or thermal conductivity, deformability, hardness, etc. Nanophase materials derived simply from consolidating the nanoparticles under pressure into a dense solid are also being studied. In these materials, the high density of grain boundaries leads to significantly different mechanical properties (e.g., ductility, fracture strength, etc.) of metal and ceramic nanocomposites.

We have been using a high power CO₂ laser to drive a pyrolysis reaction which

(continued, page 2)

Brunauer, Emmitt and Teller — The Personalities Behind the BET Method

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PART I

The famous Greek Mathematician Archimedes (circa 287-212 BC) discovered how to show whether gold objects his king had purchased were made of adulterated gold. For developing the method of measurement, he became a favorite of the king. According to legend, Archimedes arrived at his principle during his bath when he realized that the volume of water displaced was a measurement of his volume. Using this principle, anyone could measure the volume of a material with an odd shape and this, together with the weight of the object, would allow one to determine the purity of the gold object. Supposedly Archimedes, overcome with the magnitude of his idea, leapt from his bath and ran through the streets in his birthday suit, screaming to all present: “Eureka! Eureka!” This may have been the beginning of the public opinion that scientists are strange individuals who do not fit into the mainstream of human behavior. Certainly fiction, and more recently, movies and television have reinforced this view of scientists. The following brief description of three modern scientists shows that, contrary to public perception, these individuals have a range of human characteristics and do not, in fact, differ from other professions.

As material is subdivided, the extent of its surface increases. Just as with Archimedes centuries ago, scientists needed a method to measure the surface area of finely divided powders. To do this it would be necessary to measure holes that are accessible at the molecular level. The Brunauer, Emmett, Teller method (the BET method), can do this. The order of BET was a result of Edward Teller insisting that the names should appear in alphabetical order; thus the names of Stephen Brunauer and Paul Emmett preceded that of Teller. In 1938 these men developed a theory that permitted the calculation of
leads to the production of small nanoparticles via a-2-4 nm. The technique was first reported by Haggerty in 1981, and has remained largely unexplored. By adjusting the reaction conditions, we have shown that the chemical composition and particle size can be controlled. Recently, we have also demonstrated that CO\textsubscript{2} laser pyrolysis is a versatile technique, capable of preparing a variety of binary transition metal sulfides (Mo\textsubscript{3}S\textsubscript{2}, Fe\textsubscript{5}S) and carbides (Mo\textsubscript{3}C, W\textsubscript{5}C), oxides (TiO\textsubscript{2}, ZrO\textsubscript{2}), and nitrides (W\textsubscript{3}N, Mo\textsubscript{2}N) from a mixture of a metal carbonyl and a second reactant gas. Using Mo\textsubscript{3}C and Mo\textsubscript{2}N nanoparticles as examples, we present results of high resolution transmission electron microscopy (HTEM), x-ray diffraction (XRD), and x-ray photo-electron spectroscopy (XPS) which provide detailed information about the atomic order and the chemical composition of the nanocrystalline core and surface. Transition metals carbides and nitrides, such as WC and Mo\textsubscript{2}N, have been shown to have catalytic activities similar to the noble metals for CO hydrogenation and isomerization reactions. Among other investigations, we are evaluating these binary catalysts as an economical alternative, correlating their catalytic activity with structural information obtained from XPS, XRD and HTEM.

The production rates in our batch-type laser pyrolysis reactor (Figure 1) vary from 1-10 g/hr. As shown schematically, the reaction gas flows vertically through the crucible, past the horizontal laser beam, absorbing optical energy which then raises the reaction temperature to 800-1000°C. The particles nucleate and grow in a small laser-heated region, pass rapidly out of this hot zone, and are transported downstream to a particle trap. In our experiments, a typical reaction gas flow rate through a 2 mm I.D. nozzle is ~10 cm/s, which implies a 1-10 ms residence time for the particles in the "hot zone" defined by the intersection of the horizontal laser beam and the vertical reactor gas stream. The particles are also subjected to extremely high cooling rates (~10\textsuperscript{6}°C/sec) as they leave the laser field of the equipment. These data show that it is possible to use this property to quench high temperature phases not otherwise obtainable.

XRD is used to identify the crystalline phase, extract the average value of the lattice parameters and provide an estimate for the average crystallite size in the nanopowder sample. HREM lattice imaging has proven itself to be a powerful tool to probe atomic organization of a single nanoparticle, especially when the particle has a well-ordered structure. XPS is a short range probe which provides information about the composition and chemical bonding at a depth of 1-3 nm from the particle surface—thus the spectrum probes primarily the near-surface region. These three structural and chemical probes provide a relatively complete picture of the structure and composition of nanocrystalline powders.

