Electronic Supplementary Material (ESI) for Environmental Science: Nano.
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Supporting Information

One-pot Green Synthesis of Anisotropic Silver Nanoparticles

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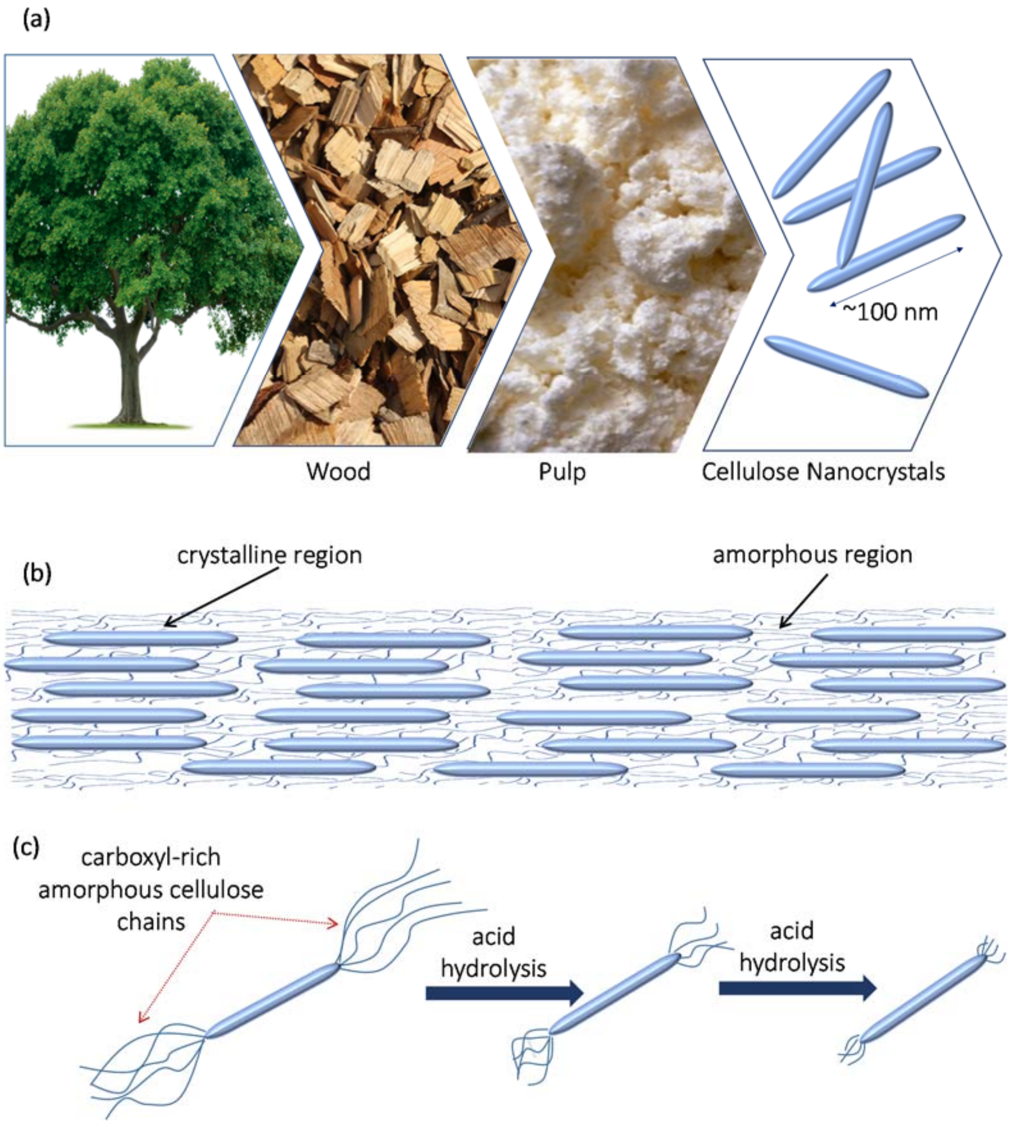

Scheme S1. (a) Schematic diagram showing the general workflow for the isolation of cellulose nanocrystals from cellulosic biomass. **(b)** Stylized representation of the structure of a cellulose fiber such as that found in wood pulp. **(c)** Structure of CNCs prepared via the two-step oxidation method and overall procedure for control of surface charge.

