Electronic Supplementary Material (ESI) for Faraday Discussions.


# Supporting information to

# Mechanochemical synthesis of Au, Pd, Ru and Re nanoparticles with lignin as a bio-based reducing agent and stabilizing matrix

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1. Experimental Details

**Materials and Reagents**

All chemicals and solvents were purchased from commercial sources and used without purification. Hydrogen tetrachloroaurate(III) hydrate, hexakis[μ-(acetato-O:O')]-triaqua-$\mu_3$-oxotriruthenium(III) (referred to as 'basic Ru(III) acetate' thereafter), palladium(II) acetate, palladium(II) acetylacetonate, and rhenium pentacarbonyl bromide were purchased from Strem Chemicals, Inc., ruthenium(III) chloride hydrate and palladium(II) chloride were purchased from Pressure Chemical. A Westvaco Chemical Division, Indulin AT Kraft pine lignin was purchased and used without further purification. This is a 99% lignin content free flowing brown powder lignin. 400-mesh carbon supported TEM grids were obtained from Electron Microscopy Science.

**Equipment**

High-resolution TEM and EDAX were performed using a Philips CM200 200 kV TEM. XPS was performed on a VG ESCALAB 3 MKII spectrometer (VG, Thermo Electron Corporation, UK) equipped with an Mg Kα source. PXRD was performed using the Bruker D2 Phaser diffractometer using as CuKα source. A Retsch Mixer Mill MM 400 was used to perform milling experiments. A Perkin Elmer Spectrum Two FTIR with a single bounce diamond ATR was used for all FTIR measurements.

**Typical procedure (synthesis of AuNP@lignin)**

In a typical reaction a 10mL stainless steel milling jar was filled with a total of 200 mg of solid reagent material, consisting of 0.1 mmol of the metal precursor with the remainder being Kraft Lignin powder. To this reaction mixture were added two stainles balls of 7 mm diameter (1.34 grams weight, total ball-to-sample weight ~13). The jar was then closed and loaded onto the Retsch MM400 mixer mill. The reactions were conducted over 90 minutes, milling at a frequency of 29.5 Hz. At the end of the reaction, the solid product was scrapped out of the jar with a spatula and weighed. The product was placed onto a Kimwipe® filter plug in a Pasteur pipette and the solid washed using three 1 mL aliquots of water, followed by three 1 mL aliquots of acetone. The solid was allowed to dry under vacuum overnight and analyses were run on the dried samples. TEM grids were prepared by suspending the powders in acetone and depositing the resulting suspensions onto a 400-mess carbon supported copper TEM grid. XPS samples were run by supporting dry samples onto carbon tape. The FTIR-ATR and PXRD measurements samples were conducted on solid dry samples.

