Supporting Information

One-pot Green Synthesis of Anisotropic Silver Nanoparticles

Zeinab Hosseinidoust\textsuperscript{a,b,c,†}, Mohan Basnet\textsuperscript{a}, Theo G.M. van de Ven\textsuperscript{b,c}, Nathalie Tufenkji\textsuperscript{‡,a}

\textsuperscript{a}Department of Chemical Engineering, McGill University, Montreal, Quebec H3A 0C5, Canada
\textsuperscript{b}Department of Chemistry, McGill University, Montreal, Quebec H3A 2K6, Canada
\textsuperscript{c}Pulp & Paper Research Centre, McGill University, Montreal, Quebec H3A 2A7, Canada
\textsuperscript{†}Current affiliation: Department of Chemical Engineering, McMaster University, Hamilton, ON, Canada

\textsuperscript{‡}Corresponding Author. Phone: (514) 398-2999; Fax: (514) 398-6678; email: nathalie.tufenkji@mcgill.ca.
Scheme S1. (a) Schematic diagram showing the general workflow for the isolation of cellulose nanocrystals from cellulosic biomass. (b) Stylized representation of the structure of a cellulose fiber such as that found in wood pulp. (c) Structure of CNCs prepared via the two-step oxidation method and overall procedure for control of surface charge.
Table S1. Methods for synthesizing anisotropic silver nanostructures

<table>
<thead>
<tr>
<th>Reduction mode</th>
<th>Ag seed particle required?</th>
<th>Additive(s) to Ag⁺ ions</th>
<th>Solution</th>
<th>Duration</th>
<th>Ref.</th>
</tr>
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<tr>
<td><strong>Photochemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Visible light</td>
<td>yes</td>
<td>NaBH₄, trisodium citrate, stabilizers (BSPP⁺ or PVP⁺)</td>
<td>aqueous</td>
<td>hours/days</td>
<td>1-10</td>
</tr>
<tr>
<td>UV, γ-irradiation (λ &lt; 400 nm)</td>
<td>no</td>
<td>2-propanol, EDTA, polymeric surfactants</td>
<td>aqueous</td>
<td>-</td>
<td>11</td>
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<tr>
<td></td>
<td>no</td>
<td>organic capping reagent (e.g., nicotinic acid, formic acid, pyridine)</td>
<td>aqueous</td>
<td>minutes ³</td>
<td>12</td>
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<tr>
<td></td>
<td>yes</td>
<td>chemical stabilizers</td>
<td>aqueous</td>
<td>10 min</td>
<td>13</td>
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<tr>
<td>Microwave</td>
<td>no</td>
<td>CNCs</td>
<td>aqueous</td>
<td>5-30 min</td>
<td>this work</td>
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<td>Ultrasonic</td>
<td>no</td>
<td>PVP, DMF ⁴</td>
<td>organic</td>
<td>10-20 min</td>
<td>14</td>
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<td>Thermal</td>
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<td>DMF, PVP</td>
<td>organic</td>
<td>30 min</td>
<td>15</td>
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<tr>
<td></td>
<td>no</td>
<td>DMF, PEG ⁵</td>
<td>organic</td>
<td>10-20 min</td>
<td>16</td>
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<tr>
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<td>yes</td>
<td>NaBH₄, PVP, sodium citrate</td>
<td>aqueous</td>
<td>10 hrs ¹</td>
<td>17</td>
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<td>yes</td>
<td>NaBH₄, sodium citrate, ascorbic acid, and CTAB ⁶</td>
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<td>hours/days</td>
<td>18</td>
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<td>NaBH₄, trisodium citrate, PVP, and H₂O₂</td>
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<td>30 min</td>
<td>22</td>
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<td>Biological synthesis</td>
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<td><em>Pseudomonas stutzeri</em> AG259</td>
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<td>48 hrs</td>
<td>23</td>
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<td>Nanosphere lithography</td>
<td>N/A</td>
<td>polystyrene nanospheres</td>
<td>-</td>
<td>-</td>
<td>24, 25</td>
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</tbody>
</table>