Table S1. Methods for synthesizing anisotropic silver nanostructures

Reduction mode	Ag seed particle required?	Additive(s) to Ag$^+$ ions	Solution	Duration	Ref.
Photochemical					
Visible light	yes	NaBH$_4$, trisodium citrate, stabilizers (BSPP[a] or PVP[b])	aqueous	hours/days	1-10
UV, ***γ-irradiation (λ < 400 nm)***	no	2-propanol, EDTA, polymeric surfactants	aqueous	-	11
	no	organic capping reagent (*e.g.,* nicotinic acid, formic acid, pyridine)	aqueous	minutes[c]	12
	yes	chemical stabilizers	aqueous	10 min	13
	no	CNCs	aqueous	5-30 min	this work
Microwave	no	PVP, DMF[d]	organic	10-20 min	14
Ultrasonic	no	DMF, PVP	organic	30 min	15
Thermal	no	DMF, PVP	organic	10-20 min	16
	no	DMF, PEG[e]	organic	17 hrs	17
	yes	NaBH$_4$, PVP, sodium citrate	aqueous	10 hrs[f]	18
	yes	NaBH$_4$, sodium citrate, ascorbic acid, and CTAB[g]	aqueous	hours/days	19-21
	yes	NaBH$_4$, trisodium citrate, PVP, and H_2O_2	aqueous	30 min	22
Biological synthesis	no	*Pseudomonas stutzeri* AG259	aqueous	48 hrs	23
Nanosphere lithography	N/A	polystyrene nanospheres	-	-	24, 25

[a]BSSP: Bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt solution, [b]PVP: poly(N-vinyl-2-pyrrolidone), [c]accompanied by boiling, [d]DMF: N-dimethylformamide, [e]PEG: poly(ethylene glycol), [f]accompanied by visible light photoreduction, [g]CTAB: cetyltrimethylammonium bromide.

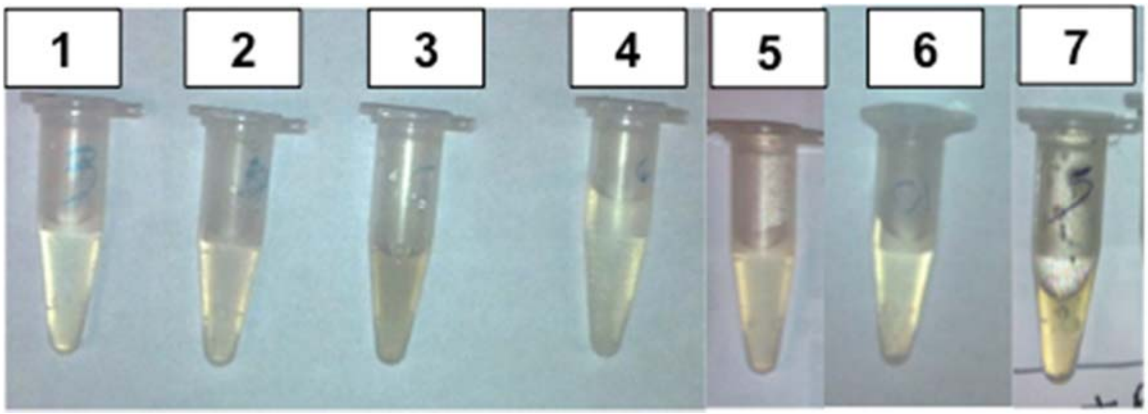

Figure S1. Photographs of colloidal dispersions of Ag nanoparticles for different samples in Table S1, (1) CNC-1, UV treated for 30 min + $AgNO_3$, (2) CNC-3, UV treated for 30 min + $AgNO_3$, (3) DCC + $AgNO_3$, (4) microcrystalline cellulose (MCC)+ $AgNO_3$, (5) only CNC-1, (6) only $AgNO_3$, (7) CNC-1+$AgNO_3$+ 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 $AgNO_3$ and sample 7 for which the image was recorded after 1 hr of heating at 40 °C.