2. TEM Measurements

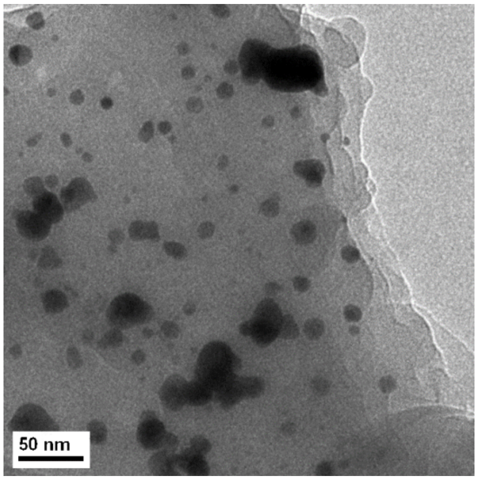


Figure S1: Representative TEM images obtained for AuNP@Lignin

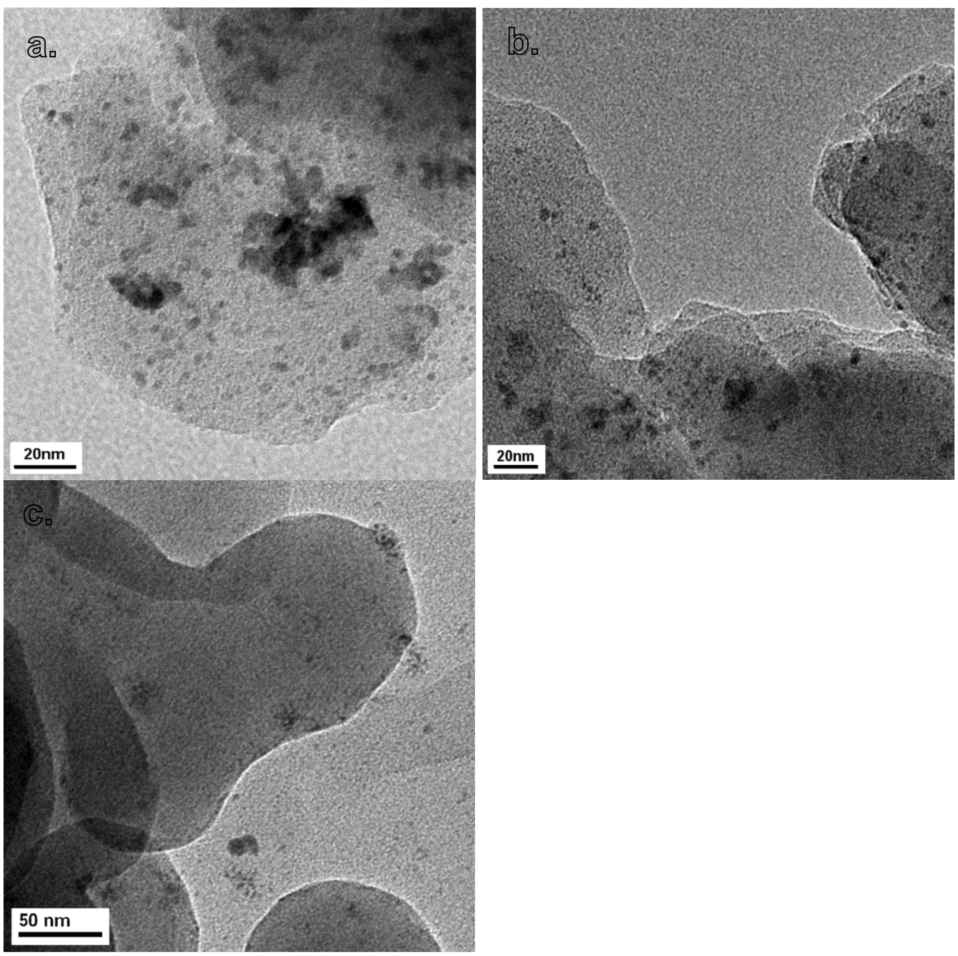


Figure S2: Representative TEM images obtained for PdNP@Lignin from the following precursors: a. Pd(II) acetate, b. Pd(II) acetylacetate, and c. Pd(II) chloride

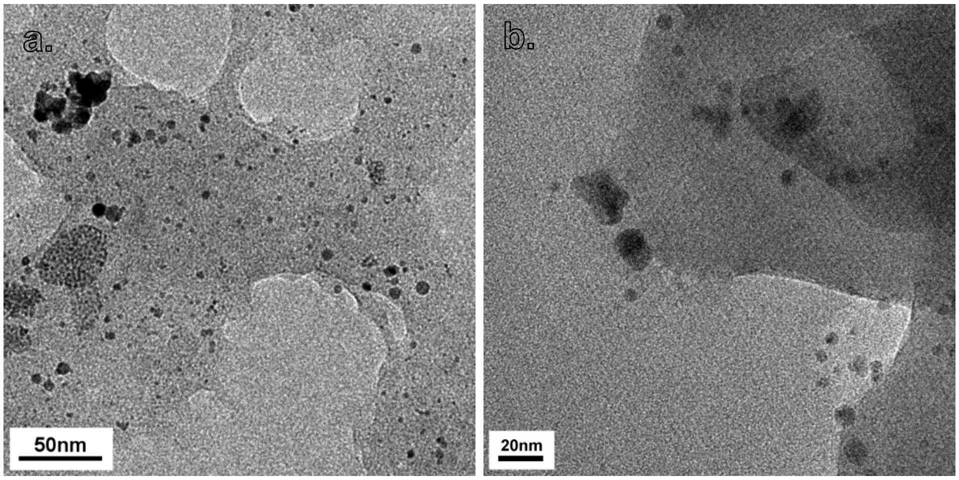

Figure S3: Representative TEM images obtained for RuNP@Lignin from the following precursors: a. basic Ru(III) acetate and b. Ru(III) chloride

