

# HUMO-NANOTUBE MEMBRANE RELATION WITH BIOPOLYMERS

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## PREFACE

With the turn of the century a flurry of activities can be noticed advancing humic acid chemistry into new directions. At that time, the micellar, supramolecular and nanotube membrane concepts were launched one after another and have been received with subdued criticism. The biopolymer concept that has dominated the science of humic acid for more than a century tends to be considered outdated by some. Perhaps because of apparent biopolymer fatigue, new concepts were anticipated by the scientists tired of the conventional theory. Claims of the concept's inability to come up with a molecular weight representing humic substances were in fact one of the major issues of concerns. Hence, many of the professionals and experts are apparently anxious to see fresh ideas, capable of propelling humic acid chemistry into new directions in accordance to recent spectacular advances in biotechnology, space and computer sciences. The established biopolymer models start with the degradation and depolymerization of large plant polymers into smaller fragments, down to micro-, nanometer and even molecular sizes more likely varying as a continuum. The idea is then that humic substances arise from the polymerization and condensation of the plant degradation products. In contrast, the new concepts are based on the principles of supramolecular chemistry, applying the theory of natural molecular self assembly without artificial guidance in formation of humic substances by the small degraded plant fragments. The latter are associated by weak bonds in the humic assemblages, which exhibit some orderly micelle- or membrane-like structures. Only a limited group of people tends to support the idea of a structureless, randomly arranged, self assembly model. In both the biopolymer and the newer self assemblage concepts, the possibility exists for some repolymerization of the broken fragments to occur during the humification process.

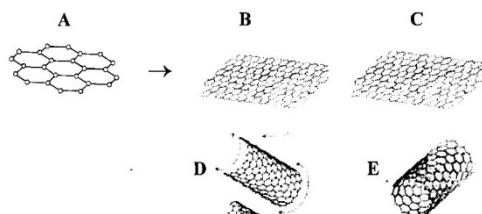
## Nanochemistry and Nanoparticles

The nanotube membrane concept is introduced in 2011 by Tan as a result of his discovery of nanotube and nanotube membrane structures of humic acids in his scanning electron microscopic (SEM) investigations (Tan, 1985; 2011a & b). The principles of *nanochemistry* are now applied in explaining formation of humic substances with such characteristic structural features. Nanochemistry is the new-

est discipline of chemistry examining assemblies and reactions of molecules at the scale of 1 nanometer, nm, ( $= 1 \times 10^{-9}$  m) to 1000 nm (Cademartiri and Ozin, 2009; Prasad, 2008). These small particles, called *nanoparticles*, are considered to have the capacity to self assemble spontaneously into assemblies varying widely in length and size from nanometers to micrometers ( $\mu\text{m}$ ). The process, known as *nanofabrications*, is expected to create supramolecular associations with distinct forms of structures. Therefore, contrary to Piccolo's (2002) concept of randomly produced assemblies, nanofabrications yield assemblies with well ordered identifiable structures. At the smallest end of the size scale they may often appear as clusters, whereas at the other (coarser) end of the size scale, the assemblies can take the shape of tubes, spheres, rods, and/or fibers, just to name a few. Hence, they are often named according to their characteristic shape and form. *Nanotubes* exhibit tubular structures and can be produced artificially or can also occur naturally. They are usually distinguished into several types, e.g., carbon nanotubes, membrane nanotubes (*cytonemes*), nanotube membranes, and nanofibers as in assemblies of peptide amphiphiles, and more. Carbon nanotubes are carbon atoms arranged as tubes and are generally  $\approx 20,000$  times thinner than human hair, but can range from 1  $\mu\text{m}$  or less to a few millimeters in length. They are generally formed by curling or warping of monolayers of graphite, called *graphene*. The process of warping can also yield imperfect tubes, hence the carbon nanotubes can assume many shapes and forms, like for example, sheets, ribbons, ellipsoids and other related bended nanostructures (Figure 1). The term "tube" implies that the particles should be tubular in shape, hence the name *fullerene* is apparently used to cover the group of nanotubes with the various shapes and forms.

