

Hybrids Based on Borate-Functionalized Cellulose Nanofibers and Noble-Metal Nanoparticles as Sustainable Catalyst for Environmental Applications

Vicente Esquivel-Peña,[‡] Valentina Guccini,^{‡h} Sugam Kumar,[†] German Salazar-Alvarez,^{‡h} Eduardo Rodríguez de San Miguel[‡] and Josefina de Gyves^{‡}*

[‡] Departamento de Química Analítica, Facultad de Química, UNAM, Ciudad Universitaria, 04510. Ciudad de México, México

[†] Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden

^h Wallenberg Wood Science Center, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

* Corresponding Author: Josefina de Gyves, degyves@unam.mx

Microwave-assisted acid digestion of MNPs/CNF samples

The content of metal supported in CNFs was measured by ICP-OES after a microwave-assisted acid digestion of the samples. Between 2–5 g of the MNPs/CNF suspensions was mixed with 10 mL of a 1:1 HNO₃ solution for the digestion of Ag NPs or 10 mL of aqua regia for the digestion of Au and Pt NPs in PTFE vessels. The samples were digested with a CEM Mars 6 equipment at 180 °C for 20 min after which 2 mL of H₂O₂ were added and a second cycle of digestion at 210 °C for 15 min was performed to assure the complete digestion of the samples. Finally, the samples were diluted to a volume of 25 mL with 1% (v/v) HNO₃. A set of aqueous standard solutions was prepared for calibrating the ICP spectrometer by serial dilution of the stock standard solutions. The analyzed metals were measured in the radial visual mode.

SAXS data analysis

In SAXS experiments, one measures intensity of the scattered X-rays as a function of the magnitude of the scattering vector, which for monodispersed scatterers can be expressed as equation S1:

$$I(Q) = \phi V (\Delta\rho)^2 P(Q) S(Q) \quad (S1)$$

where ϕ is the volume fraction of the scatterers in the scattering volume, V is the volume of the individual scatterer and $(\Delta\rho)^2$ is the scattering contrast (the square of the difference in the scattering length densities of the particle and the solvent). $P(Q)$ denotes the intra-particle structure factor (square of the form factor) which is a function of the shape and size of the particles. $S(Q)$ represents the interparticle structure factor which describes the interparticle interaction between the particles. In the absence of strong inter-particle correlations (e.g., in the case of a dilute system), $S(Q)$ may be approximated to unity

For a spherical particle having radius R , $P(Q)$ can be given in equation S2.

$$P(Q) = \left[3 \frac{\sin(QR) - (QR)\cos(QR)}{(QR)^3} \right]^2 \quad (S2)$$

For a polydispersed system, $P(Q)$ can be convoluted with a size distribution function as follows (equation S3):

$$P(Q) = \int P(Q, R) f(R) dR \quad (S3)$$

where $f(R)$ is the size distribution, which can be given by a log-normal distribution as expressed by equation S4:

$$f(R) = \frac{1}{R\sigma\sqrt{2\pi}} \exp \left[-\frac{\left(\ln \frac{R}{R_{med}} \right)^2}{2\sigma^2} \right] \quad (S4)$$

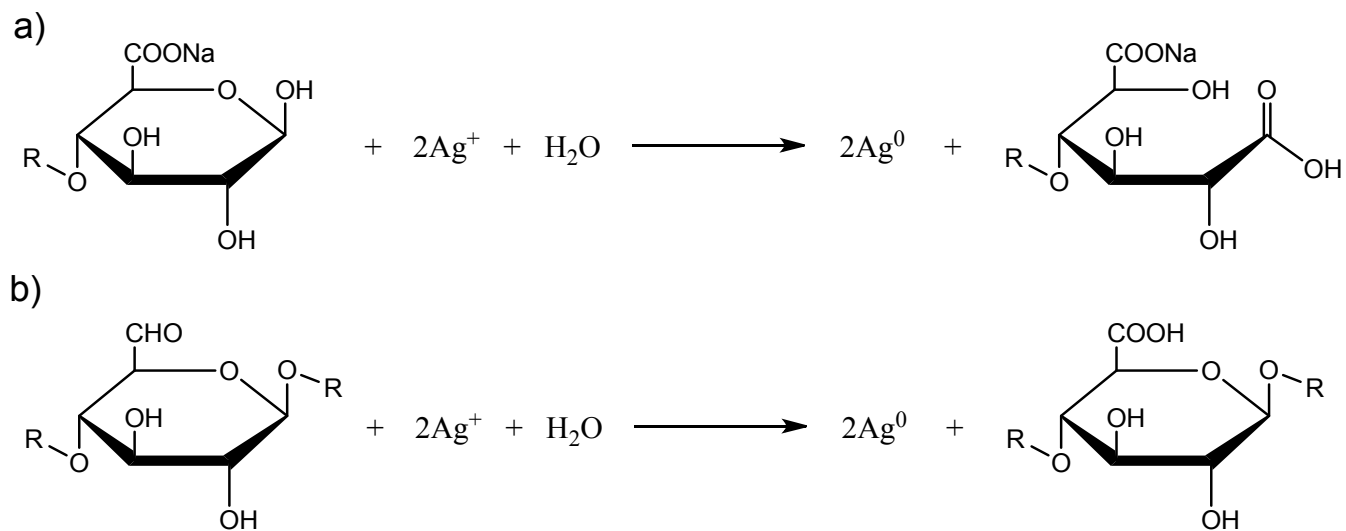
where R_{med} and σ are the median value and the standard deviation, respectively. The mean (R_m) and median values (R_{med}) are related by $R_m = R_{med} \exp(\sigma^2/2)$.

