Electronic Supplementary Information

Renewable catalyst with Cu nanoparticles embedded into cellulose nano-fiber film

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Experimental

Materials

Toluene, ethanol, acetic acid, sodium chlorite ($NaClO_2$), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), sodium bromide, sodium hypochlorite (NaClO), sodium borohydride, and sodium L-ascorbate were purchased from Acros Organics, New Jersey, USA. All reagents were used as received. Ultrapure water was used for all experiments.

Catalytic Performance

The reduction reaction of 4-nitrophenol was carried out at batch mode. An aqueous solution of 4-nitrophenol (5 - 20 mg/L) was initially mixed with $NaBH_4$ (500 mg/L). When the Cu-loaded TEMPO-oxidized wood holocellulose nano-fiber (Cu-TOCNF) film (2.5 mm diameter) was immersed in the solution, the reaction proceeded with gentle stirring at room temperature. At set of intervals, small aliquots of the solution were taken and analyzed by using a ultra-violet (UV-Vis) spectrophotometer.

Analyses

Fourier transform infrared absorption spectra were obtained using a Nicolet 6700 FT-IR spectrometer. A UV-Vis spectrophotometer (Jasco V-670) was used for monitoring the absorbance of light. The X-ray photoelectron spectra were recorded using a VG Scientific Model ESCA Lab 250 XPS spectrometer. Transmission electron microscopic (TEM) images were taken using a Hitachi H-7000 equipped with a CCD camera, operating at a voltage of 100 kV. The specimen for TEM was prepared by dropping a sample solution onto a carbon-coated copper grid and drying in air.

Table S1. Reports of 4-nitrophenol reduction.

Catalyst	references
Ag nanoparticles	1
Dendrimer-Au nanocomposites	2
Pd nanoparticles in polyelectrolyte brush and core-shell microgel	3
Au nanoparticles on polymethylmethacrylate	4
core-shell nanorods	5
Pt and Au nanoparticles	6
Au nanoparticles on hollow spheres	7
Cu nanoparticles in cellulose nanofiber film	present

References

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Table S2: Rate constants based on the first-order kinetic reaction for 4-nitrophenol conversion on Cu-TOCNF film.

4-nitrophenol concentration (mg/L)	Rate constant (min^{-1})	R^2 Value
5 (1st Run)	1.44	0.999
10 (1st Run)	0.378	0.997
20 (1st Run)	0.102	0.994
20 (2nd Run)	0.102	0.992
20 (5th Run)	0.099	0.995
20 (10th Run)	0.098	0.997

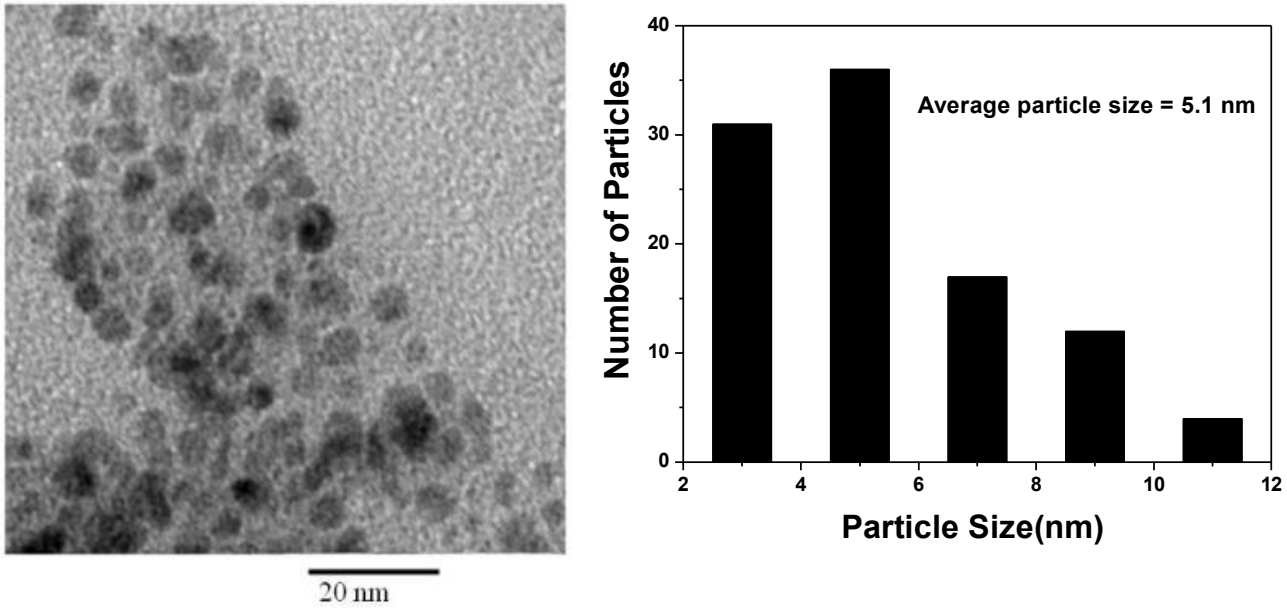

Fig. S1: (Left) A TEM image of Cu nanoparticles prepared using ascorbic acid as a reducing agent and (right) a histogram of particle size distribution.