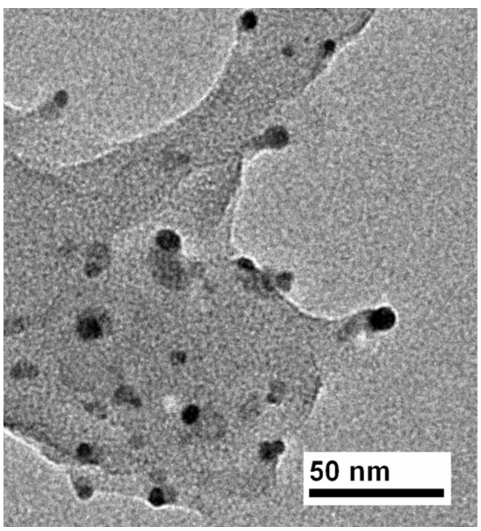

Figure S4: Representative TEM images obtained for ReNP@Lignin

3. FTIR-ATR

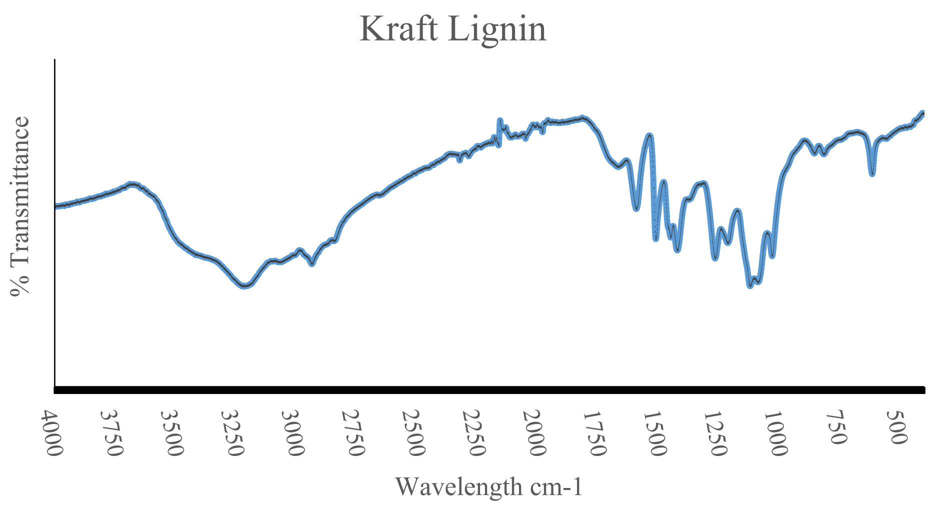


Figure S5: FTIR-ATR spectra of Kraft pine lignin

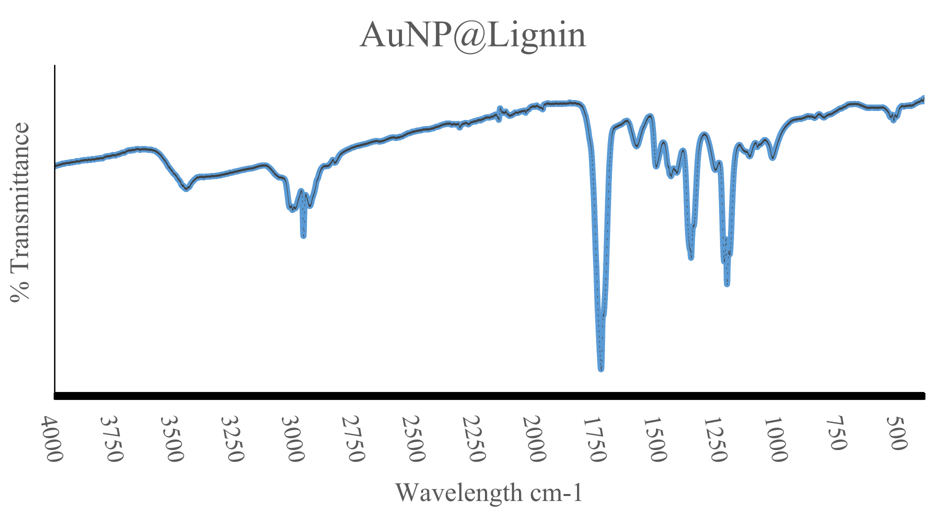


Figure S6: FTIR-ATR spectra of AuNP@Kraft lignin

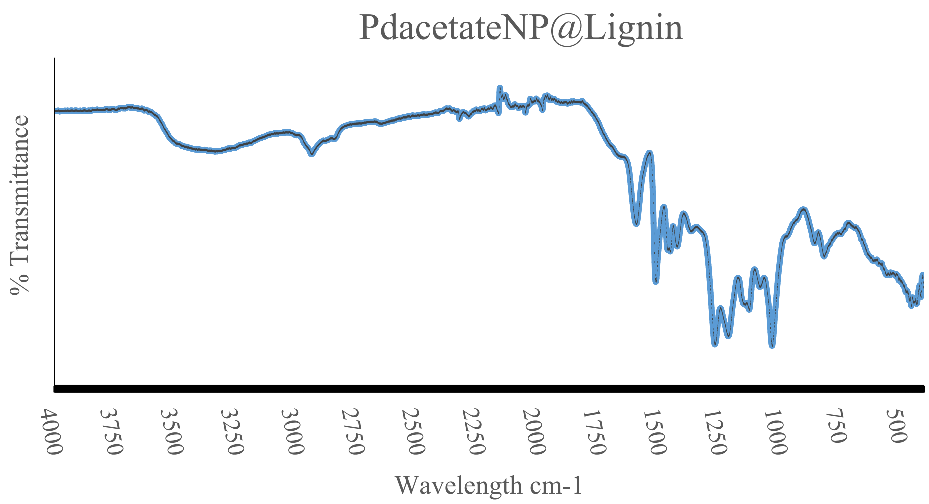


