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A SCANNING ELECTRON MICROSCOPY STUDY OF THE MACRO-CRYSTALLINE STRUCTURE OF 2-(2,4-DINITROBENZYL) PYRIDINE

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ABSTRACT

The compound, 2-(2,4-dinitrobenzyl) pyridine, was synthesized in the laboratory; an introductory level electron microscopy study of the macro-crystalline structure was conducted using the scanning electron microscope (SEM). The structure of these crystals was compared with the macro-structure of the crystal of 2-(2,4-dinitrobenzyl) pyridinium bromide, the hydrobromic salt of the compound which was also synthesized in the laboratory. A scanning electron microscopy crystal study was combined with a study of the principle of the electron microscope.

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Theory of Color Change

Sandy colored crystals of the 2-(2,4-dinitrobenzyl) pyridine have the unusual property of turning a deep blue color when exposed to sunlight. The deep blue color can then revert again to sandy color when kept in the dark. This color change from sandy to deep blue takes only a few minutes; however, the color change from deep blue back to sandy takes about one day in the dark. Observations show that the interconversions are reversible an unlimited number of times. The phenomenon is explained by the formation of a tautomeric form by the action of light.

In the presence of light the sandy colored dinitro compound rearranges to the deep blue colored acid-nitro tautomer. In doing so, the sandy colored compound undergoes intramolecular hydrogen bonding. A proton (H+) is transferred from the methyl group to the oxygen of the nitro group. This results in extended conjugation of multiple bonds in the blue tautomer (shown in the encircled group). This chromophore is responsible for producing the color in the blue tautomer.

Visible ultraviolet spectroscopy, providing information of conjugation, confirms that the blue tautomer has a greater degree of conjugation. Maximum absorption of radiation is expected to take place at a longer wavelength for the compound with the greater number of conjugated multiple bonds. Maximum absorption occurs at a wavelength of 248 nm for the sandy compound and 567 for the blue compound.

Superiority of the Electron Microscope Over the Light Microscope

The macro-crystalline structures of the photochromic compound, 2-(2,4-dinitrobenzyl) pyridine and its salt, 2-(2,4-dinitrobenzyl) pyridinium bromide, were studied using the scanning electron microscope (SEM). The SEM along with a high speed-camera was used to magnify, photograph, study, and compare the small details of the macro-structure of the crystals. It is the overwhelming superiority of the electron microscope that allows the observation of minute details, such as the inner structure of tiny crystals (note micrograph 3.8), which exceeds the scope of the light microscope.

The principle of this 20th century invention reveals its high degree of superiority over the light microscope. With the optical microscope, it is the wave length of light that places an ultimate limit to the resolution or the smallest distance between two points at the object that can be seen separately through a microscope. The overwhelming superiority of the electron microscope is due to the fact that the wavelength of the electron can be many thousand times smaller than the wavelength of light.

Whenever the size of an object in front of a wave is about the same size as the wavelength of the wave, the wave will bend or diffract around it. To project the outline of an object on a screen, one must use a wave whose wavelength is very small compared with the object. Visible light has a wavelength of about 0.5×10^{-6}m so it is hard to see the outline of a body whose diameter is about 0.5×10^{-6}m. The

electron can have a wavelength of 10^{-10}m so the outline of an atom whose diameter is 10^{-10}m is barely perceptible for this wavelength. Electrons will form a sharp shadow of viruses having a diameter of about 10^{-6}m, while visible light will diffract around them. A small wavelength gives the most accurate measurement of a body's position. The behavior of electrons in this manner is an example of the wave-particle duality set forth by Louis de Broglie in 1924.

The more powerful lens microscope can magnify an object only about 2,000 times its own diameter. An electron microscope magnifies about 200,000 times, or 100 times as much as an ordinary microscope. This image can also be photographed and magnified to approximately 800,000 times the original diameter, or 400 times as much as a regular microscope magnifies. The electron microscope has a theoretical resolution of about 3A which is about the distance between atoms in solids. The scanning tunneling electron microscope can attain an amazing vertical resolution of about 0.1A. At the same time, the great depth of focus, which is about 300 times that of a light microscope, endows images of objects with a life-like, three dimensional quality. This is lacking in the light microscopes of the same magnification. Operation at the ultimate peak of performance requires a well-experienced microscopist.