²BSPP: Bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt solution, ³PVP: poly(N-vinyl-2-pyrrolidone), ⁴accompanied by boiling, ⁵DMF: N-dimethylformamide, ⁶PEG: poly(ethylene glycol), ¹accompanied by visible light photoreduction, ⁷CTAB: cetyltrimethylammonium bromide.
Figure S1. Photographs of colloidal dispersions of Ag nanoparticles for different samples in Table S1, (1) CNC-1, UV treated for 30 min + AgNO₃, (2) CNC-3, UV treated for 30 min + AgNO₃, (3) DCC + AgNO₃, (4) microcrystalline cellulose (MCC)+ AgNO₃, (5) only CNC-1, (6) only AgNO₃, (7) CNC-1+AgNO₃+ heat (no UV treatment). Images were recorded immediately after 1 hr of UV treatment except for samples 1 and 2 for which the images were taken after 30 min of incubation with AgNO₃ and sample 7 for which the image was recorded after 1 hr of heating at 40 °C.

Figure S2. UV-vis spectra for a UV-treated mixture of silver nitrate and Avicell microcrystalline cellulose beads.
Figure S3. TEM images for initial nanoparticle seeds showing no spherical particles after 5 mins of UV irradiation for AgNO₃ mixed with (a, b) CNC-1 (scale bars: 2 μm), (c, d) CNC-2 (scale bars: 1 μm and 0.5 μm, respectively), and (e) CNC-3 (scale bar: 200 nm). Panel (b) is a magnified section of panel (a) and panel (d) is a magnified section of panel (c).

Note: Because of the dispersed nature of the nanoparticles, higher magnification micrographs were very sparse and did not adequately represent the shape distribution of the population, whereas micrographs with magnification low enough to show a greater number of particles were not suitable to showcase the shape of the particles. Micrographs such as panel (e), with a high density of overlapping particles, were prepared by altering the sample preparation protocol for TEM and air-drying larger volumes of the sample on a single grid.
Figure S4. TEM images of three representative silver structures prepared with (a) CNC-1, (c) CNC-2 and (e) CNC-3, along with the corresponding EDS spectra showing a clear Ag peak for each particle (b, d, f).
Figure S5. Particle size distribution histograms for silver particles formed using (a) CNC-1, (b) CNC-2, and (c) CNC-3. Particle size was determined by analysis of over 200 particles in TEM images. The diameter plotted is the equivalent spherical (i.e., the diameter of a sphere that would surround the particle, fitted and measured using ImageJ).

Figure S6. (a) Normalized absorption ($A_{664}$ nm at each time point divided by $A_{664}$ nm at time zero) versus time for degradation of methylene blue (18.2 mg/L) by NaBH$_4$ in the presence of silver nanoparticles synthesized using a mixture of AgNO$_3$ and CNC-1, CNC-2, CNC-3, or rhamnolipids (RL) compared to that in the absence of silver catalyst (control, no Ag); (b) normalized absorption for methylene blue degradation in the presence of each CNC fraction alone, without AgNO$_3$. (c) Specific reaction rate $\left(\frac{1}{S} \frac{d(C)}{dt}, \frac{A}{A_0}, S: catalyst surface area\right)$ versus time.
Figure S7. Photographs of colloidal dispersions of Ag nanoparticles. All samples were UV treated for 30 min. (1) CNC-3 + AgNO₃, both solutions were degassed to remove dissolved oxygen before mixing and UV treatment, (2) CNC-3 (not carboxylated) + AgNO₃, (3) CNC-3, UV treated for 30 min + AgNO₃, kept in dark, (4) CNC-3, UV treated for 30 min + AgNO₃, not kept in dark, (5) CNC-1, UV treated for 30 min + AgNO₃, not kept in dark, (6) rhamnolipids + AgNO₃. Images were recorded 4 hrs after UV treatment except for samples 3 and 4 for which the images were taken after 4hrs of incubation with AgNO₃.

Figure S8. Extinction spectra for a mixture of pre-UV treated (a) CNC-1 and (b) CNC-3, with silver nitrate. The CNCs were UV-treated for 30 min and spectra were recorded at different time points after being mixed with silver salt.
Figure S9. TEM images for initial nanoparticle seeds showing no spherical particles after 5 mins of UV irradiation for (a, b) CNC-1, (c-e) CNC-2, and (f-i) CNC-3.
References