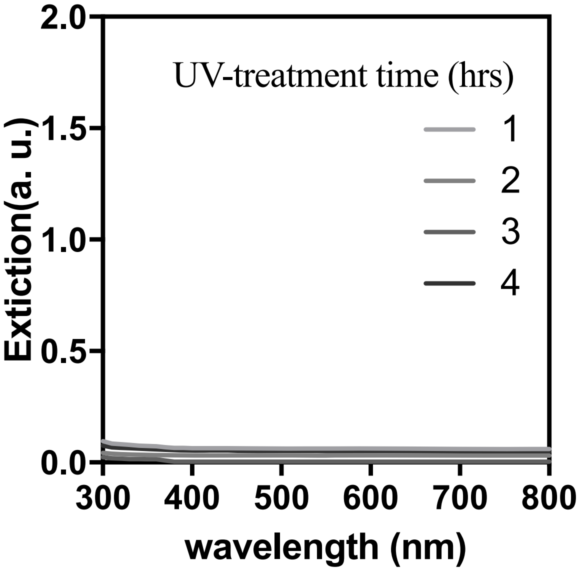

Figure S2. UV-vis spectra for a UV-treated mixture of silver nitrate and Avicell microcrystalline cellulose beads.

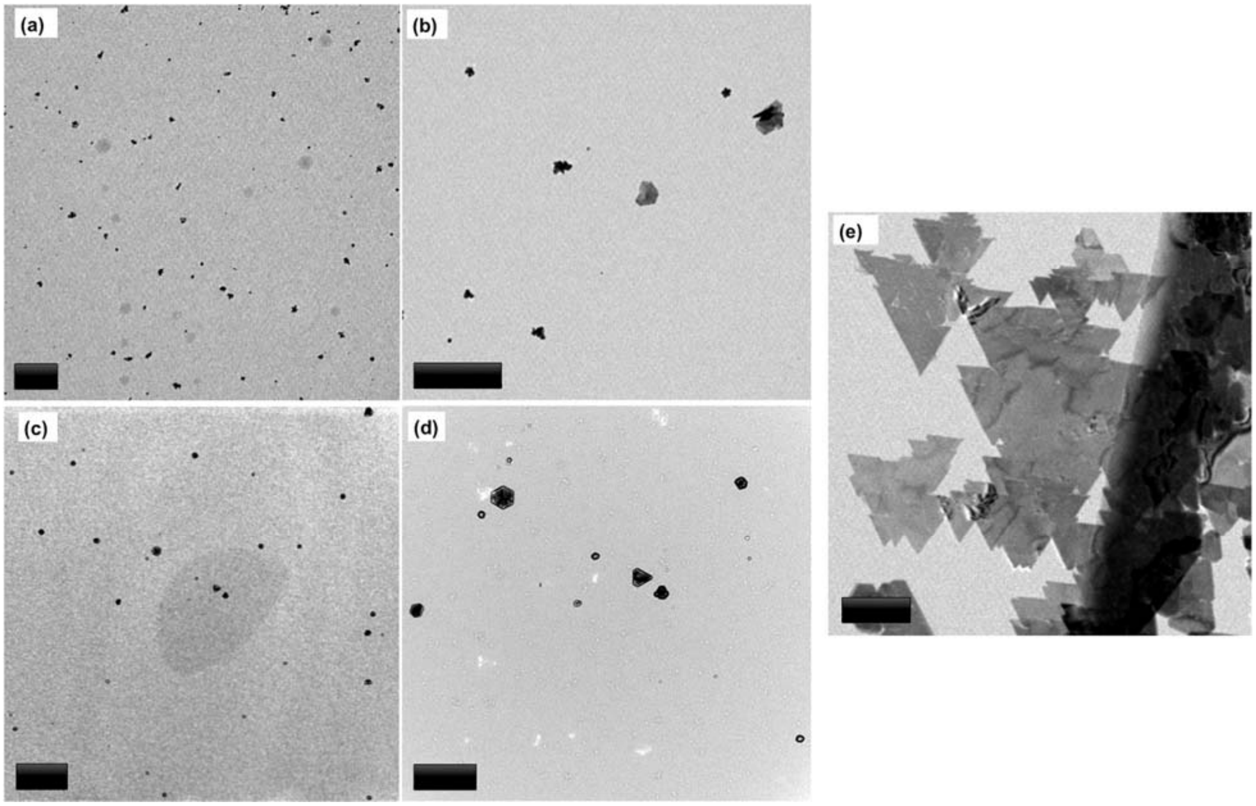

Figure S3. TEM images for initial nanoparticle seeds showing no spherical particles after 5 mins of UV irradiation for $AgNO_3$ mixed with (a, b) CNC-1 (scale bars: 2 µm), (c, d) CNC-2 (scale bars: 1 µm and 0.5 µm, respectively), and (e) CNC-3 (scale bar: 200 nm). Panel (b) is a magnified section of 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.