As a first attempt, the data were analyzed by considering the system as a dilute suspension of polydispersed nanoparticles in the solvent. In this model, equations (S2-S4) were used in equation (S1) and $S(Q)$ was taken ~ 1 . The resulting fitted curves (black lines) are shown in Figure 2a. The fitted curves almost reproduced the scattering profiles in the intermediate- and high- Q region ($Q > \text{nm}^{-1}$, indicated by the dotted line in Figure 2a) but were not able to account for the low- Q scattering intensity, which may be a result of the presence of some small nanoparticle aggregates, as also observed in the TEM images. The data, therefore, can be analyzed by summing a power-law behavior (arising from the aggregates) and scattering from polydispersed nanoparticles. The scattering intensity can be written in equation S5.

$$I(Q) = \frac{I_c}{Q^\alpha} + \phi V (\Delta\rho)^2 P(Q) S(Q) \quad (S5)$$

where the first term (I_c is a Q independent constant) represents scattering from particle aggregates while the second represents scattering from individual particles [$P(Q)$ is the same as in equations S2-S4 and $S(Q) \sim 1$].

The data have been analyzed by comparing the calculated scattering from different models to the experimental data and the fitting parameters were optimized by a nonlinear least-squares fitting program.



Scheme S1. Proposed silver reduction mechanism (AgNPs formation) by a) cellulose hemiacetal groups and b) cellulose C6 aldehydes.

Table S1. Metal content for mono- and bi-metallic NPs/CNF obtained by ICP-OES after acid digestion. Results are expressed in mol of metal/g of material obtained.

Sample	$C_{\text{Ag}} \times 10^5$ (mol g ⁻¹)	$C_{\text{Au}} \times 10^5$ (mol g ⁻¹)	$C_{\text{Pt}} \times 10^5$ (mol g ⁻¹)
Ag NPs/CNF	9.89 ± 0.35	----	----
Au NPs/CNF	----	5.16 ± 0.28	----
Pt NPs/CNF	----	----	5.21 ± 0.08
Ag@Au NPs/CNF	8.12 ± 0.35	2.10 ± 0.31	----
Ag@Pt NPs/CNF	9.03 ± 0.16	----	1.72 ± 0.05

