

Supporting Information

Black Phosphorus-Polyglycerol Nanohybrid for Precious Metal Recovery

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Experimental

Materials

RP (99.7 % purity) was obtained as a powder from Merck and used without further purification or processing. Glycidol (≥ 96.0 %, SigmaAldrich) underwent distillation before use and was stored at 4 °C over molecular sieves and under an argon atmosphere to maintain inert conditions. Anhydrous N-methyl-2-pyrrolidone (NMP, with a purity of 99.5%, SigmaAldrich) was used without any additional purification. Argon and nitrogen gas were used to maintain inert conditions for all air-sensitive experiments. Iron (10.0 g/L, in 2.0 % HNO₃, *TraceCERT*®) and zinc (1.0 g/L, in 2.0 % HNO₃, *TraceCERT*®) standard solutions for AAS were obtained from SigmaAldrich. Copper, nickel, and chromium (all 1.0 g/L, in 2.0 % HNO₃, ROTI®Star) standard solutions for AAS were obtained from Carl Roth GmbH. Gold (1.0 g/L, in 2.0 % HCl, ROTI®Star) standard solution for AAS was obtained from Carl Roth GmbH. Gold(III) chloride (solid powder, 99.0 %) was obtained from ABCR GmbH. Palladium(II) chloride (solid powder, ≥ 99.0 %) was obtained from Merck. Chloroplatinic acid hexahydrate (solid powder, ≥ 99.95 %), copper(II) chloride dihydrate (solid powder, ≥ 99.0 %), chromium(III) chloride hexahydrate (solid powder, ≥ 98.0 %), and nickel(II) chloride hexahydrate (solid powder, ≥ 98.0 %) were obtained from SigmaAldrich. Iron(III) chloride (solid powder, 98.0 %) was obtained from Riedel de Haën (Honeywell International Inc). Zinc(II) chloride (solid powder, ≥ 98.0 %) was obtained from Alfa Aesar GmbH (Thermo Fisher Scientific). Ultra-high purity synthetic-grade water was acquired from the Milli-Q® Advantage A10 Water Purification System. All additional chemicals and reagents were obtained from various commercial suppliers and used as-is without additional purification, unless specified otherwise.

Methods

Synthesis of mBP, sBP, and cBP

mBP

mBP was prepared via HEPBM using the Pulverisette 6 ball-mill device from Fritsch GmbH. 1 g of RP was placed in an 80 mL stainless-steel ball-mill chamber together with 100 g of stainless-steel ball-mill medium (100:1 ball-to-powder w/w ratio) under

argon. The RP was milled at 600 rpm for a total of 4 hours before collecting the mBP product under argon.

sBP

sBP was prepared solvothermally from RP and ethylenediamine. 150 mg of RP was immersed in 10 mL of anhydrous ethylenediamine under argon. The dry mixture was placed in a solvothermal autoclave reactor which comprises a polytetrafluoroethylene (PTFE) chamber jacketed by a steel autoclave. The reactor was then placed in an oven and heated at 200 °C for 7 days before letting it cool down to room temperature. The reactor was transferred back to an argon glovebox and the solvent was extracted removed by decanting. The sBP powder was then washed with methanol 4 times via centrifugation before lyophilizing it to remove the solvent.

cBP

cBP was prepared via CVT from RP, tin, and tin(II) iodide. 500 mg of RP was placed in a glass ampule together with 4 mg of tin powder and 8 mg of tin(II) iodide under argon and sealed with a flame. The ampule was then placed in a muffle furnace before heating it to 650 °C over one hour. The temperature of the furnace was first reduced to 550 °C over 1 hour, then to 500 °C over 8 hours, and then to 200 °C over 4 hours, before turning off the heating and letting the ampule cool down to room temperature. The ampule was then transferred to a glovebox and opened to extract cBP crystals. The crystals were then crushed manually using a mortar and pestle before immersing them in anhydrous NMP (5 mg mL⁻¹) and subjecting them to ultrasonication for 4 hours under argon. The sonicated dispersion was then centrifuged at 1500 rpm for 45 min and the supernatant was extracted to collect the cBP nanoflakes and separate them from bulk BP. The supernatant was then flushed with argon and stored at 4 °C for further use.