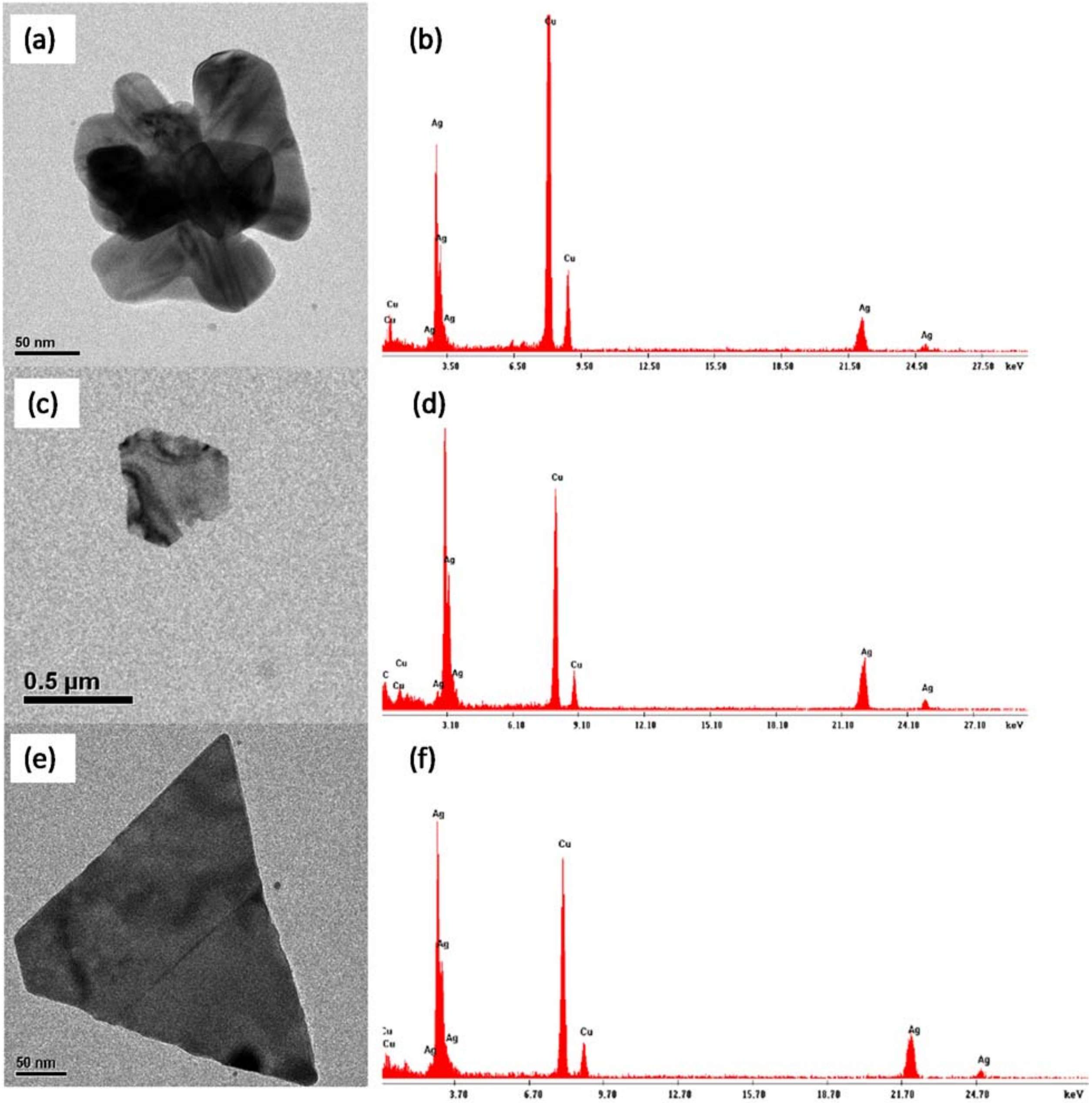

Figure S4. TEM images of three representative silver structures prepared with (a) CNC-1, (c) CNC-2 and (e) CNC-3, along with the corresponding EDS spectra showing a clear Ag peak for each particle (b, d, f).