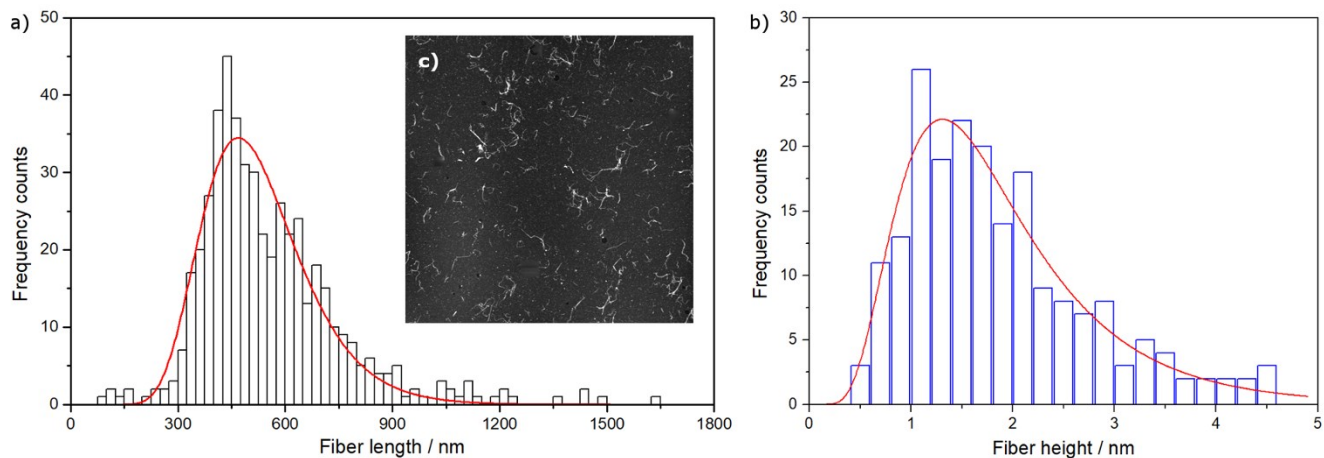


Figure S1. Physical characterization of cellulose nanofibers: (a) length distributions, (b) height distribution and (c) AFM image for CNFs.

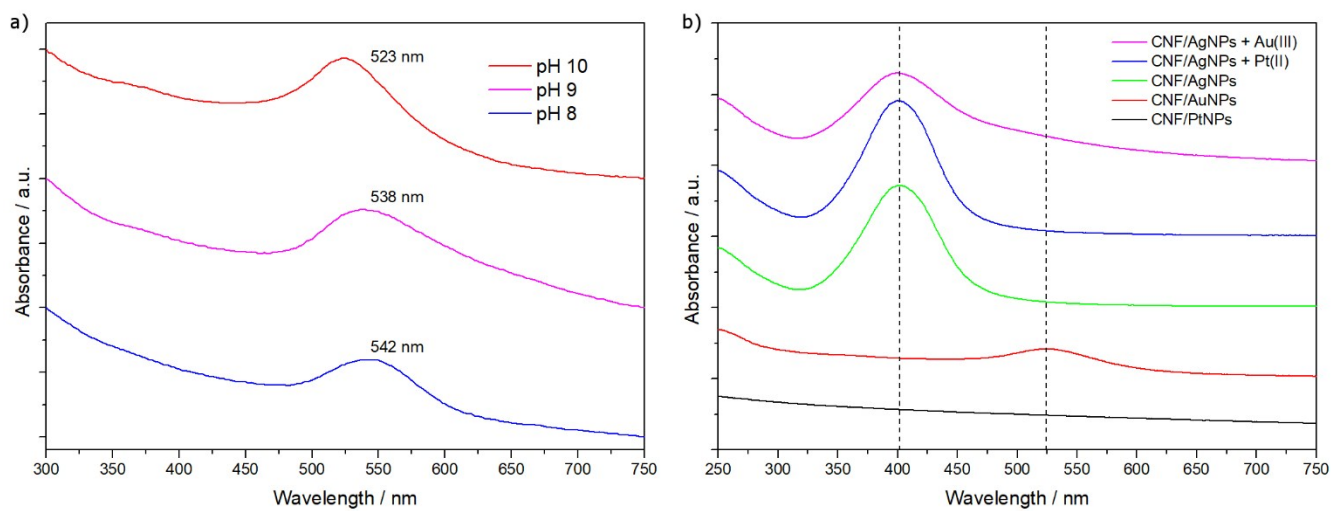


Figure S2. Surface plasmon resonance for: (a) AuNPs/CNF as a function of pH, and (b) mono and bimetallic NPs.