Yield: 20-30 %, 1 mg mL⁻¹

Synthesis of BP-PG

BP-PG was prepared mechanochemically via HEPBM using the Pulverisette 6 ball-mill device from Fritsch GmbH. 500 mg of previously prepared mBP and 500 mg of anhydrous distilled glycidol were placed in a stainless-steel ball-mill chamber together with 100 g of stainless-steel ball-mill medium under argon. The mixture was then treated by HEPBM at 600 rpm for 1 hour to obtain BP-PG. The BP-to-glycidol ratio

was varied for some reactions (i.e. 1:2, 1:10, and 10:1 w/w). Moreover, a 1-step approach was tested by directly using RP with glycidol (1:1 w/w), but with the milling parameters used for the allotropic transformation of RP to BP (4 hours milling total).

Synthesis of BP@PG

To synthesize BP@PG, 500 mg of previously prepared mBP was dispersed in 15 mL of anhydrous NMP and heated to 120 °C while stirring before adding 500 mg (~0.45 mL) of anhydrous distilled glycidol over 30 min using a syringe pump (1 mL/hr). The mixture was stirred at 120 °C for 72 hours and cooled down to room temperature thereafter. The solvent was extracted by lyophilization and the residue was washed by an water/acetone mixture (1:3 v/v) via centrifugation 4 times. The final product was dried under vacuum.

Metal Removal

A simulated electronic waste leachate was prepared by mixing equal amount of equal concentrations (w/v) of chromium(III) nitrate, copper(II) nitrate, iron(III) nitrate, zinc(II) nitrate, nickel(II) nitrate, and gold(III) chloride in acidic Millipore-quality water. The electronic waste leachate was then diluted 10-fold with pH 1 water before adding BP-PG directly to form BP-PG-in-EWL dispersions with 250-1000 $\mu\text{g mL}^{-1}$ concentrations. The dispersions were left to stir for 5-60 min depending on the experiment. The stirring was then turned off and the BP-PG nanoparticles were left to sediment for some time to separate the nanoparticles from the EWL mixture, and the supernatants were collected for analysis. To recover the gold nanoparticles, the AuNP@BP-PG was either left to degrade over time under ambient conditions, or forcibly oxidized by treatment with hydrogen peroxide (H_2O_2 5-30% w/w) solution to finally obtain a purple-pink dispersion of gold nanoparticles.

Metal Selectivity

Equal concentrations (1.0 mg mL^{-1}) of gold(III) chloride, chromium(III) nitrate, copper(II) nitrate, iron(III) nitrate, zinc(II) nitrate, and nickel(II) nitrate were placed in glass vials. A dispersion of BP-PG in pH 1 water (2.0 mg mL^{-1}) was added to the $[\text{M}]^+$ solutions to finally form mixtures of 0.5 mg mL^{-1} of $[\text{M}]^+$ and 1.0 mg mL^{-1} of BP-PG, which were kept at room temperature until the sedimentation of the BP-PG nanoparticles. The supernatants were then extracted for analysis using AAS, and the sediment analyzed and the recovered AuNPs via XPS, UV-Vis, and SEM.

The metal adsorption percentages were determined by comparing the initial and final concentrations of metal ions in the solutions, as described in Equation 1.

$$[M]^+ \text{ Concentration After Treatment} = \frac{C_f}{C_i} \times 100 \quad (1)$$

C_f is the final concentration of $[M]^+$ after BP-PG treatment, and C_i is the initial concentration of $[M]^+$ before treatment with BP-PG.

Pd²⁺ and Pt⁴⁺ Removal

A dispersion of BP-PG in water (250 µg mL⁻¹, pH 1) was mixed with a series of aqueous palladium(II) chloride and chloroplatinic(IV) acid hexahydrate solutions ($[M]^+ = 125, 250, 500, 750, \text{ and } 1000 \text{ µg mL}^{-1}$, pH 1) for 60 min at room temperature. The nanoparticles were left to sediment for some time before collecting portions of the supernatants for UV-Vis analysis and the sediment for XPS analysis.