Principle of Electron Microscopes

Electrons are strongly scattered by all forms of matter including air. Therefore, the electron microscope must be evacuated to about 10^{-4}mm Hg (10^{-7}atmospheric pressure). The lenses cannot be material in nature. They are electric or magnetic fields, which are symmetrical about the axis of the instrument. The source of electrons is housed in the electron gun which shoots beams of electrons toward the object. The electron source relies on high temperatures to enable a fraction of the free electrons in the cathode material to overcome the barrier of the work function and leave. In effect, the electrons are "boiled out" of the cathode material. The electron source is an incandescent, hairpin-shaped filament of tungsten (W) or lanthanum hexaboride (LaB_6), surrounded by electrodes which accelerate and collect the electrons in a narrow, intense beam. The electron gun can operate at voltages of 1-100kV.

Highly accelerated beams of electrons from the electron gun are focused by the electron lens into a tiny spot. The electric or magnetic field, or a combination thereof, which comprises the lens, acts upon an electron beam in a manner analogous to that in which an optical lens acts upon a light beam.

The condenser and objective or probe-forming electron lenses serve to demagnify the image of the crossover, the narrowest cross section of the beam from the electron gun. The condenser lens determines the beam current, and the probe-forming lens determines the final spot size of the electron beam which impinges upon the sample. The electron beam is focused by the electromagnetic field of the magnetic lens as the electrons travel down the column or bore of the lens.

In the axially symmetrical condenser lens, solenoid windings of copper wire are used to induce a magnetic field (when traversed by electric current). The solenoid windings are surrounded by an iron mantle, except for a gap in the iron core representing the distance between the north and south pole pieces of the lens. The magnetic strength of the lens is stronger by the presence of the iron core than in its absence. At the gap, the concentrated magnetic field forms the electron lens having a focal length of one eighth to about one sixteenth of an inch, which is inversely proportional to the strength of the lens. The lens height is 10-15 cm in a 30 Kv SEM. The strength (or intensity of the magnetic field) of the magnetic lens in the gap is proportional to the flow of current through the lens, as well as the number of turns in the solenoid winding.

197

Production of a minimum electron spot size begins with the reduction of the electron beam at crossover (50 um for a tungsten hairpin) to a greatly reduced scale. An electron image of the crossover passes through the condenser lens, and it is focused to a smaller intermediate diameter. The distance the electrons are focused is varied by changing the strength of the condenser lens system. If the current is increased, then the strength of the lens increases, and the demagnification increases (the focused spot gets smaller). Also, the divergence of the electron ray from the focused spot will increase. Less beam current will enter the final probe-forming lens, to obtain a minimum probe size which improves resolution. The condenser lens can be focused to allow most of the electron beam to pass through the aperture of the objective lens, to obtain maximum beam current and signal. Consequently, one can decide between maximum beam and current signal, or lose current but have minimum probe size for optimum resolution.

In the scanning electron microscope a fine electron beam is focused on a thick specimen and the pattern of the reflected electrons is displayed on a television-like image tube. A mechanical stage allows scanning of the object. The image can be photographed on regular photographic film. However, the problems and complexities of high-voltage electron microscopes limit their application.

Scanning Electron Microscopy Crystal Study

Sample preparation for observation in the electron microscope involved mounting the sample on a specimen stub with silver paint, and coating the crystal sample with a thin film of conducting material of gold-palladium by the process called sputter coating. This was done to eliminate or reduce the electric charge which can build up in a non-conducting sample when scanned by a high-energy electron beam. The coating provides a conducting path and should help eliminate the problems associated with charging.

The electron micrographs show the expected variations in crystal shapes, sizes, and lengths for crystals not grown in a controlled environment. Micrograph 1.1, for example, shows crystals of various shapes and sizes at low magnification.

