Interaction and Redox Processes between Cytochrome c and Semiconductors: Applications in Spintronics and Micro/Nanorobots

Spintronics is developing technology in which information is carried by both electronic charge and electron spin.(1–5) The spintronic-based electronics combine standard microelectronics with spin-dependent effects. The spin effect results from the interaction between the spin of the carriers and external magnetic fields and breaks the paradigm in which storage is based on magnetism and the information processing is based on charge. The field of spintronic emerged fast since the discovery of giant magnetoresistance (GMR). GMR discovery in 1988 awarded A. Fert and P. Grunberg with the Nobel Prize in Physics in 2007. The more recent advance in spintronic was the chiral induced spin selectivity (CISS) effect. The CISS effect allows the injection of spin-polarized current without the use of a permanent magnetic layer and results that electron transport is spin-selective through chiral molecules.(6) The CISS effect is obtained with peptides since they are chiral molecules with a helical structure that acts as spin filters. Cytochrome c is an interesting molecule for application in energy conversion and spintronics.(7–9) Dias et al. published an study demonstrating the molecular interaction of cytochrome c with two TiO_2 structures: P25 TiO_2 NPs and titanate nanotubes.(9) Both the TiO_2 materials promoted photoreduction of the cytochrome c heme iron that was re-oxidized by peroxides and could be reversibly reduced. In these systems, the UV-illumination of the semiconductor materials promotes the formation of the electron (e^-) hole (h^+) pair and a similar processes occurred with nanoparticulated hematite.(8) The cytochrome/semiconductor system is a mimetic of the photosynthesis. The efficient reduction of cytochrome c by the semiconductors suggests its action as a spin filter. The mechanism of water splitting promoted by semiconductors has a competitive production of hydrogen peroxide and molecular oxygen having both the hydroxyl radicals as intermediates. The hydroxyl free radical can combine to form hydrogen peroxide or molecular oxygen and two protons that accept electron of the conduction band and is reduced to hydrogen gas. However, in the latter process, molecular oxygen is produced in the singlet excited state adding an energy barrier of 1eV to the hydrogen production. The presence of a chiral molecule such as cytochrome c can act as a spin filter in the electron transfer favoring the production of the ground state triplet molecular oxygen. The capacity of cytochrome c act as a spin filter in these systems is an interest of our group.

The interaction of proteins and whole cells with metallic nanostructures for the development of nano/micromotors and robots is also another important question under investigation in our group.(10) An important characteristic of micro/nanorobots for biological applications is biocompatibility that can be attained with the use of cells and biomaterials such as proteins. In this regard, our research group got functionalization of microtubes and microwires decorated with gold nanoparticles with fluorescent PEG-SH and adherence of two cell lineages smooth muscle cells and keratinocytes.

The Fe_2O_3/Fe_3O_4 microtubes decorated with gold nanoparticles were functionalized with FTIC-PEG-SH 8000 (fluorescein polyethyleneglycol) (Fig 2).

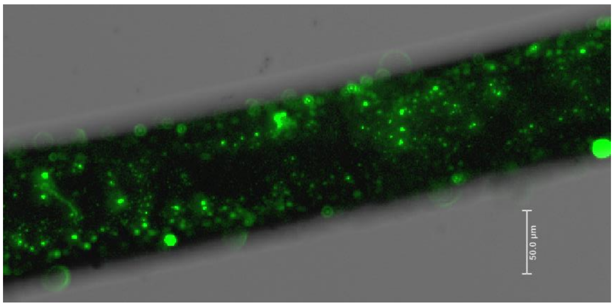

Figure 2. Snapshot of merged phase contrast and fluorescence images of the Fe_2O_3/Fe_3O_4 microtubes functionalized with FTIC-PEG-SH.

The Fe_2O_3/Fe_3O_4 microtubes decorated with gold nanoparticles exhibited excellent biocompatibility and allowed the growing and adherence of aortic smooth muscle cells and keratinocytes on their surfaces.

The applications of MNRs are extensive such as theranostics, remediation, nanofabrication, repair of materials among others. Among the energy sources that MNMs can serve, light is highly attractive.(4) Light-powered MNMs can utilize energy from an external source and surrounding chemicals to achieve efficient propulsion through a photocatalytic process. These devices thus constitute the photo micro/nanomotor (FMNMs). The basic principles that respond by the self-propulsion of the photocatalytic MNMs can be explained by the Janus model (Fig. 4).

Figure 5. Self-propelling mechanisms of Janus micromotors. From left to right until the third representation the photocatalytic mechanisms are presented, and in the central representations, the oxygen is formed by the oxidation of hydrogen peroxide in solution. In the right representation, irradiation with infrared light on the nanostructured gold layer creates a thermal gradient due to the plasmonic effect. Warming promotes agitation of water molecules that generate one-way movement.

In the present project we are studying the interaction and redox processes of cytochrome c with the hematite surface of microtubes and microwires, hematite/iron/hematite foils as well as ZnO/Zn plates. We had preliminary results of photo-induced electron transfer from nanoparticulate hematite to cytochrome c, as well as the effect of isotopic substitution of water, i.e., deuterium dioxide. Now we started the studies with cytochrome c and the hierarchically layered Fe_2O_3/Fe_3O_4 microtubes regarding the adsorption and electron transfer processes.

In this condition, the protein that remained in the solution was completely reduced. Replacement of water by deuterium dioxide impaired the heme iron reduction (Fig. 5).

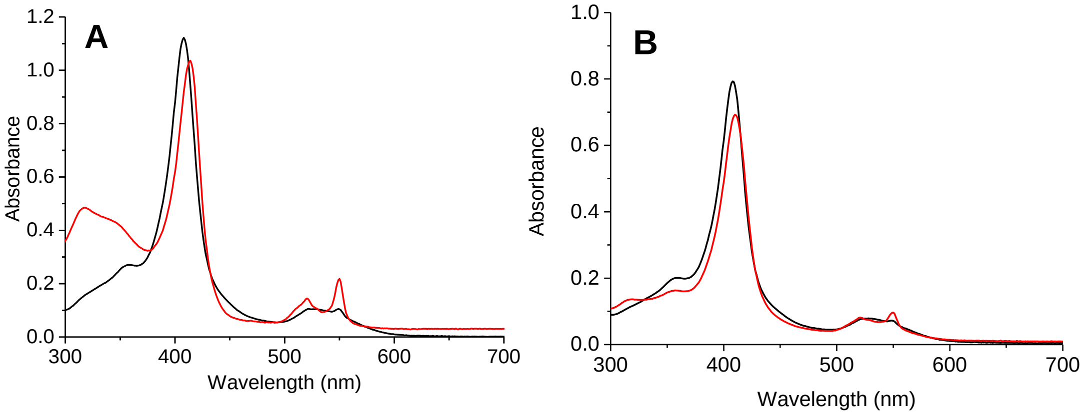

Figure 5. Electronic absorbance spectra of oxidized (blue line) reduced (red line) cytochrome c. Panel A shows the spectra before and after irradiation with sunlight simulator and panel B shows the spectra before and after irradiation in deuterium oxide.

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