Gold Recovery Capacity of BP-PG, mBP, BP@PG, BP + PG, and AC

Dispersions of mBP, BP@PG, and BP-PG in water (250 µg mL⁻¹, pH 1) were mixed with a series of aqueous gold(III) chloride solutions ($[M]^+ = 125, 250, 500, 750, \text{ and } 1000 \text{ µg mL}^{-1}$, pH 1) for 60 min at room temperature. The nanoparticles were left to sediment for some time before collecting portions of the supernatants for analysis.

The recovery capacity was calculated using the following equation:

$$\text{Recovery Capacity} \left(\frac{\text{mg}}{\text{mg}} \right) = \frac{(C_i - C_f) \times V}{m} \quad (2)$$

where C_i is the initial concentration of the Au^{III} solution, C_f is the final concentration of the Au^{III} solution, V is the volume of the treated solution, and m is the mass of the nanomaterial used for the treatment.

Raman Spectroscopy

Raman spectroscopy measurements were conducted utilizing a Horiba Xplora spectrometer equipped with an x/y piezo stage. The laser excitation wavelength for all measurements was set at 532 nm and delivered through a 100x objective (Nikon®). To prevent thermal heating or sample degradation, the laser power was limited to 1% of the intensity for all measurements. Each spectrum was measured with an

accumulation time of 1 second. Samples were drop-casted on silicon dioxide/silicon wafers (1 cm x 1 cm).

Statistical Raman spectroscopy (SRS) involved the measurement of Raman maps across sample regions deposited on Si or SiO₂/Si substrates. Average spectra were derived from the maps, excluding Si-only spectra. The accumulation time for each spectrum in the mapping process was set to 1 second. Substrate movement during mapping was achieved using the motorized x/y piezo stage.

Powder X-Ray Diffraction

The measurements were conducted employing a Panalytical Empyrean diffractometer from Malvern Panalytical Ltd. A Cu (1.5406 Å) source was utilized for sample measurement within the (10 - 90) Degrees 2 theta range, with a measurement step size of 0.255 Degrees per step. Each sample underwent a 19-minute measurement duration. Fe plates served as the background, and self-printed white polylactic acid holders were used for securing the samples.

Infrared Spectroscopy

Infrared spectroscopy of the prepared nanomaterials and other reagents was conducted using a PerkinElmer Spectrum Two FT-IR Spectrometer.

XPS

NAP-XPS experiments were performed with an EnviroESCA spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany), equipped with a monochromatic Al K α X-ray source (Excitation Energy = 1486.71 eV) and a PHOIBOS 150 electron energy. Samples for XPS analysis were prepared on indium foil. The spectra were measured in normal emission, and a source-to-sample angle of 60° was used. All spectra were acquired in fixed analyzer transmission (FAT) mode. The binding energy scale of the instrument was calibrated, following a technical procedure provided by SPECS Surface Nano Analysis GmbH (calibration was performed according to ISO 15472). For quantification, the survey spectra were acquired at ultra-high vacuum conditions with a pass energy of 100 eV, and the spectra were quantified utilizing the empirical sensitivity factors that were provided by SPECS Surface Nano Analysis GmbH (the sensitivity factors were corrected with the transmission function of the spectrometer). For charge compensation, the highly-resolved XP spectra were

acquired under near-ambient pressure conditions (5 mbar H₂O) with a pass energy of 50 eV, and the respective data were fitted using UNIFIT 2020 data processing software. For fitting, a Shirley background and a Gaussian/Lorentzian sum function [peak shape model GL (30)] were used. If not denoted otherwise, the L-G mixing component was set to 0.30 for all carbon peaks and 0.40 for all heteroatom peaks. All binding energies were calibrated to the signal observed for the aliphatic C–C bond component ($E_{bind} = 285$ eV) if not stated otherwise.

³¹P-MAS-NMR

Solid-state phosphorus nuclear magnetic resonance spectroscopy was carried out on RP, mBP, sBP, cBP, BP@PG, and BP-PG using a JEOL ECZ600 spectrometer operating at a 600 MHz proton resonance frequency, equivalent to 11 × 6/5 Tesla. Measurements involved normal single pulses at spinning rates of 12 and 16 kHz to verify the origin of sidebands, with a relaxation delay of 5 seconds. The rotor used had a diameter of 3.2 mm, and 1024 data points were acquired for this measurement.