The samples were coated by the process of sputter coating. By this process, an energetic ion or neutral atom of argon gas accelerates towards and strikes the surface of the negatively biased gold-palladium target and imparts momentum to the atoms. Some of the atoms of the target may receive enough energy in the collision to break bonds with neighboring atoms and be carried away from the solid, if the velocity imparted to them is sufficient. Electrons are ejected from the negatively charged target, discharging a glow normally associated with sputter coating. As the electron accelerates towards the positive anode, under the influence of an applied voltage, it may collide with a gas molecule, leaving behind an ion and an extra free electron. The positive ions then accelerate towards the negatively biased gold-palladium target where they cause sputtering as the atoms lying near the surface of the target are ejected in this collision and sputtered onto the sample as a thin film deposit of gold-palladium.

Micrograph 1.1 shows one of the advantages of sputter coating. The target atoms, after collision, are traveling in all directions as they sputter coat on the surface of the sample. In this way, the target atoms are able to "go around corners" and achieve a complete coating without the need of rotating or tilting the sample. An artistic pile-up of crystals can be adequately coated by sputter coating.

Some disadvantages of sputter coating can be seen in micrographs 3.4 and 3.8. These include thermal damage due to heat of radiation from the target and electron bombardment of the sample.

Another potential problem is surface etching. It is attributed to either stray bombarding gas ions, or metal particles hitting the surface with sufficient force to erode it away. In micrograph 3.2 the crystal in the center contains many small holes sometimes found in sputter coated samples. At a magnification of about 2,000, micrograph 3.8 shows surface erosion and sample destruction at a pitted area. It is not known for certain whether the very small holes found in sputter coated samples, examined at high resolution, are the result of surface etching or just thermal damage. Thermal damage, when it occurs, is manifested as melting, pitting, and in extreme cases, complete destruction of the sample. But this is thought to be mainly due to the sample being subjected to inordinately high power fluxes.

Thermal damage can also be caused by excessive heating in the electron microscope, which results in specimen or sample movement and instability to breakdown and destruction. It is manisfested as blisters, cracks, and holes in and on the surface of the sample.

Micrograph 3.9 exhibits beam damage by the appearance of blisters on the surface of the crystal specimen. The blistering effect is only obtained, or at least seen, under higher magnifications of about 2,000 or greater. A vertical fracture near the lower center of micrograph 3.9 may be due to beam damage. Hair-like fibers extend from one side of the fracture to the other as the crystal breaks and melts under the heat of the electron beam, resulting in sample breakdown and destruction. Problems of thermal damage can be reduced by working at lower beam currents. Sample heating from the probe current in the picoampere range is expected not to be a problem for samples in the SEM. An alternative is to coat with a thin film of copper, aluminum, silver, or gold.

Crystals of the protonated compound (hydrobromic salt of the photochromic compound), 2-(2,4-dinitrobenzyl) pyridinium bromide, can be seen in micrograph 4.13. In comparison, the gold-palladium coated sample of salt crystals appear to be wider and flatter than the crystals of the unprotonated photochromic compound. The width of the long, wide, diagonal crystal in the lower right of micrograph 4.13 is 53 microns. Holes in the crystals of the salt compound are smooth and precise. Inner layers are not found in the holes of the salt crystals, as can be found in the unprotonated photochromic compound from which they were prepared. Additionally, the salt crystals do not exhibit properties of photochromism.

An interesting outcome of the study is the detection of inner layers in the macro-crystalline structure of the photochromic compound, 2-(2,4-dinitrobenzyl) pyridine. A very interesting layering effect is seen in the crystal on the right side of micrograph 1.4. The long horizontal crystal on the right, in micrograph 3.2, is similarly layered. However, the former appears to have more inner layers as compared to the hollow appearance of the latter. Micrograph 2.11 is that of an uncoated crystal sample, and exhibits a great deal of charging. Nevertheless, thermal damage has exposed many inner layers of the crystal. These layers are calculated to be less than 1.7 microns in thickness.

The relationship of the inner layers to the color change for these photochromic crystals remains to be determined. Additional study may reveal a relationship between layering phenomenon and the color change, along with the action of light, by which the compound is able to undergo intramolecular hydrogen bonding, allowing it to rearrange to the deep blue tautomeric form. Layers of 2-(2,4-dinitrobenzyl) pyridine as thin as 0.015 mm have been crystallized between fused silica plates.[2] Layers of crystalline films reduced to 0.004 - 0.008 inches thick can be investigated by transmission microscopy for the study of structure and structural defects.