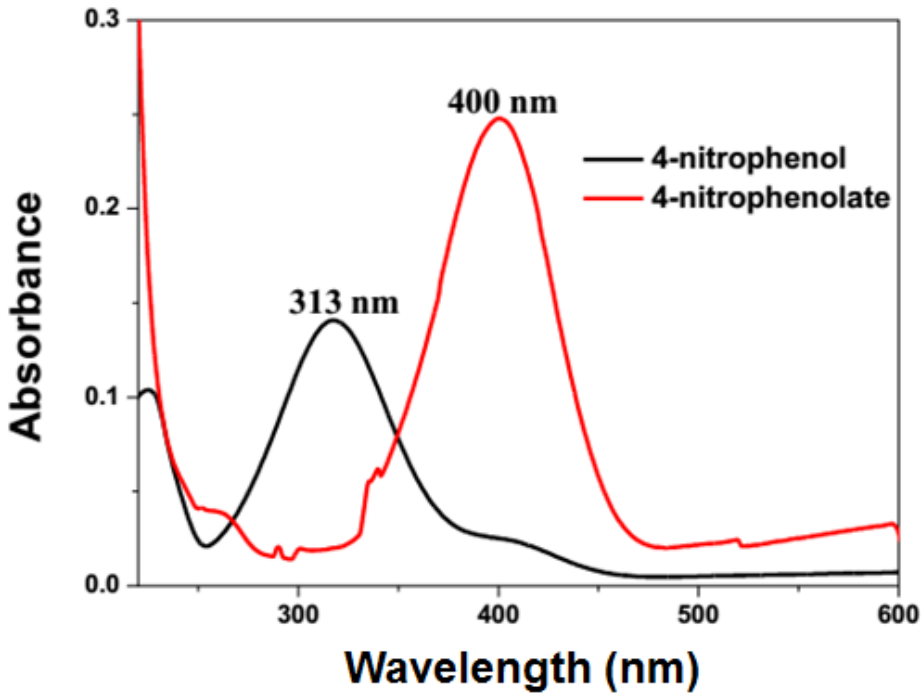

Fig. S2: UV-Vis spectra of 4-nitrophenol and 4-nitrophenolate ion.

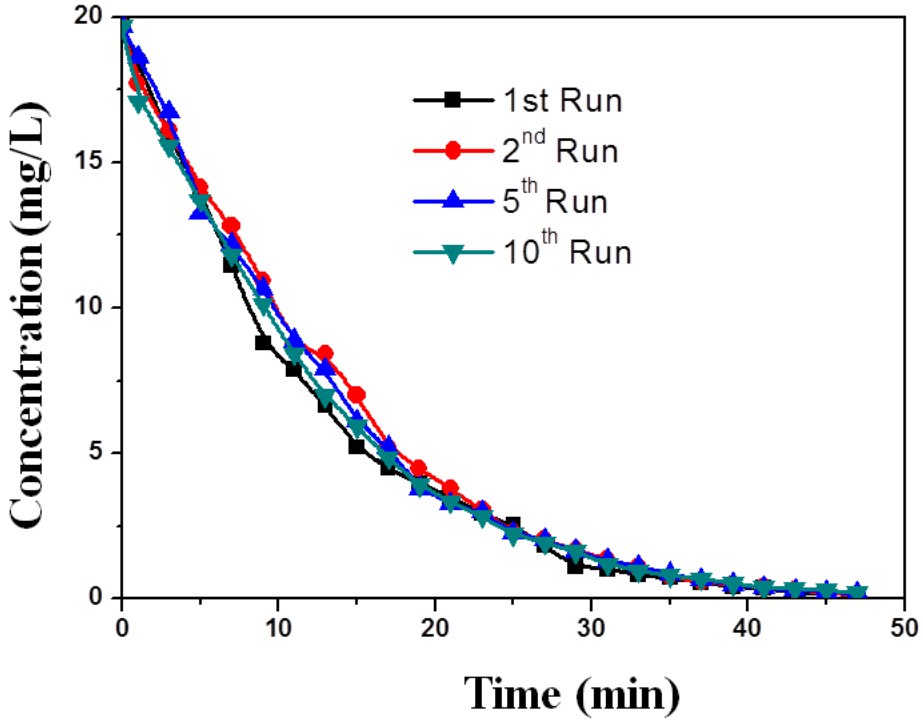

Fig. S3: Plot of concentration versus time of 4-nitrophenol reduction for multiple runs (1, 2, 5, 10) on the same Cu-TOCNF film.

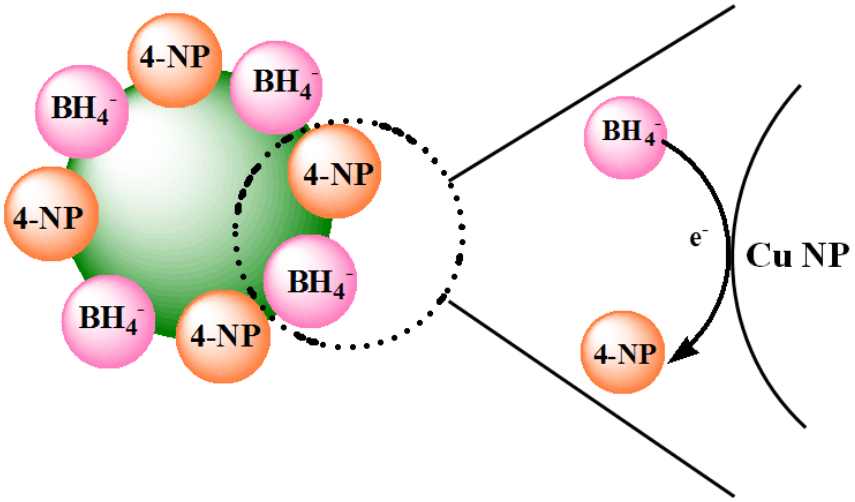

Fig. S4: Schematic representation of catalytic process occurring on Cu nanoparticles embedded in TOCNF film.