To further ensure sample purity, a total suppression of spinning sidebands (TOSS) experiment was conducted, suppressing rotational sidebands with 1024 data points, a 5-second relaxation delay, and a rotational frequency of 16 kHz. Data processing included apodization (single exponential multiplication of 20 Hz for ³¹P), and zero-filling up to 2k.

For the prepared BP@PG and BP-PG, measurements were performed using a normal single pulse at a spinning rate of 14 kHz, with a 3-second relaxation delay. The rotor, made of zirconium dioxide, had a diameter of 3.2 mm, and 2048 data points were acquired. Data processing involved apodization (single exponential multiplication of 20 Hz) and zero-filling up to 4k. All reported chemical shifts are relative to Adamantane (¹³C) used as an external reference.

Liquid NMR Spectroscopy

NMR spectra were acquired using either a Bruker AMX 500, Bruker Avance 400 spectrometer, or Jeol ECP 500. Tetramethylsilane at 12 MHz, with full proton decoupling, was used for internal calibration.

Zeta Potential

Zeta potential (ZP) profiles were assessed using the Malvern Zetasizer Nano apparatus (Brookhaven Instruments Corp.) under room temperature conditions (25 °C). The samples were prepared at a concentration of 1 mg mL⁻¹ in Millipore-quality water. The samples were introduced into disposable Folded Capillary Zeta Cells (DTS 1070, Malvern Panalytical). Each sample underwent three measurement runs, and the average of the recorded results was used.

Dynamic Light Scattering

Dynamic light scattering (DLS) measurement were performed using the Malvern Zetasizer Nano apparatus (Brookhaven Instruments Corp.) under room temperature conditions (25 °C). The samples were prepared at a concentration of 1 mg mL⁻¹ in Millipore-quality water. The samples were introduced into 12mm Square Polystyrene Cuvettes (DTS0012, Malvern Panalytical). Each sample underwent three measurement runs, and the average of the recorded results was used.

Thermogravimetric Analysis

The samples underwent thermogravimetric analysis using the PerkinElmer TGA 8000 thermobalance instrument. The measurements were carried out under a nitrogen atmosphere, and a consistent heating rate of 5 °C per minute was applied for all analyses. The temperature range for the analysis spanned from 30 °C to 800 °C. Aluminum oxide (Al₂O₃) crucibles were used to hold all samples, each weighing <25 mg.

Lyophilization

Freeze-drying of all items was carried out using a Christ Alpha 1-2 LDplus device and Christ Alpha 3-4 LSCbasic for aqueous solvent removal and for organic solvent removal, respectively. The products were frozen with liquid nitrogen before mounting on the device.

Scanning Electron Microscopy

The scanning electron microscope (Hitachi SU8030, Japan) was used to examine the surface morphology of the nanomaterials. The examination was conducted at an accelerating voltage (V_{acc}) of 15.0 - 30.0 kV, a current of 10.1 μA, and a working

distance (WD) approximately set at 10.0 mm. Size distribution analysis of recovered Au⁰ species was done using ImageJ software.

UV-Vis Spectroscopy

UV-Vis analyses were conducted using the PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer in the wavelength range of 200-900 nm. The samples were assessed using a UV Macro-Cuvette (Type 100-QS, 10 mm, Quartz Glass SUPRASIL® 200-2500 nm, Hellma Analytics). Millipore-quality water was used for all measurements.

Atomic Absorption Spectroscopy

The elemental analysis of metal concentrations in the samples was performed using AAS on a PerkinElmer AAnalyst 200 instrument. The samples were brought to a known volume with deionized water. Standard solutions of gold, chromium, copper, iron, zinc, and nickel were used to measure calibration curves. The samples and standards were introduced into the flame atomizer, and the absorbance signals were recorded at the characteristic wavelength for each metal. The instrument parameters, including the flame conditions and lamp currents, were optimized for maximum sensitivity and accuracy. All measurements were performed in triplicate, and the results were expressed as the mean $\pm$ standard deviation.