Figure 2 displays powder XRD data (dots) for Mo\textsubscript{2}C nanopowder. The solid curve represents a sum of Lorentzian lineshapes used to simulate the data. The Lorentzian peak positions and areas are consistent with the standard powder diffraction data file. For simplicity, a single linewidth is used for all the XRD peaks. The overall agreement between the data and the calculated results for the standard indicates that our phase identification is correct. A broad peak at 20° = 27° is attributed to Mo\textsubscript{3}S\textsubscript{2}, which forms during the surface passivation process.

Similar data were collected for Mo\textsubscript{3}N and W\textsubscript{3}N; these particles also exhibit a cubic structure, whereas W\textsubscript{5}C is tetragonally amorphous.

Using the Debye-Scherrer formula (D=0.9λ/μcosθ), and the Bragg's law (2dsinθ=λ), where μ, λ, and θ are, respectively, the angular position of the (111) line and the x-ray wavelength, we have determined the average crystallite size D and the lattice spacing (d) along the 111 direction for Mo\textsubscript{3}N, W\textsubscript{3}N and Mo\textsubscript{2}C single crystal nanoparticles, as given in Figure 3. In the case of Mo\textsubscript{3}C and W\textsubscript{3}N nanoparticles, significant differences were found to exist between the standard intensities and our data. This is attributed to: possible metal atom vacancies and to slight displacements in the metal atom sublattice near the particle surface. Further work with the synchrotron light source at Brookhaven National Laboratory will be initiated to see if we can extract quantitative information about these interesting deviations from crystallinity. The clear shift in Figure 2 of the diffraction data toward lower 2θ relative to the standard positions indicates a lattice expansion which has taken place in the nanoparticles relative to the bulk phase.

![Diagram](image)

**Figure 3. Average crystalline size (D) and lattice spacing (d) along the (111) direction, derived from XRD and HREM measurements.**

Mo\textsubscript{3}N | W\textsubscript{3}N | Mo\textsubscript{2}C | W\textsubscript{5}C
---|---|---|---
D\textsubscript{111} (Å) | 25 | 19 | 21 | Amorphous
D\textsubscript{111} (Å) | 25 | 27 | 20 | Amorphous
θ\textsubscript{111} (°) | 20 | 23 | 20 | 23 | 23 | 23 | NA
θ\textsubscript{111} (°) | 20 | 23 | 23 | 23 | NA

*The value is approximate, due to significant particle agglomerates.*

(continued, page 3)
In Figure 4, we show HRTEM lattice images for MoC nanoparticles. The atomic planes appear like interference fringes. As can be seen, these lattice fringes are present in the majority of the particles, which shows directly that each particle is a nanocrystal. Although the XRD and XPS both find structure in the data associated with metal-oxide formation on the surface, no evidence for these surface, or near-surface modifications have been observed in HRTEM. We thus conclude that the oxide layers must be thin (monolayer or sub-monomolayer) and disordered enough so that they are not easily seen under HRTEM. In particular, the MoC particles which are produced by the reaction of the carbynol and C, do not appear to have a carbon coating on the surface. In contrast to this finding, FeC nanoparticles (dia. ~ 10 nm) produced similarly, exhibited up to 10 well defined graphic layers in HRTEM. This is understandable, since FeC is known to be very active for producing graphic carbons from the decomposition of Fe, H, using the HRTEM data, values for the (111) lattice spacings, d, are also listed in Figure 1. It is clear from Figure 3 that the crystallite sizes estimated from the finite-size-induced line broadening in XRD are in good agreement with the HRTEM images, indicating that within each nanocrystallite, there is little disorder.

Figure 5 shows the XPS spectra for Mo,N and Mo,C. The particles in this particular image are agglomerates. Nevertheless, the interference patterns from atomic planes are still evident.

Figure 5. XPS data (surface specific) for Mo,N and Mo,C.

at 228.58 eV in Fig. 5a and 5c to the Mo-N and Mo-C local environment, respectively; whereas the peaks at 232.5 eV in Fig. 5a and 5c are from the x +1 oxidation state of molybdenum, which indicates the presence of MoO3 on the surface. Deconvolution of the data gives 90% of surface Mo in the form of MoO3 for both Mo,N and Mo,C. The carbon 1s peak located at 284.5 eV in Figs. S8and 5d corresponds to carbon deposited on the particle surface during synthesis. Note that the surface-MoO3 and carbon are not resolved in HRTEM due to their poor crystallinity, which emphasizes the importance of employing multiple tools in the nanoparticle characterization. Despite the surface-oxide and carbon these Mo,N and Mo,N particles, their activity for heteroatom (NO,Si) removal was found to be comparable to commercially available catalysts.