Figure S7: FTIR-ATR spectra of PdNP@Kraft lignin made from Pd(II) acetate

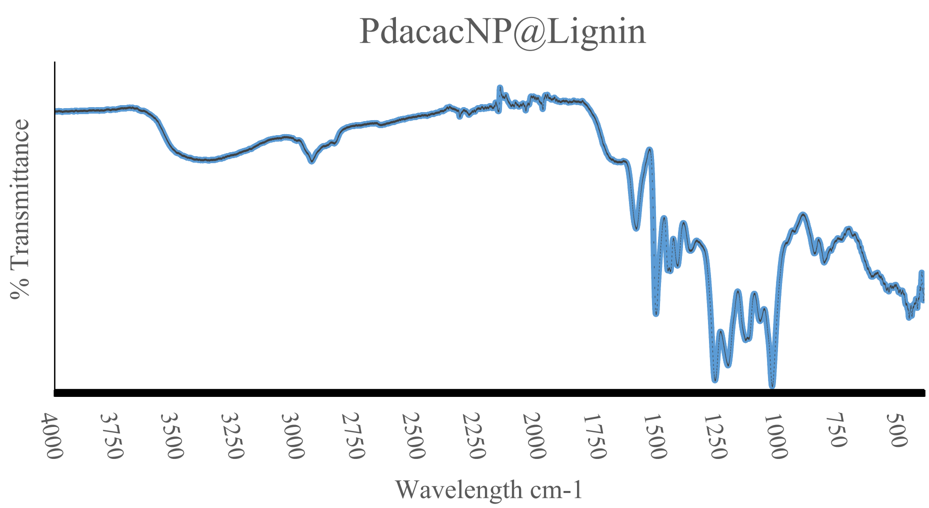


Figure S8: FTIR-ATR spectra of PdNP@Kraft lignin made from Pd(II) acetylacetate

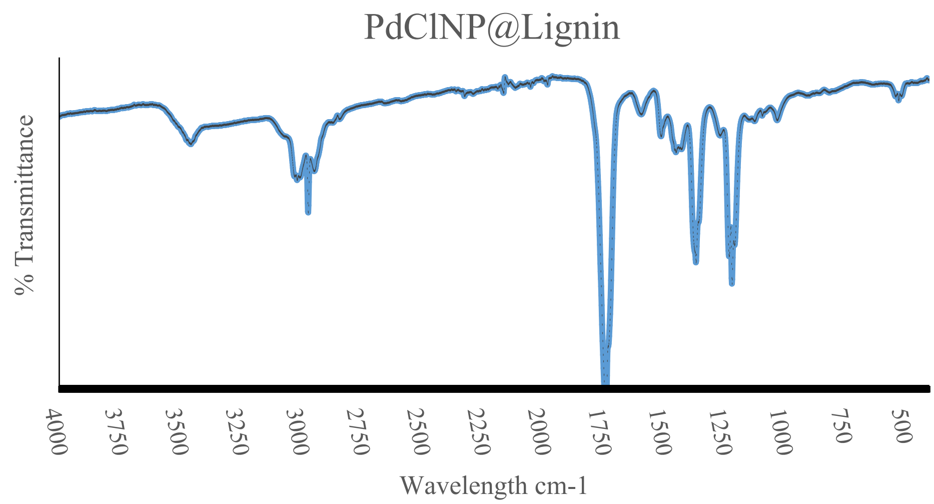


Figure S9: FTIR-ATR spectra of PdNP@Kraft lignin made from Pd(II) chloride

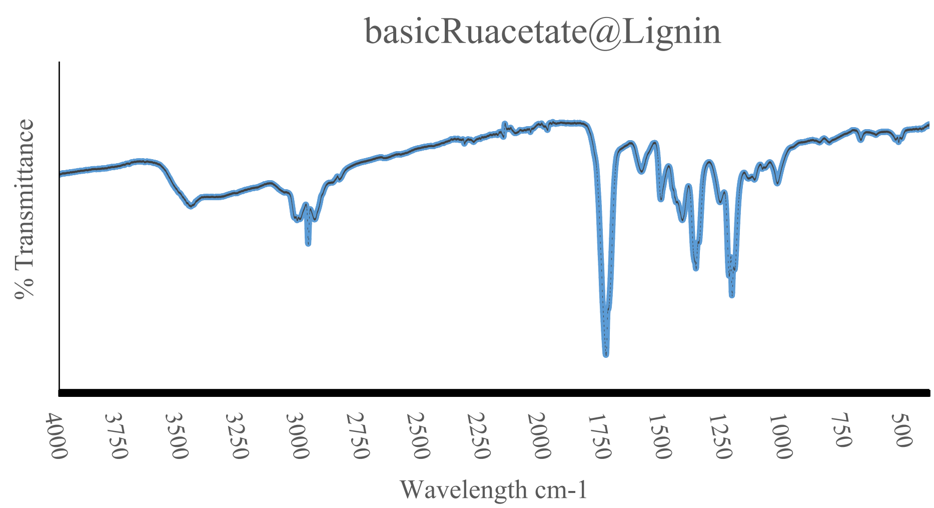


