Microscopy and spectroscopy characterization of carbon nanotubes functionalized with Spirulina for application in artificial photosynthesis.

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Recently there is a growing interest in the search for new alternative and sustainable energy sources. The combination of semiconductors with photocatalytic biological materials represents a novel alternative for hydrogen production by means of water splitting. Spirulina alga (*Arthrospira máxima*) is a microorganism with various pigments, such as chlorophyll a, b and phycocyanin, that allow the development of photosynthetic processes. These pigments act as antennas that capture the required photons for the photosynthetic processes. Spirulina nanoparticles can be produced from dry algae. They promote an increase of the electronic transfer efficiency when used to functionalize carbon nanotubes. Thus, the aim of this work is to functionalize single wall carbon nanotubes (SWCNT) with Spirulina nanoparticles that work as antenna to harvest sunlight for an artificial photosynthesis device and produce H_2.

SWCNT were purified and activated with a sulfo-nitration process and functionalized by adsorption of Spirulina nanoparticles by means of ultrasound. The obtained biocatalyst material was characterized by High Resolution Electron Scanning Microscopy (HRSEM), High Resolution Electron Transmission Microscopy (HRTEM), Energy Dispersion Spectroscopy (EDS), UV-Vis Diffuse Reflectance, Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Emitted Photoelectron Spectroscopy (XPS). Additionally, the system was characterized by electrochemical techniques to evaluate photo-electrocatalytic processes. HRSEM and HRTEM corroborated the functionalization of the SWCNT with the Spirulina nanoparticles. While, EDS allowed to characterize the distribution of the chemical elements of Spirulina in the nanotubes. C, N, O, Ca, Mg, P, Fe and Cr were detected. These elements are attributed to the carbohydrate, protein and mineral content in Spirulina, especially Mg corresponds to the prosthetic group of chlorophylls a and b that function as photonic antennas. FTIR complements the characterization of functional groups characteristic of Spirulina on the SWCNT (Carbohydrates: 1530 cm^{-1}, Mg bounded to carbohydrates 1658 cm^{-1}, amides 1030 cm^{-1}). Uv-Vis spectroscopy of diffuse reflectance was useful to determine the band gap of Spirulina (1.7 eV), which has a value similar to other semiconductors used for artificial photosynthesis (GaAs, CdSe). The photo-electrocatalytic tests demonstrate that the Spirulina-SWCNT heterostructure is a suitable photocatalytic system, since it provides a response rather similar to traditional semiconducting systems. Likewise, the chlorophyll and phycocyanin contents allow that this biofotocatalyst can be used in the visible range. The evolution reaction of H_2 was measured by linear voltammetry. It generates a slope of Tafel 235 mV / dec, this shows that the device has a performance similar to the new systems of artificial photosynthesis based on inorganic compounds. These characteristics represent important advantages in the design of low cost artificial photosynthesis devices. The biological character photocatalysts that are being currently investigated are abundant and not limited by high cost and rarity as in the case of noble metals. Finally, both microscopy and spectroscopy techniques used were efficient for the characterization of the artificial photosynthesis system based on biological materials.

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