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Two-page extended abstracts will be due March 31, 1995, but prospective authors should supply 50-word statement of title and subject matter as soon as possible.
Stephen immigrating was that, in the upheaval in Hungary that followed WWI, enrolment in Hungarian universities was limited to 5% Jewish students, their percentage of the general population at that time. In New York City, Stephen found that the City College of New York did not charge tuition whereas Columbia University had a substantial registration fee. Wanting his degree from the more prestigious Columbia University, he would alternate schools each semester. He worked and saved enough during his semester at City College to afford to attend Columbia the next semester. He could not speak or read English when he came to the U.S. Nevertheless, Brunauer obtained a double major, in chemistry and in English. He graduated magna cum laude—from Columbia.

Brunauer took chemistry and engineering graduate courses at both Columbia and City College. During his undergraduate/graduate student days, he became involved with the Hungarian Young Workers' League, a group supported by the Communist Party. At that time the Communist Party was a young organization that was just starting to become a force in international politics. The group that Stephen chose to support in the Young Workers' League eventually followed a political course that conflicted with the International Communist Party. Stephen became disillusioned and by the time that he obtained a job with the fixed Nitrogen Laboratory (FNL) a federally supported research laboratory in Washington, DC, he had left the Young Worker's Club. However, he retained his interest in politics and in liberal causes.

His early involvement in the Communist Party would come back to haunt him in the decades to come as the American political arena of the 1950s was shaken by a scandal from Wisconsin named Joseph McCarthy.

The Hungarian Young Worker's League served to provide social functions as well as a political role frequently the social and political roles were combined. Intellectually oriented meetings were frequently held followed by a Hungarian dinner at a subsidized price that even students could afford. Brunauer, a very assertive individual, entered the debates at these meetings, and this attracted him to the leadership. He was soon engaged as a reporter for the local Hungarian newspaper. At that time the newspaper was the second largest Hungarian newspaper in the U.S., serving the Hungarian populace of New York City and the surrounding area. Most Hungarian immigrants lived in isolation, even in New York City and did not learn English; thus, the Hungarian language newspaper had considerable influence on this population.

Brunauer began working for Paul I. Emmett, the E of B at the Fixed Nitrogen Laboratory (FNL) in 1929. He obtained this position by making the highest score on the civil service exam. Because he attended some meetings that had liberal leanings in Washington, and met Esther Cailkin, who became his wife, at one of them. From then until (continued, page 5)
COMMENTARY

MAN BYTES DOG!

Frank Derbyshire
Director, for Applied Energy Research

It is now December, 1944. A good time to think about writing the editorial that I promised some time ago to my Editor (to borrow a phrase, "she who must be obeyed"). But not as good as scoring some time ago, which is when I was supposed to have done it.

After years of stoic resistance in the face of inexorable budgeting from my more computerize colleagues, I have capitulated and joined the computer communications club. To those who know what this means, I have been connected (via computer, that is) to E-mail and Internet. To those who don't know what this means (this included myself until recently), I can send and receive messages by computer to and from destinations throughout the world, and I can also potter through all manner of information - text, image, video, music, the spoken word - that is made available by various suppliers, also located globally.

My change of stance isn't due to the acquisition of new skills (I still cannot program my home video or answering machine), and I refuse to attribute it to some aberrant manifestation of mid-life crisis. I could conjure any number of other plausible reasons, but the real one is simply that some software designeres have had the foresight to make it easy for those of us on the periphery of computer use to be brought into the fold. All that is required is to point the mouse to the appropriate icon and click. Even I can do that, I discovered. I couldn't resist. It is such a welcome change from having to wade through some enormously thick, cryptic manual that is apparently written for aliens or, worse, ask one of the members of the inner circle of the computer cognoscenti to explain what to do. Many people will have had some such harrowing experience. There will then follow an inintertempl monologue consisting of strange words - lan, bit, ram, baud, byte, rom - that sound as though they might form a familiar speech pattern, (e.g. man bytes dog) but are soon discovered to form an unintelligible stream. If one is stupid enough to request clarification, the expert will often smilignly oblige, and produce yet another torrent of what might as well be Swahili.

No matter. Despite my sorry lack of qualifications, I have become one of a growing number of pedestrians who are stepping gingerly onto the information superhighway. In so doing, I have become acutely aware of the ability to access an astonishing diversity of data whose quality can rest anywhere between the truly excellent and the truly abysmal, and whose quantity and rate of delivery can be overwhelming. If one is able to eliminate the trivia and focus on one's objectives, these vast resources can be a tremendous asset to progress in all fields of endeavor. The danger lies in the temptation to select only the information that suits one's purpose.