Figure S10: FTIR-ATR spectra of RuNP@Kraft lignin made from basic Ru(III) acetate

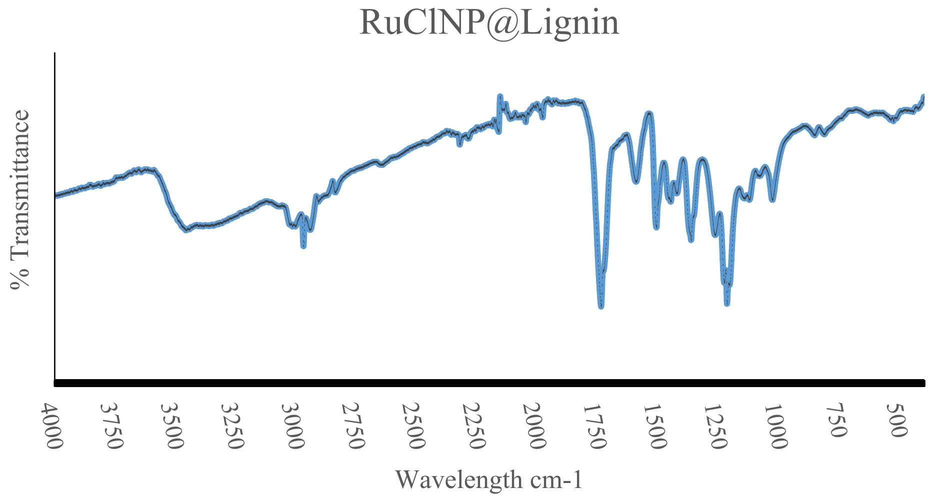


Figure S11: FTIR-ATR spectra of RuNP@Kraft lignin made from Ru(III) chloride

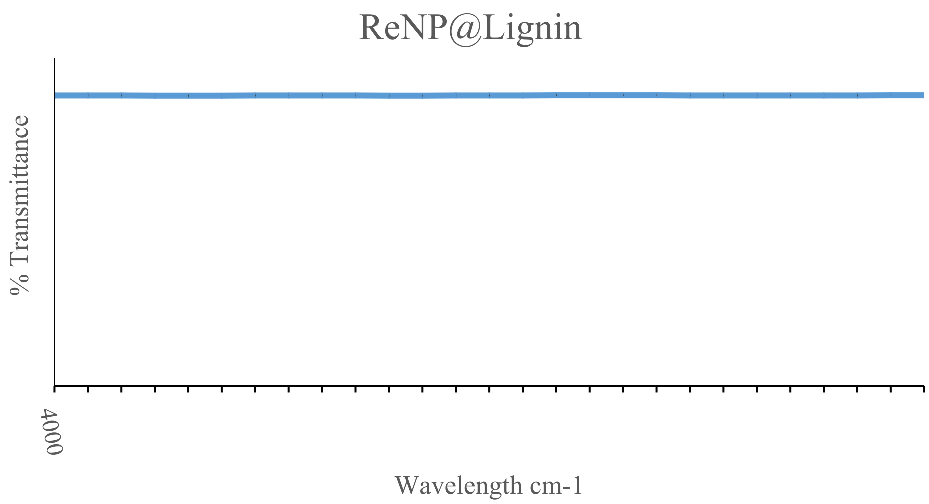


Figure S12: FTIR-ATR spectra of ReNP@Kraft lignin made from rhenium pentacarbonyl bromide