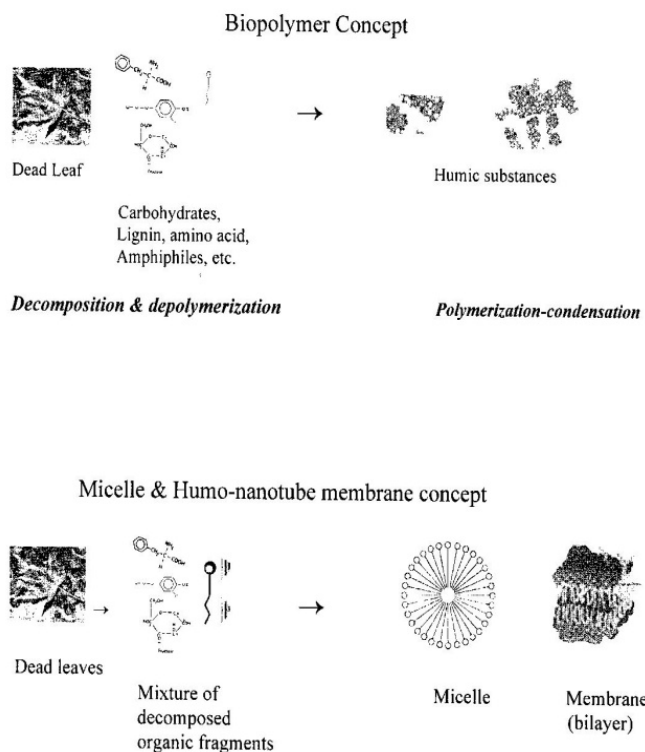
### Nanotube Membranes and Micelles

Nanoparticles containing both hydrophilic properties at one end and hydrophobic characteristics at the other end — known in colloid chemistry as *amphiphiles* (Tan, 2011) — are of particular interest in the formation of micelles and membranes in humic acid chemistry. The micellar concept in humic acid science was introduced by Wershaw (1986; 1999) and examined by Tan (2011a & b), who called the process of micelle formation *micellization*, and also showed that the micelles formed can assume different sizes and shapes, from single spheres, rectangulars to cylinders and bilayers. The bilayers of micelles are called *membranes*. Nanotube membranes can also take the form of open-ended single nanotubes or can also be composed of an array of nanotubes arranged perpendicularly to the surface of a micellar film matrix like the cells of a *beehive honeycomb*. Because honeycomb structural features have been discovered in recent humic analyses by SEM (Tan, 2011b), the micellar concept is extended and applied at the nano- and micrometer scale by the present author. As explained originally by Wershaw, decomposition of plant residue provided a great amount of small broken decomposed fragments. Some of them are

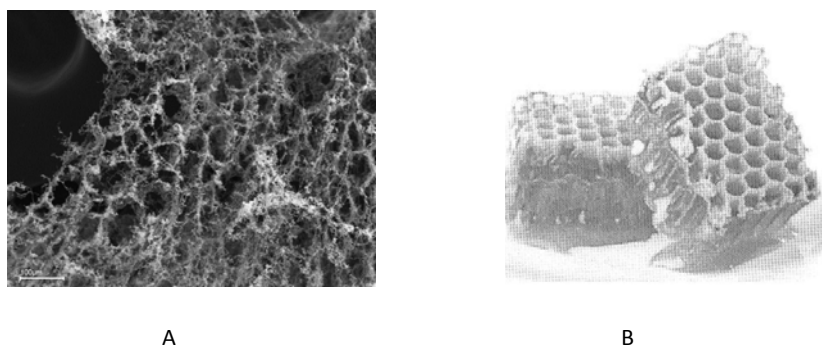


**Figure 1** Examples of different types of carbon nanotubes formed from graphene: (A) Graphene, enlarged by author's hand drawing to show the hexagonal arrangement of carbon atoms, resembling benzene and phenolic structures; (B) Single nanotube sheet showing relation with grapheme; (C) Bilayer, considered a membrane; (D) Graphene warped into a "curled" nanotube; (E) Rolled-up into a tubular nanotube.

Sources: [http://en.wikipedia.org/wiki/Nanotube\\_membrane/](http://en.wikipedia.org/wiki/Nanotube_membrane/), accessed 12/15/12; Hurlbut and Klein (1971); <http://www.sciencedaily.com/releases/2005/11/051104085644.htm> accessed 1/1/2013.