Lastly, several potential areas of usefulness of the photochromic compound, 2-(2,4-dinitrobenzyl) pyridine, exist in the deformation of dye laser pulses,[4] in the photographic screen stencil printing process,[1] and in information storage.[3]

Acknowledgments

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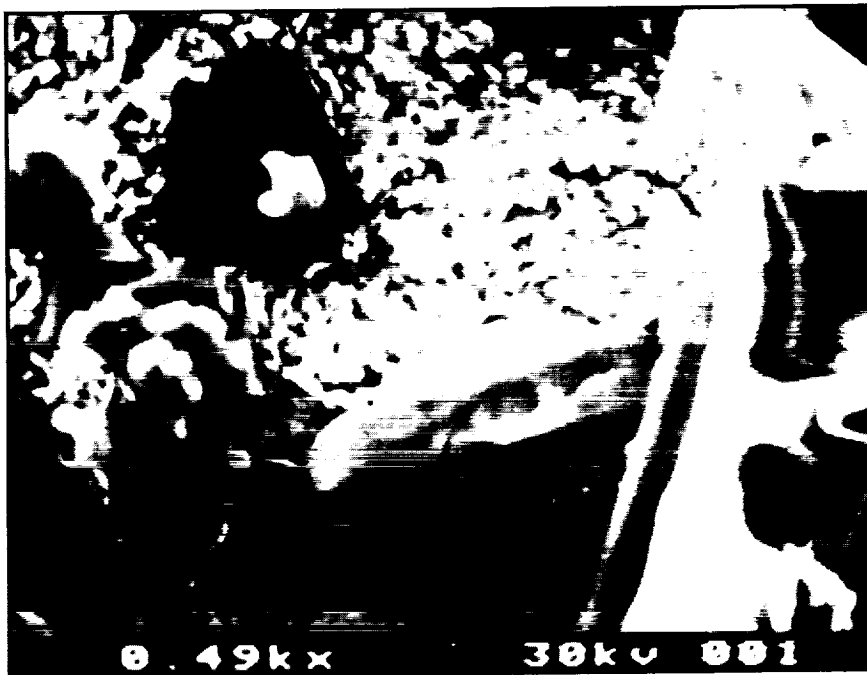
Micrograph 1.1