4. XPS Data – All XPS data were referenced to a C1s peak at 284.5eV

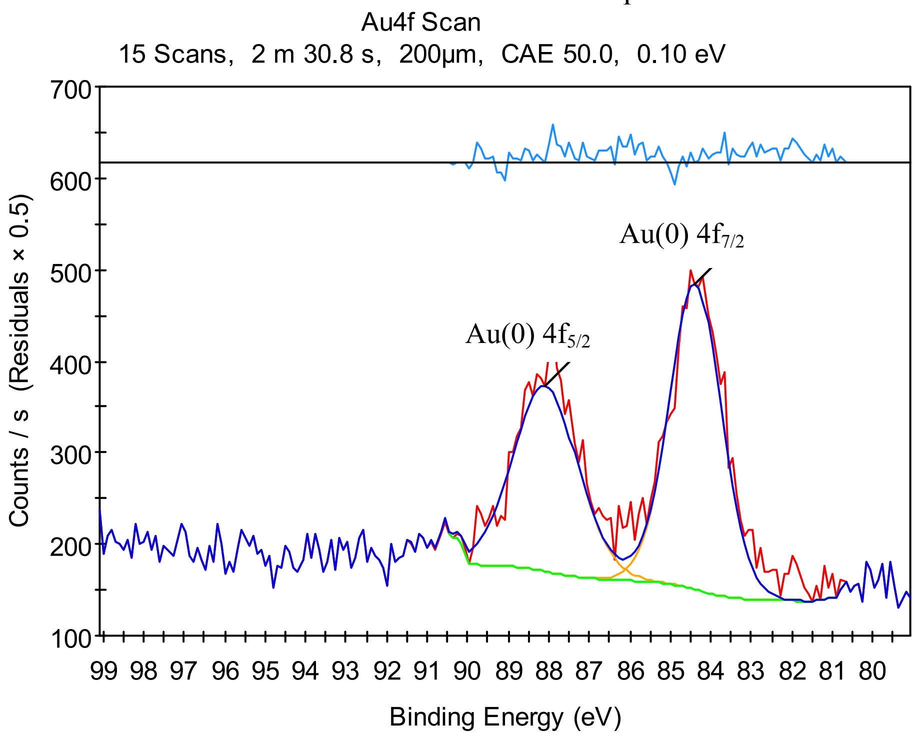


Figure S13: XPS spectra of AuNP@Lignin

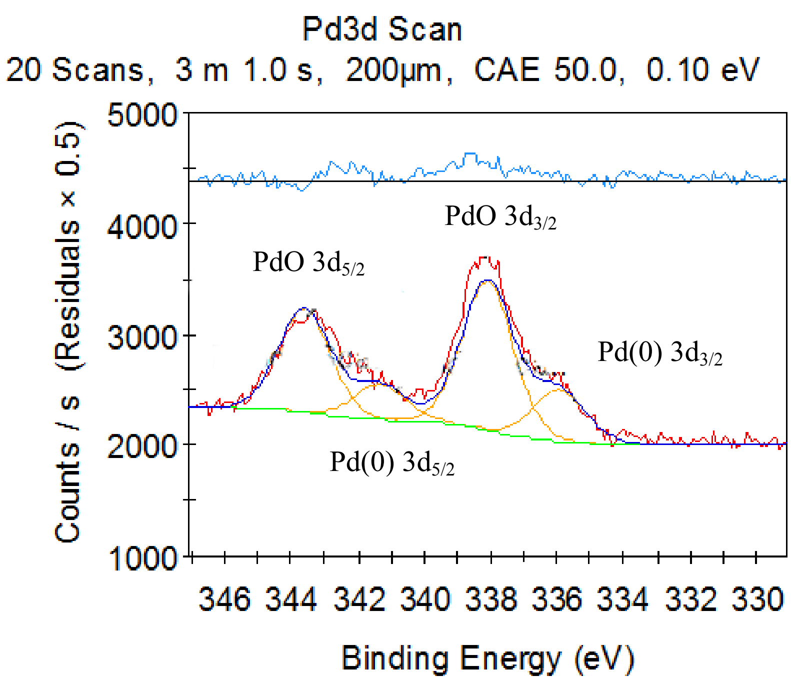


Figure S14: XPS spectra of PdNP@Kraft lignin made from Pd(II) acetate

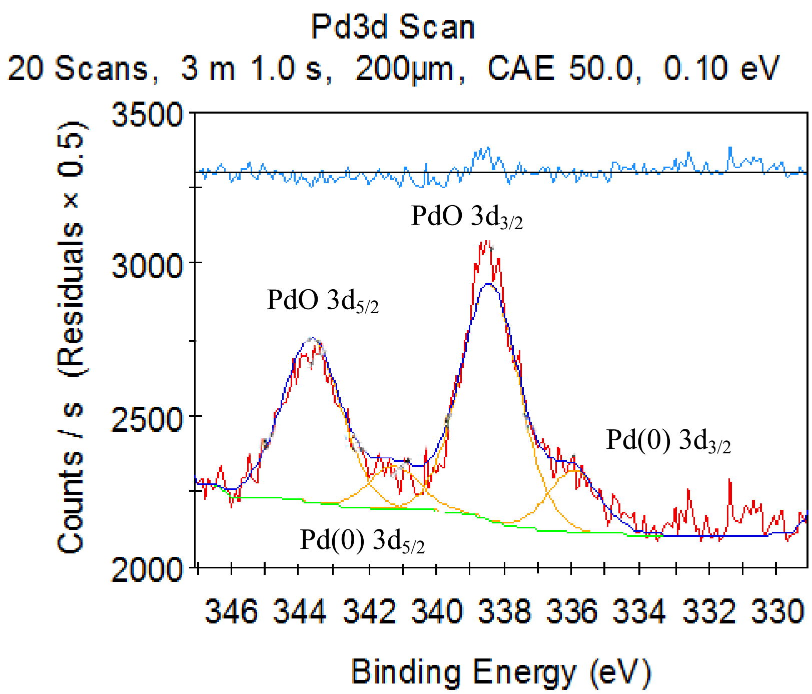