The same is true of all the data that are laid before us, whether they arrive by computer screen or otherwise, and the process of filtering the fotsam and jetsam is difficult enough when considering factual information, let alone when there is subjective content. The largest and most ubiquitous volume of information is conveyed by the news media, and here there are problems caused by competition between the news suppliers and the limited attention span of the average customer. To attract attention, news is selected and "packaged" to appear sensational, novel and crowd-pleasing. The downside of news advertising and vending strategies is that important (but currently non-catataymci) events are ignored, complex issues are oversimplified and hence distorted or misrepresented.

The selective reporting of spectacular findings or events generally does nothing to excite the public perception of science. A consequence of inmoder--

BET, (continued)

1946. Esther managed the international education programs for the American Association of University Women.

They moved to Baltimore during 1951 so that Stephen could spend a year in full-time study to obtain his Ph.D. at Johns Hopkins University. He approached graduate school as he approached most things in his life. In two years, Stephen obtained his M.S. by attending night classes at George Washington University. He applied for a fellowship at Johns Hopkins University, soliciting letters from many people. Even today, he is known for saving the thickest application folder in the university's history. In any event, he finished his work in less than a year.

Esther had obtained a Ph.D. in history from Stanford. She gained a fellowship to study in Germany during 1933, and was there with Stephen when Hitler came to power. During this visit she was able to arrange an interview with Hitler as part of her study. Returning from Europe, both Brunauers became even more active in political meetings. It is amazing that he found time during this period to complete the experimental work that would become the BET method. It is even more surprising that Stephen would take an evening class taught by Edward Tellier at George Washington since he was working full-time for Emmett, teaching an evening course at George Washington and was a new father. However, he did, and this included telling Tellier the theoretical basis for his work. Tellier disagreed. Undaunted, Brunauer challenged Tellier to provide the experimental basis for the practical work that had been completed by Brunauer and Emmett. Tellier did the work, although he did not in the manner that some credit him. In this version, Tellier took a number of coins, placed them on the floor and, crawling around, arranged them in possible configurations until he arrived at the correct solution. It is almost certain that Tellier solved this problem as he did many others, with the direct concentration that enabled him to focus intense energy upon a problem.

This is part one of a two-part series. Dr. Drake will continue his account of the fathers of the BET Method in the January issue of Energia. The author wishes to acknowledge Dalmus Brunauer for her contributions to this article.

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Commentary, (continued)

are reporting is to generate immediate expectations. Advances in research are usually made in a steady progression of steps, each in itself of relatively minor consequence. The "major breakthrough" is a rarity. Even in these instances, success is the result of effort and dedication, as well as talent, and because of the existence of the background of gradually accrued knowledge. Difficult as it may be to accept, less fortunate researchers can spend days, weeks, even whole careers, toiling in the gloom of some derelict laboratory at public expense and not discover the antigravity principle or invent a pocket time machine. The failure to present scientific endeavor in its true context creates a climate where the public or funding to support a realistic expectation of steady progress will not find advocates. Instead, researchers are obliged to oversell their concepts, to predict dramatic findings, and generally to promise more than they can deliver. The almost inevitable shortfall only serves to propagate this cycle and widen the existing credibility gap.

Scientific data can also be selectively presented to serve political purposes. Without appropriate qualification, such information is misleading and can be detrimental. For example, the prospect of global warming due to the increase of carbon dioxide in the atmosphere has become a highly visible and politically significant issue in many countries. It has led to enacted or pending legislation intending to place a punitive tax on emission sources. Yet, while it has been established that the concentration of carbon dioxide is slowly increasing, scientific opinion is clearly divided on the question of whether or not it will be harmful to life on earth. Eventually, we should learn whether we are facing a long-term problem or not, whether our leaders have acted with intuitive foresight, or have caused us to waste considerable time and effort in premature overreaction. In either case, immediate decisions appear to have been made on a slowly evolving situation, prompted more by emotionally-driven considerations than hard data.

The foregoing could simply represent my biased opinions. But to show that I am not entirely alone, I will make mention of an article that appeared recently in Chemical and Engineering News (November 7, 1996), and which helped to inspire this editorial. It described the results of a survey in which it was reported that "U.S. scientists think public confidence in science and research has dropped..." that "...science is used too often to fulfill a political agenda..." and that "...government agencies often use scientific research to support predetermined viewpoints."

The character Chicken Licken of nursery fable felt an acorn fall on his head and concluded that the sky was falling. His basic problem (apart from being a panic merchant) was an inability to balance his information. That is basically the point that I am trying to make - that somehow we need to restore some balance in the way in which information is conveyed and used, and to restore some faith in the value of investing in science education and research.

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