Cellulose Nanocrystals: Novel Templates for Synthesis of Nanostructures

Abstract. Biological systems such as proteins, viruses, or DNA have been most often reported as templates for the synthesis of functional nanomaterials, while the properties of widely available biopolymers, such as cellulose, have been much less exploited for this purpose. Here, we report for the first time that cellulose nanocrystals (CNC) can assist in the synthesis of metallic and semiconducting nanoparticle chains. A cationic surfactant, cetyltrimethylammonium bromide (CTAB), was critical for nanoparticle stabilization and CNC surface modification. Silver (Ag), gold (Au), copper (Cu), platinum (Pt), cadmium sulfide (CdS), zinc sulfide (ZnS), and lead sulfide (PbS) nanoparticles were synthesized on CNCs. The nanoparticle density and particle size were controlled by varying the CATB concentration, the pH of the salt solution, and the reduction time.

Keywords. Cellulose nanocrystals, functionalization, nanoparticles, surfactants.

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Introduction. The synthesis of functional nanomaterials through biominalization and biotemplating is attracting a tremendous amount of interest because it promises to achieve better control over positioning and to connect different functional nanostructures into complex nanodevices. Starting several years ago with the use of biomolecular structures such as viruses, proteins, or DNA, template synthesis of nanomaterials has received much attention in the scientific community. Although most of these molecules are difficult to obtain, natural biopolymer fibers, such as cellulose, are abundant in biomass and are easily accessible from a range of sources such as forest products, grasses, tunicates, reeds, or stalks. Cellulose-based materials are relatively cheap, renewable, abundantly available in a variety of forms, and endowed with hydroxyl groups accessible for chemical modification. The size and morphology of cellulose nanocrystals (CNCs) offer a useful template for the formation and design of nanostructures synthesis.

Figure 1. TEM images of Ag nanoparticle synthesis on tunicate CNC with a carbon-coated copper TEM grid substrate. Synthesis took place in the (a) absence of CTAB and (b) presence of CTAB. When CTAB is used, Ag precipitation takes place preferentially on CNC rather than on the TEM grid [2].

Fabrication of nanoparticles onto the surface of a biological template often uses electroless deposition techniques, in which the driving force for nanoparticle deposition relies on the difference between the redox potentials of the precursor salt and of the biomolecule template structure. However, CNC surfaces display mostly neutral hydroxyl groups, and the negatively charged sulfate groups on the CNC (as a result of sulfuric acid hydrolysis) may not interact with cations sufficiently to cause significant precipitation of nanoparticles on the CNC surface. This work has investigated the effect of adding a cationic surfactant, cetyltrimethylammonium bromide (CTAB), to facilitate nanoparticle precipitation on CNC surfaces.
1.6 Self-Assembly and Miscellaneous Applications

**Methodology.** A multi-step electroless deposition process was used to synthesize inorganic nanoparticles (Ag, Au, Cu, Pt, CdS, ZnS, PbS) on the surfaces of tunicate CNCs, as described in detail in [1,2]. The same synthesis procedure was used successfully for nanoparticle decoration of CNCs in two different types of configurations: a) CNCs were first deposited on a carbon-coated copper transmission electron microscopy (TEM) grid, and the resulting samples were used for TEM analysis; and b) CNCs were first dispersed in deionized water brought to an acidic pH, and the resulting samples were used for UV-vis analysis. The morphology and size of the nanoparticles deposited on CNC surfaces were characterized by TEM. The presence of a given inorganic material (Ag, Au, Cu, Pt, CdS, ZnS, PbS) on the CNC surface was confirmed by the electron energy-loss (EELS) spectrum and the UV-vis spectrum.

**Results.** It was demonstrated for the first time that by using a modified reductive deposition procedure involving the cationic surfactant CTAB, a reproducible procedure for nanoparticle decoration of tunicate CNC can be successfully designed [1,2]. The addition of CTAB promoted the formation of inorganic nanoparticles on the CNC surface (Figs. 1 and 2). The surface of the tunicate CNCs were decorated along its entire length with inorganic nanoparticles (Fig. 3). For the first time, a cationic surfactant (CTAB) was used, not only as a stabilizer of inorganic nanoparticles, but also as a vehicle for the positioning of these particles on the CNC surface. The nanoparticles were polydispersed, which was believed to result from a competing nucleation and growth mechanism that dominates their formation. The average size of the nanoparticles and their coverage on the CNC was controlled by varying the concentration of the surfactant and the salt solution and the reaction time and pH of the salt solution.

**Conclusions.** It is possible to synthesize inorganic nanoparticles (Ag, Au, Cu, Pt, CdS, ZnS, PbS) on the surfaces of tunicate CNCs with a high degree of surface coverage. The stabilizing properties of surfactants (CTAB) facilitated the fabrication of these inorganic materials. The results indicate that the same platform could be extended to serve as an alternative universal platform for engineering a variety of functional materials at the nanoscale.

**References**


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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!
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