Figure S15: XPS spectra of PdNP@Kraft lignin made from Pd(II) acetylacetate

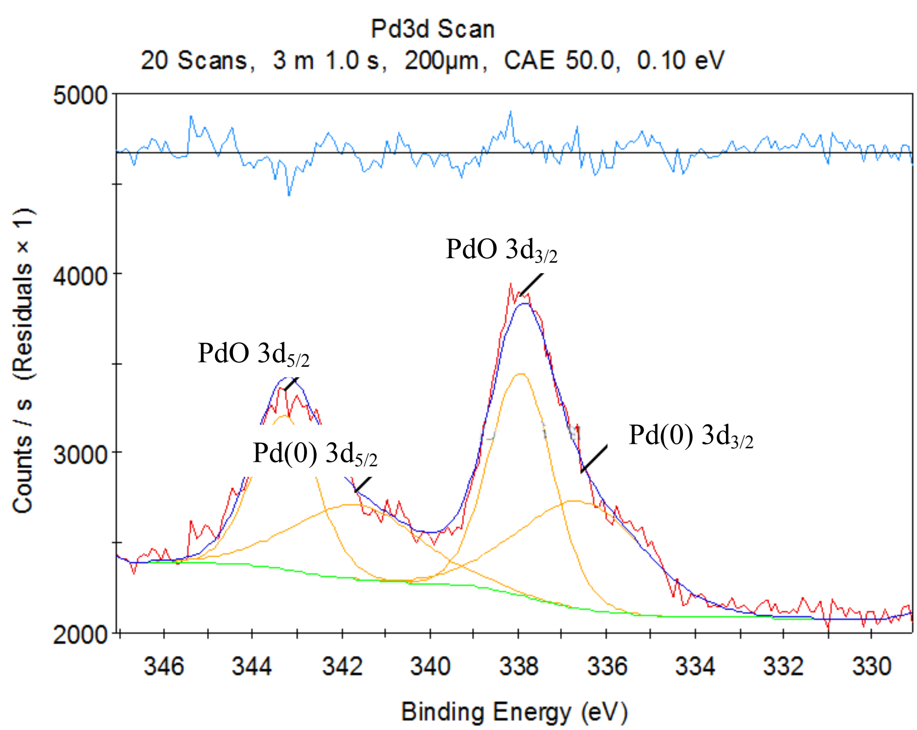


Figure S16: XPS spectra of PdNP@Kraft lignin made from Pd(II) chloride

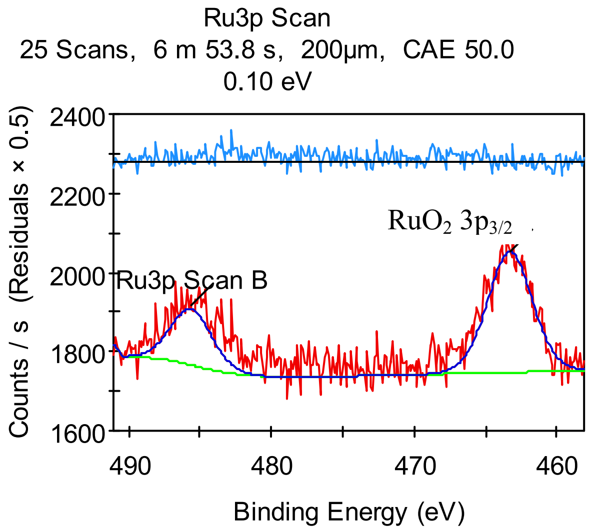


Figure S17: XPS spectra of RuNP@Kraft lignin made from basic Ru(III) acetate