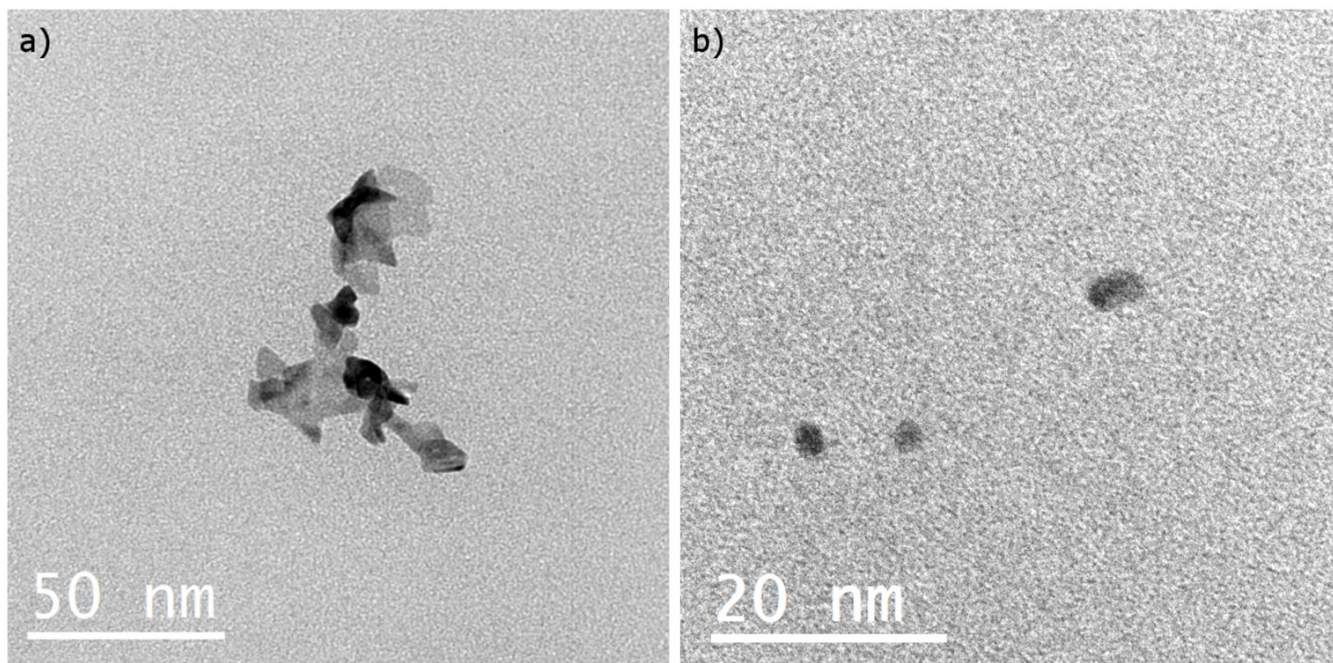


Figure S3. TEM images for Pt NPs reduced by (a) cellulose nanofibers and (b) sodium borohydride.

Table S2. Mean size of metal nanoparticles obtained by SAXS

Sample	Mean size (nm)
Ag NPs/CNF	5.3 ± 1.5
AgAu NPs/CNF	5.4 ± 1.5
AgPt NPs/CNF	5.4 ± 1.5