**Figure 2** Humification processes by: (Top) Biopolymer Concept illustrating direct condensation-polymerization of small decomposed organic fragments; (Bottom) Micellar and Membrane Concepts showing formation of micelles and membranes. The micelle is the humic substance by Wershaw's (1986) concept. The size of the micelle is determined by its radius, which equals the length of the amphiphile. In the humo-nanotube concept it is  $\approx 2-10$  nm. The number of amphiphiles determines the mass of the micelle. The thickness of the membrane above is  $2x$  the length of the amphiphile.



**Figure 3** (A) Scanning electron micrograph of humic acid extracted from lignite (Tan, 2011b) showing nanotube membrane structures resembling a beehive honeycomb as shown in (B)

in the forms of amphiphiles which in solution can aggregate to form micelles, but in the presence of clay minerals can form bilayers of micelles, called membranes by Wershaw. These micelles and membranes are Wershaw's idea of humic substances. According to the older biopolymer concept, the plant degradation fragments would react, and the reaction products are then subjected to condensation-polymerization reactions producing the humic substances. In polymer chemistry, a *condensation-polymerization reaction* is polymerization with the loss of  $H_2O$  — condensation— in the process. The two different humification processes are illustrated for comparison in Figure 2. The version of the biopolymer concept in the Figure above relates perhaps to the AC (*abiotic condensation*) concept presented by Hedges (1988). Most of the scientists consider humic substances to be new organic compounds in soil humus, synthesized by processes involving *polymerization* (Schnitzer and Khan, 1972; Flaig, 1975; Stevenson, 1994). Since many of the original plant materials are biopolymers, often the term *biopolymer concept* is used for the humification process instead of *polymerization concept*. The authors above and many others meant to indicate with this concept that humic acid is synthesized using the small fragments. Degradation of organic matter is a required prerequisite for the creation of these “precursors,” or raw materials. However, the polymerization (biopolymer) concept does not consider humic acid a slightly degraded form of a bio- (plant) polymer as suggested by Hedges (1988) in his *biopolymer degradation* (BD) concept. It is difficult to realize or assume a broken weathered lignin particle as a humic acid molecule. Hedges' (1988) BD concept is based on a different rationale because of his

idea for his “humic acid” to decompose and be reconstructed again into humic acid (see Figure 1, page 47 of the article).

### Humo-Nanotube Associations

The great variety of nanotubes grouped under the name of fullerene as discussed above, including nanotube fibers, nanotube micelles and membranes, occur in nature. They can be formed by the decomposition of plant and animal tissue. As indicated above, decomposition of plant and animal tissue will break them down into smaller fragments. The large plant biopolymers are depolymerized in the process, yielding broken fragments of polymers, oligomers, monomers, and smaller particles. In the author’s opinion the decrease in particle sizes looks more likely as a continuum. The decomposition process will no doubt also produce a lot of nanoparticles, capable of self assembling. The presence of peptides and other amphiphilic nanofibers, as indicated earlier, is needed in the formation of nanotube membranes. Together with carbon nanotubes they are essential in the production of humic substances. The hexagonal arrangements of carbon in the carbon nanotubes — closely resembling benzene and phenol monomer structures — are providing the aromatic carbon structure, whereas the peptide nanofibers and membranes satisfy the nitrogen requirement for the synthesis of humic substances. This concept looks closely related to the conventional ligno-protein or biopolymer theory by underscoring polymerization involving strong intermolecular chemical bonding holding the humic molecules together. However, the humo-nanotube concept suggested by the present author considers molecular self assembly with weak chemical bonds as the main forces in formation of humic substances. In the process, some repolymerization of the small fragments may perhaps also take place. Evidence for the humo-nanotube associations in natural ecosystems has been presented by Tan (2011a & b; 1985). In his most recent analysis of humic acid by scanning electron microscopy, the presence of the distinctive honeycomb pattern of a beehive (Figure 3) is clearly demonstrated. The humo-nanotube membrane structure is presumably the most stable thermodynamic association that can be attained by self assembly. Such an orderly structural pattern relates better than Piccolo’s random bundles in explaining issues of consistent carbon and nitrogen contents and reproducible spectroscopic features of humic substances published in various journals. The sizes of the humic micelles and membranes can be calculated as indicated in Figure 2, providing perhaps the key toward solving the issue of molecular weights.

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