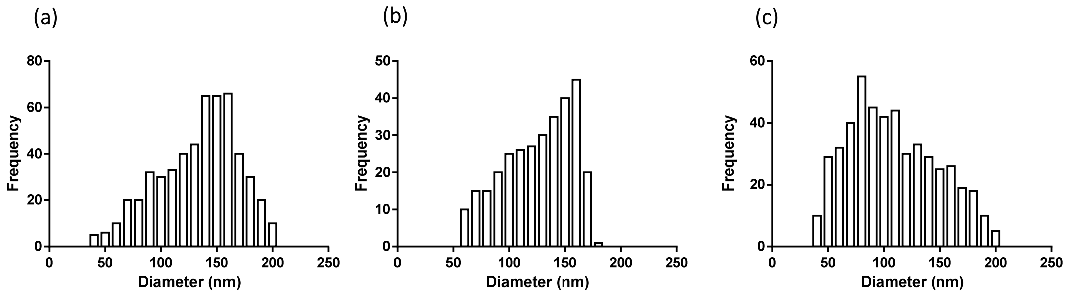

Figure S5. Particle size distribution histograms for silver particles formed using (a) CNC-1, (b) CNC-2, and (c) CNC-3. Particle size was determined by analysis of over 200 particles in TEM images. The diameter plotted is the equivalent spherical (*i.e.*, the diameter of a sphere that would surround the particle, fitted and measured using ImageJ).

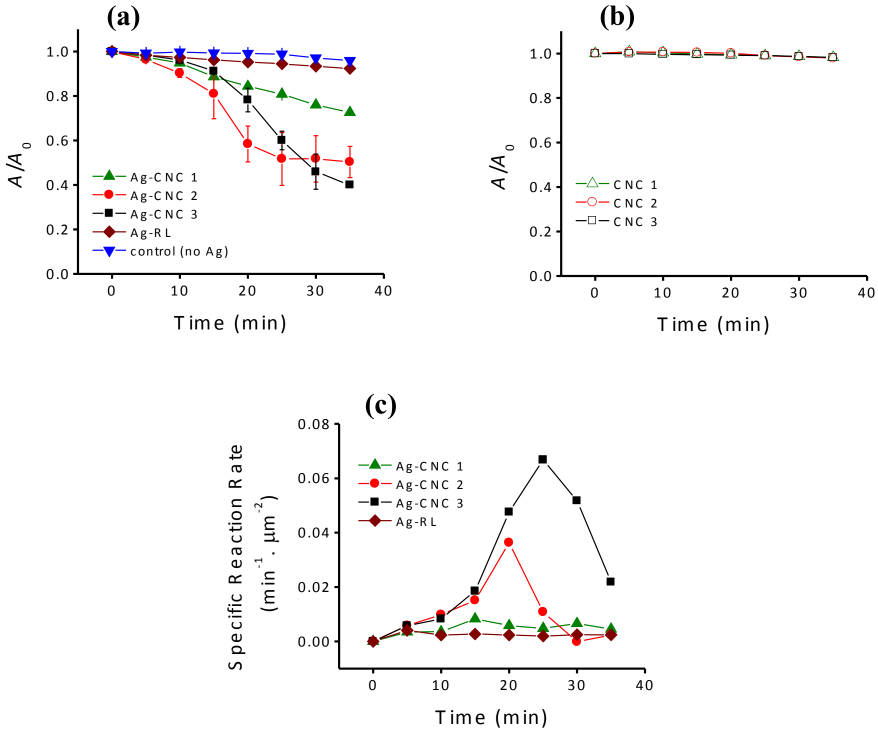

Figure S6.(a) Normalized absorption (A_{664} nm at each time point divided by A_{664} nm at time zero) versus time for degradation of methylene blue (18.2 mg/L) by $NaBH_4$ in the presence of silver nanoparticles synthesized using a mixture of $AgNO_3$ and CNC-1, CNC-2, CNC-3, or rhamnolipids (RL) compared 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 $(\frac{1}{S}\frac{d(C)}{dt}, C = \frac{A}{A_0}, S{:}\, catalyst\ surface\ area)$ versus time.