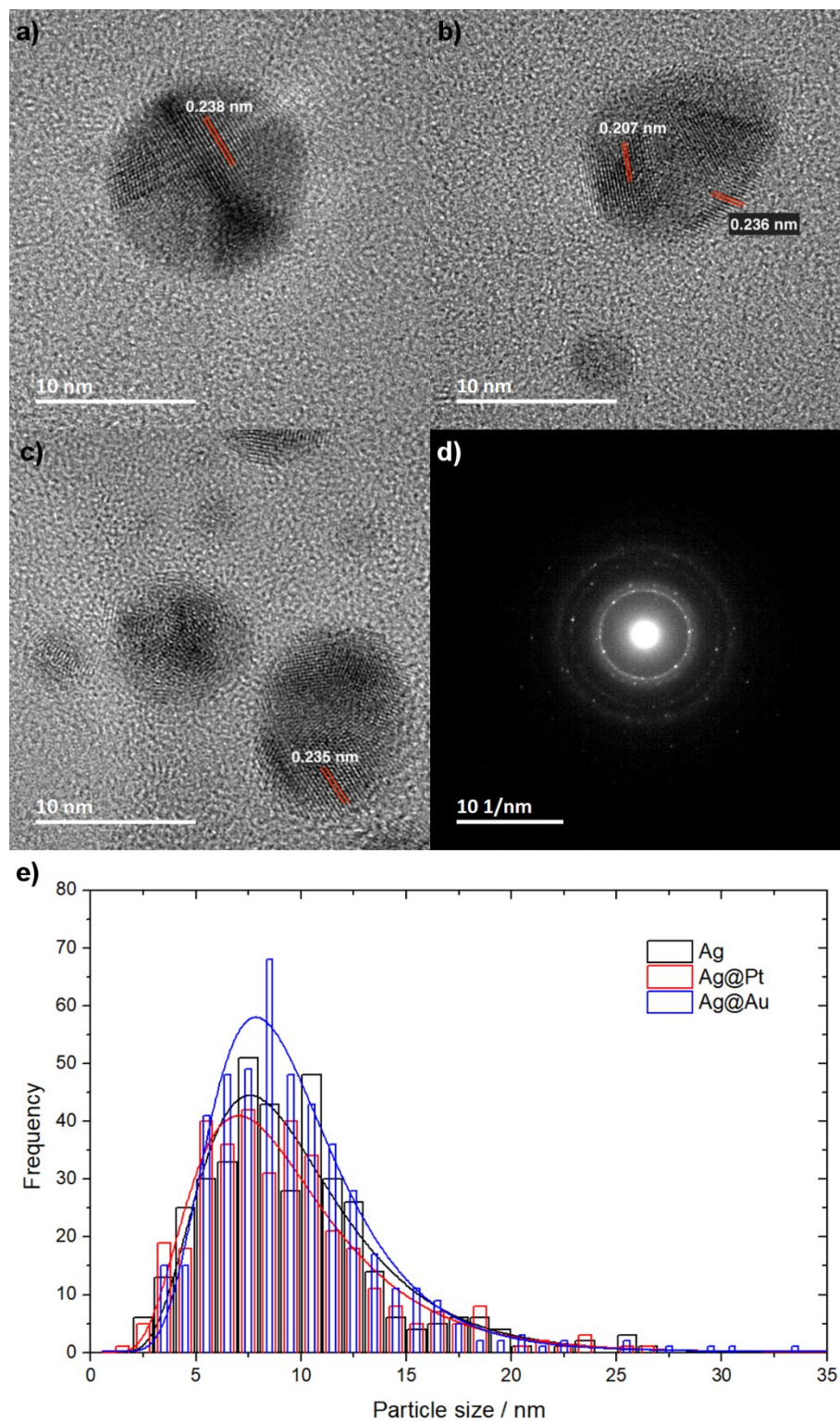


Figure S4. HRTEM images for (a) Ag NPs/CNFs, (b) Ag@Au NPs/CNF, and (c) Ag@Pt NPs/CNF, (d) electron diffraction pattern for Ag@Au NPs/CNF, and (e) size distribution of Ag, Ag@Au and Ag@Pt NPs/CNF measured by TEM.

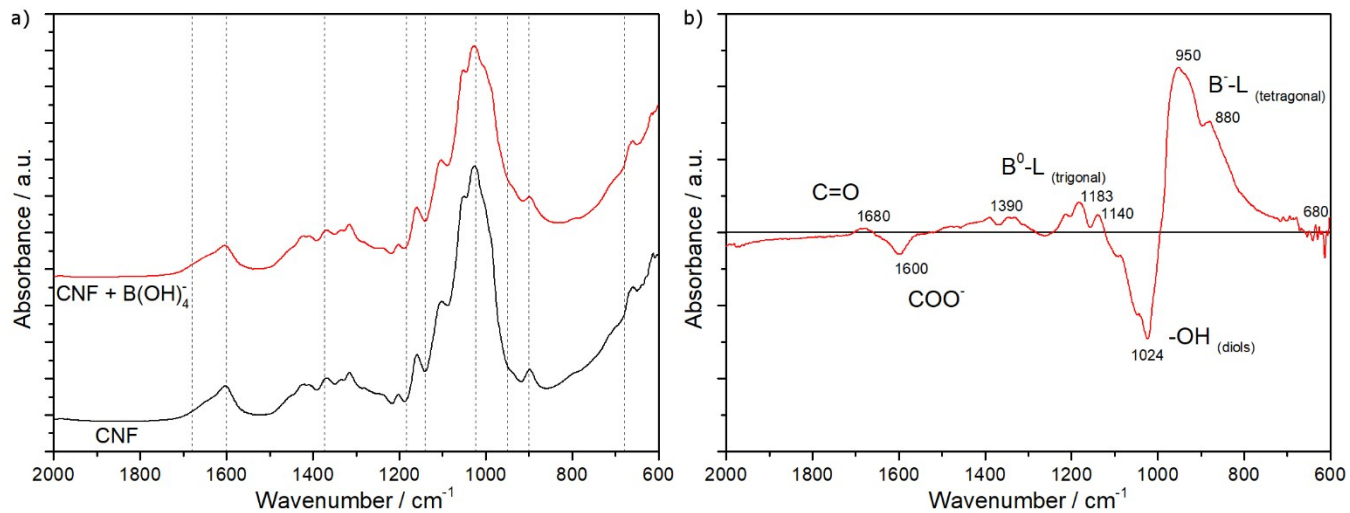


Figure S5. (a) FTIR spectra of CNF with and without borate ions as cross-linking agent and (b) differential FTIR spectrum of CNF with and without borate ions as cross-linking agent.