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Biologically Derived Nanoparticle Arrays via an Electrochemical Reconstitution of Ferritin and Their Applications

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The immobilization of biomolecules on electrode surfaces is of great importance and interest in research areas for biosensors<sup>1</sup> and bioelectronics<sup>2</sup> applications. The ferritin used in this work is a natural iron storage protein that presents a high degree of structural similarity across a wide range of biological species.<sup>3</sup> The ferritin molecule is

- composed of 24 organic subunits that build <u>a</u> segmented hollow protein shell with an outer diameter of 12.5 nm and an inner diameter of 7.5 nm. The mineral core of naturally existing ferritins is composed of an antiferromagnetic iron oxide (ferrihydrite) within its hollow and spherical protein interior.<sup>4</sup>
- In this work, nanoparticle arrays biologically derived from an\_electrochemically-controlled, site-specific biomineralization were fabricated on a gold substrate through the immobilization process of biomolecules. The work reported herein includes the immobilization of ferritin with various surface modifications, the electrochemical biomineralization of ferritins with different inorganic cores, and the fabrication of self-assembled 2-D arrays with thiolated ferritin (see Fig. 1). Protein immobilization on the substrate is achieved by anchoring thiolated ferritins with dithiobis-N-succinimidyl propionate (DTSP). A reconstitution process of site-specific electrochemical biomineralization with a protein cage loads ferritins with different core materials (see Fig. 2). The ferritin acts as a nano-scale template, a biocompatible cage, and a separator between the nanoparticles. Biomineralization and electrochemical characterization of some other metals (Pt, Co, Mn, and Ni) in the ferritin cavity are also reported. This first demonstration of electrochemical reconstitution of biomolecules provides a new tool for biomineralization and opens the way to fabricate biologically derived nanoparticle arrays.

The nano-sized metal-cored ferritins on a gold substrate displayed a good electrochemical activity for the electron transport and storage, which is suitable for bionanobattery applications.

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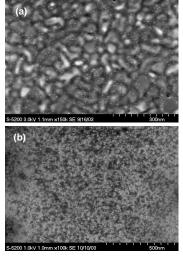
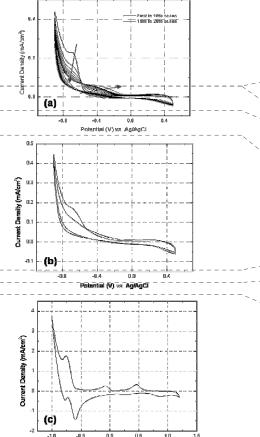


Figure 1. FE-SEM images of immobilized ferritin on (a) DTSP and mercaptopropanol (MPOH) modified Au electrode and (b) self-assembled monolayer of thiolated ferritin.



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site-specific electrochemical biomineralization with a protein cage, ferritins are

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Figure 2. Cyclic voltammograms of immobilized ferritin on (a) DTSP and MPOH-modified Au electrode in 0.05 M phosphate buffer (pH 7.5) (b) containing with 0.01 M EDTA. (c) CV of platinum reconstituted ferritin in 0.05 M phosphate buffer.

al (V) vs. Ag/AgCl