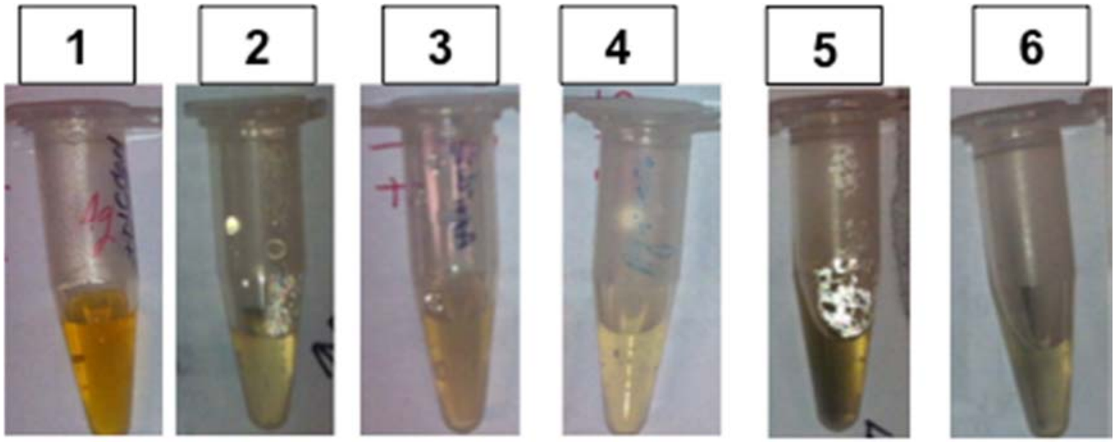

Figure S7. Photographs of colloidal dispersions of Ag nanoparticles. All samples were UV treated for 30 min. (1) CNC-3 + $AgNO_3$, both solutions were degassed to remove dissolved oxygen before mixing and UV treatment, (2) CNC-3 (not carboxylated) + $AgNO_3$, (3) CNC-3, UV treated for 30 min + $AgNO_3$, kept in dark, (4) CNC-3, UV treated for 30 min + AgNO3, not kept in dark, (5) CNC-1, UV treated for 30 min + $AgNO_3$, not kept in dark, (6) rhamnolipids + $AgNO_3$. 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 $AgNO_3$.

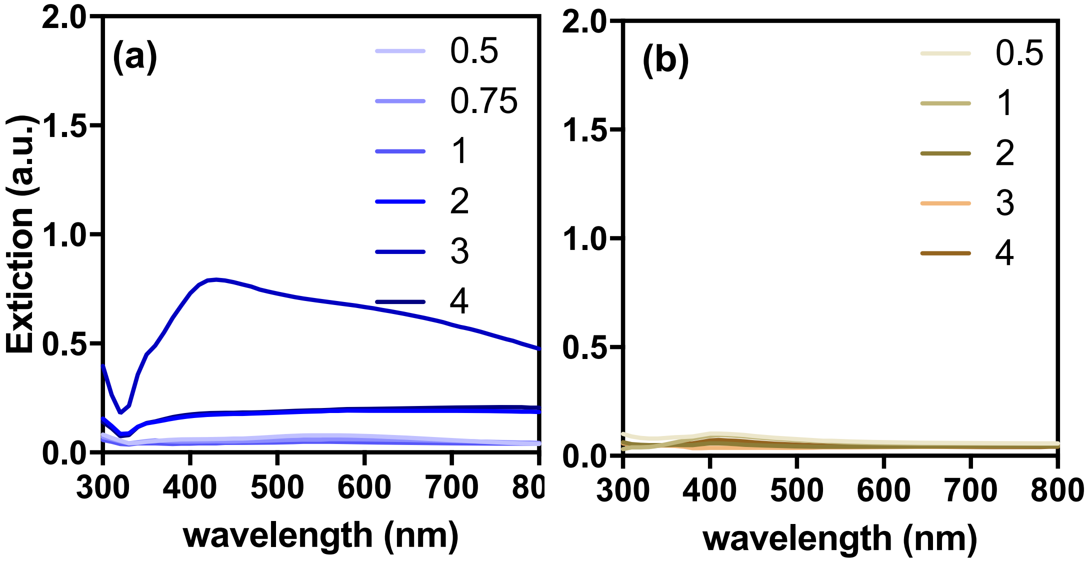

Figure S8. Extinction spectra for a mixture of pre-UV treated (a) CNC-1 and (b) CNC-3, with silver nitrate. The CNCs were UV-treated for 30 min and spectra were recorded at different time points after being mixed with silver salt.