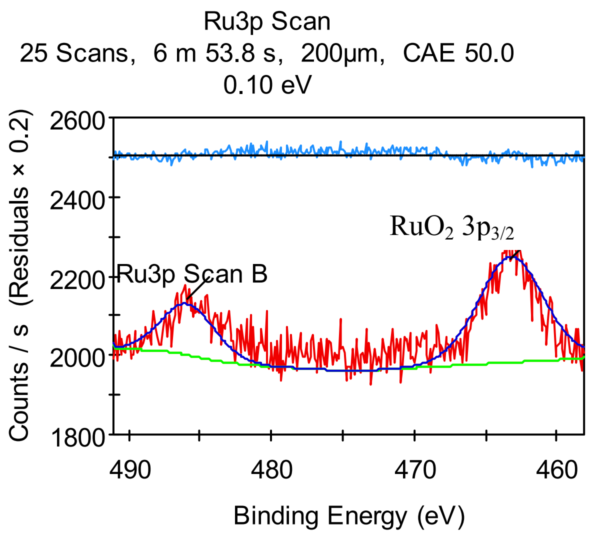


Figure S18: XPS spectra of RuNP@Kraft lignin made from Ru(III) chloride

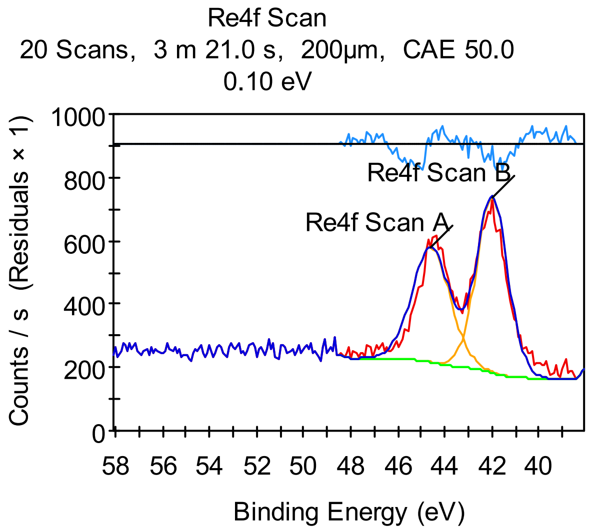


Figure S19: XPS spectra of ReNP@Kraft Lignin

5. PXRD Data

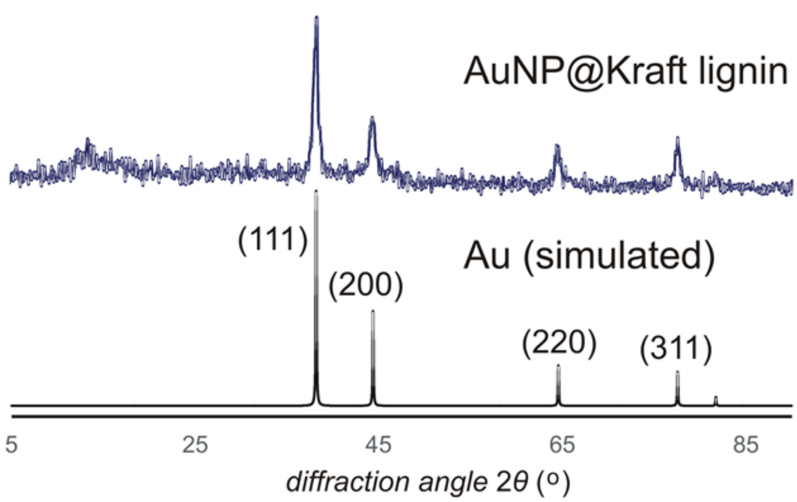


Figure S20: PXRD spectra of AuNP@Lignin