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## Multifunctional silk: from fabrication to application

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Abstract		
<p>Silk fibers offer untapped internal structures to template the formation of nano-objects and active coatings. So far, access to all or part of the internal and organized structures has been a significant challenge. The aim of the thesis is, therefore, to identify and exploit silk templating ability to create value-added multifunctional hybrid materials with enhanced conductive and catalytic properties. The application of nanotechnology in textiles is limited by the difficulties of loading the textile fibers with nanoparticles (NPs), and by the uncontrolled leakage of the loaded NPs. We first demonstrate using supercritical carbon dioxide (sc-CO<sub>2</sub>) impregnation that the four major commercially available Indian silk (mulberry, eri, tasar and muga) could be loaded without leakage with standard gold NPs sized between 5-150 nm.</p> <p>Next, we developed a one-step synthesis and impregnation of metal oxides in the silk fibers using mild sonication. Here we sonochemically reduce potassium permanganate (KMnO<sub>4</sub>) to manganese oxide (MnO<sub>2</sub>) in silk fibers. The obtained MnO<sub>2</sub>-Silk hybrid fibers effectively decomposed hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and oxidized the typical horseradish peroxidase substrates, such as o-phenylenediamine (OPD), and 3,3',5,5'- tetramethylbenzidine (TMB) in the presence or absence of H<sub>2</sub>O<sub>2</sub>. The oxidative properties of MnO<sub>2</sub>-Silk fiber hybrid showed an enzyme-like behavior for the catalase-like activity, oxidase-like activity, and peroxidase-like activity. The operational stability of the MnO<sub>2</sub>-Silk fiber hybrid over ten cycles showed a constant residual activity of about 25-30 % after 2-3 cycles indicating that MnO<sub>2</sub>-Silk fiber hybrid could be used as a satisfactory oxidoreductase enzyme mimics. We used potentiometric titration to understand the surface charges on the MnO<sub>2</sub>-Silk hybrid materials. We identified the reactive species as <math>Mn_{1-x}^{4+}Mn_x^{3+}O_{2-x}(OH)_x</math> with a pK of approximately 5.2.</p> <p>We further developed an <i>in-situ</i> UV-Visible spectroscopy based method to study the mechanism of formation of MnO<sub>2</sub> on a silk film and its associated enzymatic activity. The results suggested a three components route for sonication and auto-reduction (as control) to form MnO<sub>2</sub>-Silk from KMnO<sub>4</sub>. Overall, we found that the smaller size, more mono-dispersed, and deeper buried MnO<sub>2</sub> NPs in silk film prepared by sonication, conferred a higher catalytic activity and stability to the hybrid material.</p> <p>The dimensions and oxidation states of the MnO<sub>2</sub>-Silk hybrid material were determined by the use of X-rays structural and spectroscopic methods: a small-angle X-ray scattering (SAXS), anomalous small-angle X-ray scattering (ASAXS), and near-edge X-ray absorption fine structure (NEXAFS). ASAXS allowed us to analyze the MnO<sub>2</sub> alone. We found that the MnO<sub>2</sub> NP had a size below 20 nm. NEXAFS (pre-peak and main peak) confirms the formation of Mn(IV) oxide.</p> <p>Finally, we demonstrated that the combination of scCO<sub>2</sub> impregnation and sonochemistry could yield new or improved multifunctionality. Here we fabricated a soft working electrode for the simultaneous degradation and detection of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The multifunctional silk hybrid showed an enzyme-like behavior for the degradation of H<sub>2</sub>O<sub>2</sub> with a Km of about 13 mM. Together these studies suggest that judicious access and use of silk internal structures can enhance silk already remarkable properties.</p>		
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