Micrograph 1.4
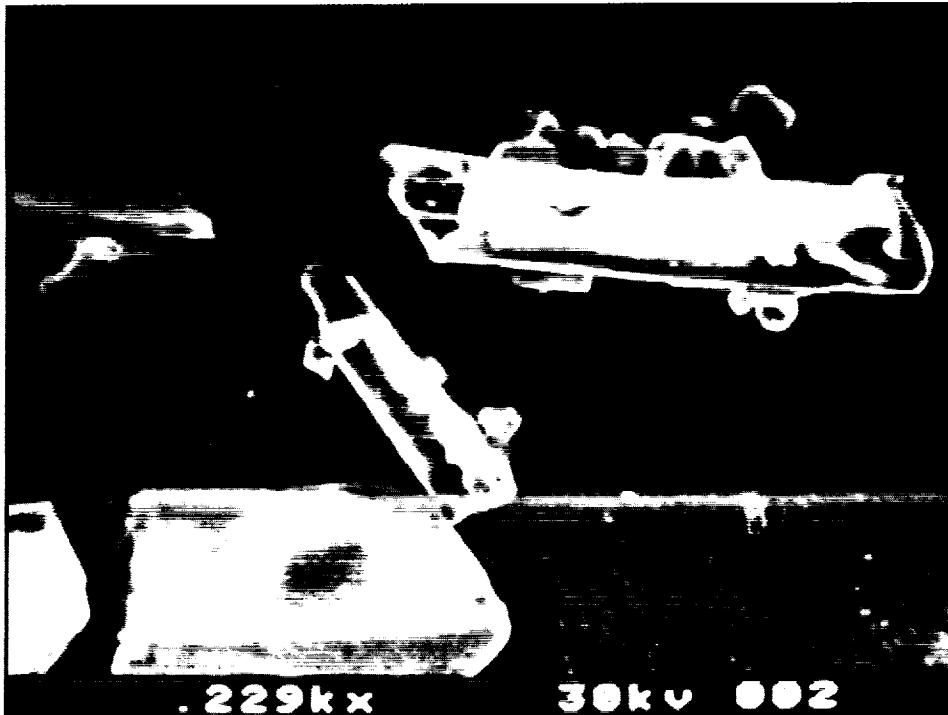
Micrograph 2.11

Micrograph 3.2
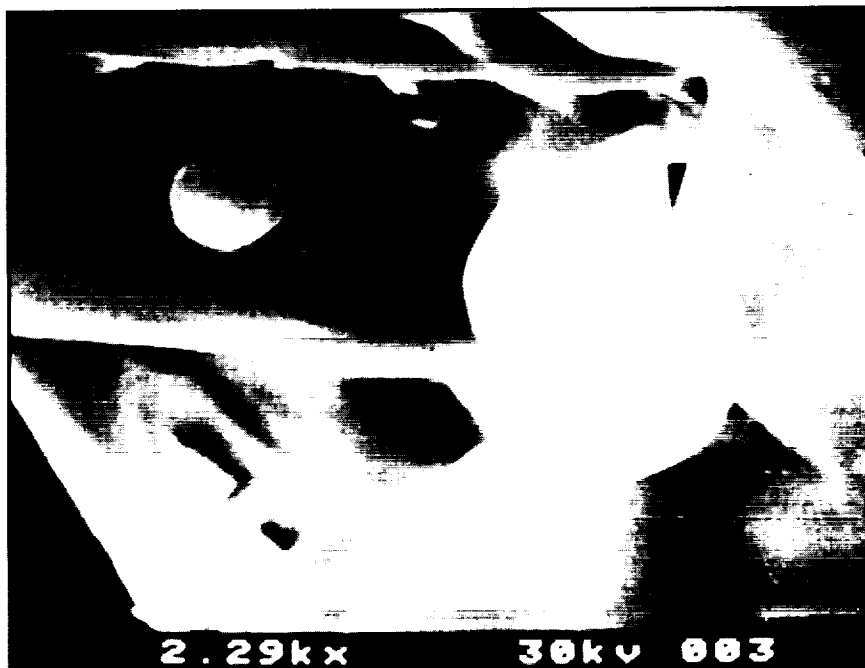
Micrograph 3.4

Micrograph 3.8
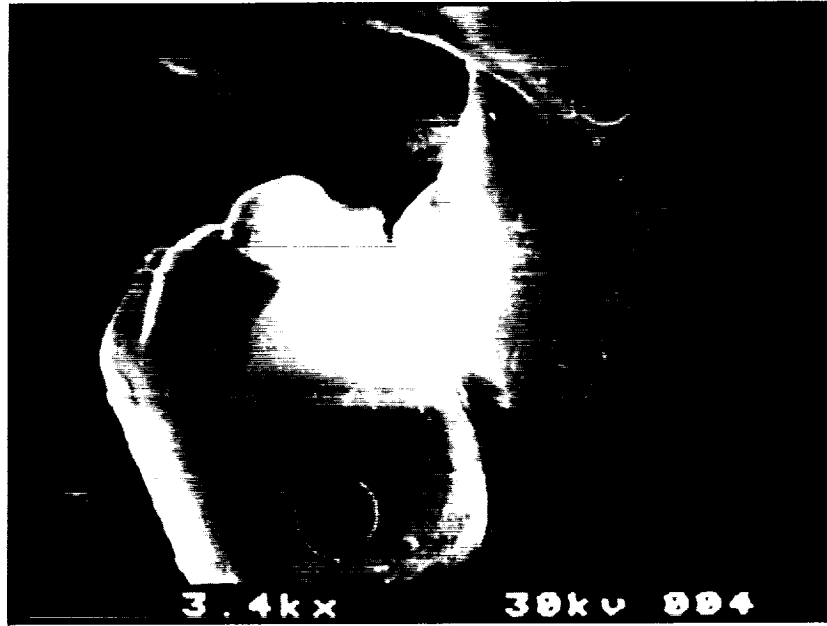
Micrograph 3.9

Micrograph 4.13