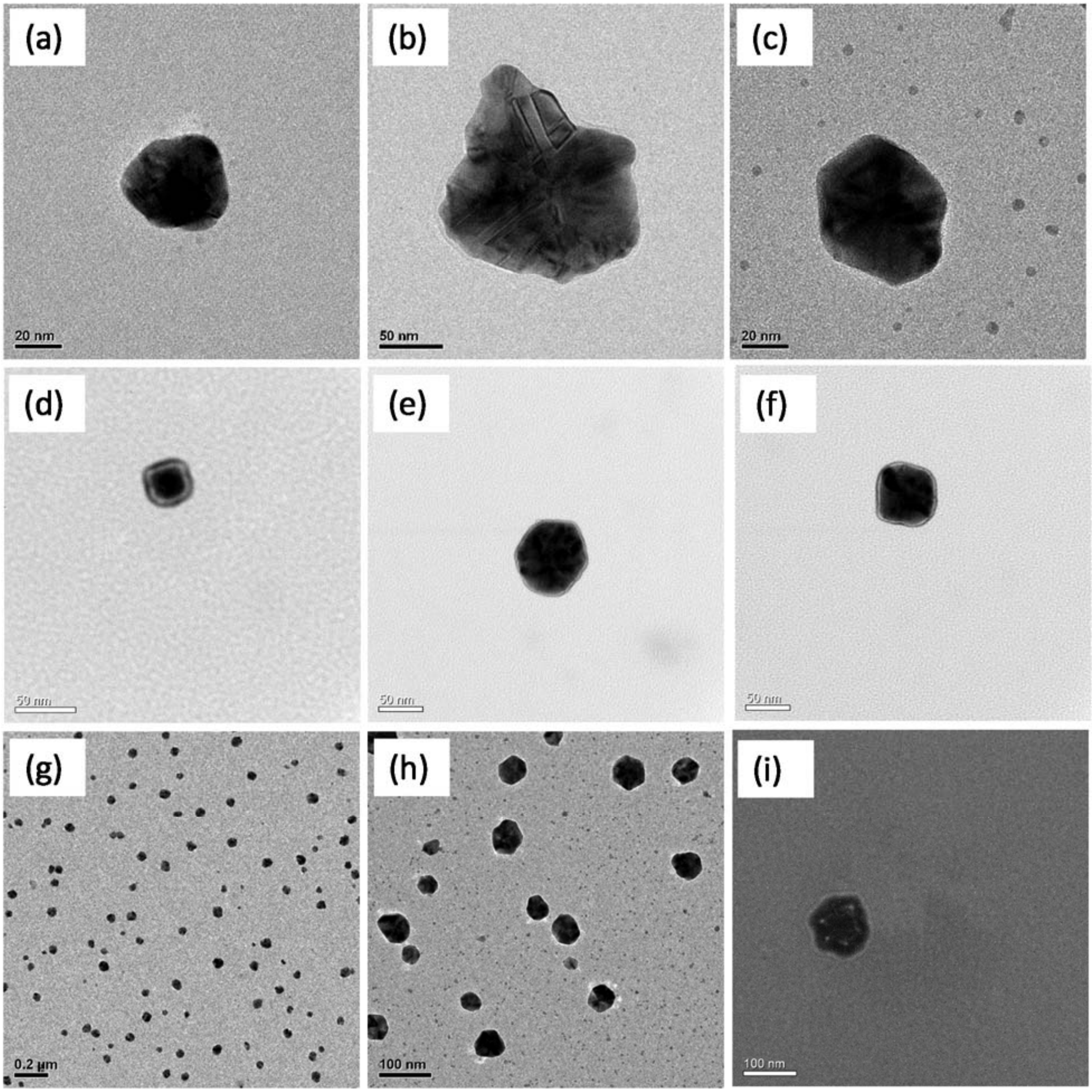

Figure S9. TEM images for initial nanoparticle seeds showing no spherical particles after 5 mins of UV irradiation for (a, b) CNC-1, (c-e) CNC-2, and (f-i) CNC-3.

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