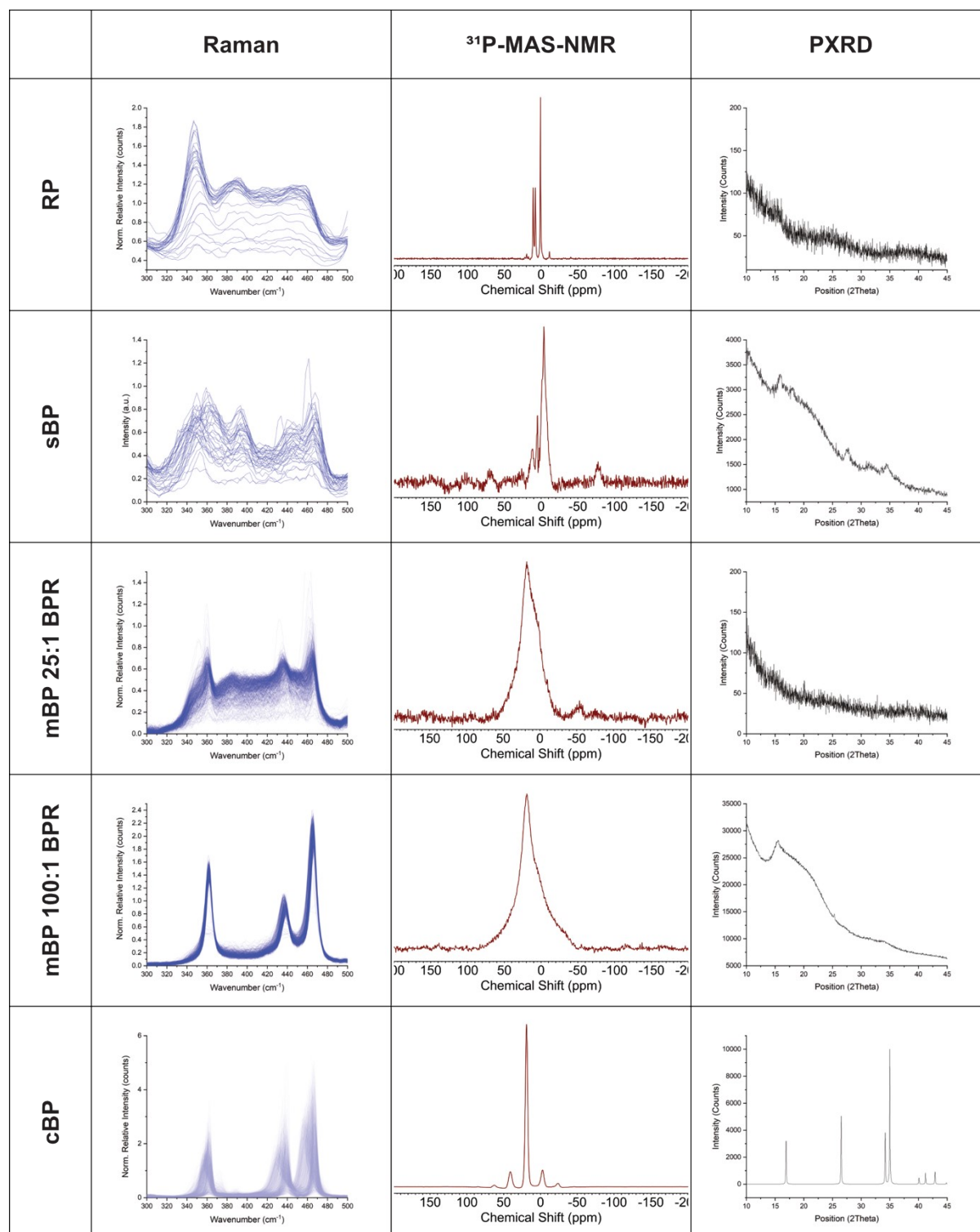
Mercury Porosimetry

Mercury intrusion porosimetry (MIP) was performed using an AutoPore V instrument from Micromeritics Instrument Corporation. The MIP method is based on the principle that mercury, being a non-wetting fluid, can only enter the pore throats of a solid under increasing pressure. The pore diameter is inversely proportional to the applied pressure, as described by the Washburn equation. For this study, measurements were conducted across a low-pressure range from 0.0036 MPa to 0.3 MPa and a high-pressure range up to 400 MPa. This allowed for the determination of the pore size distribution across a range of approximately 3.6 nm to 400 μ m. The principles underlying this technique are well-documented in the literature (Washburn, 1921; ISO 15901-1, 2016).

Cyclic Voltammetry

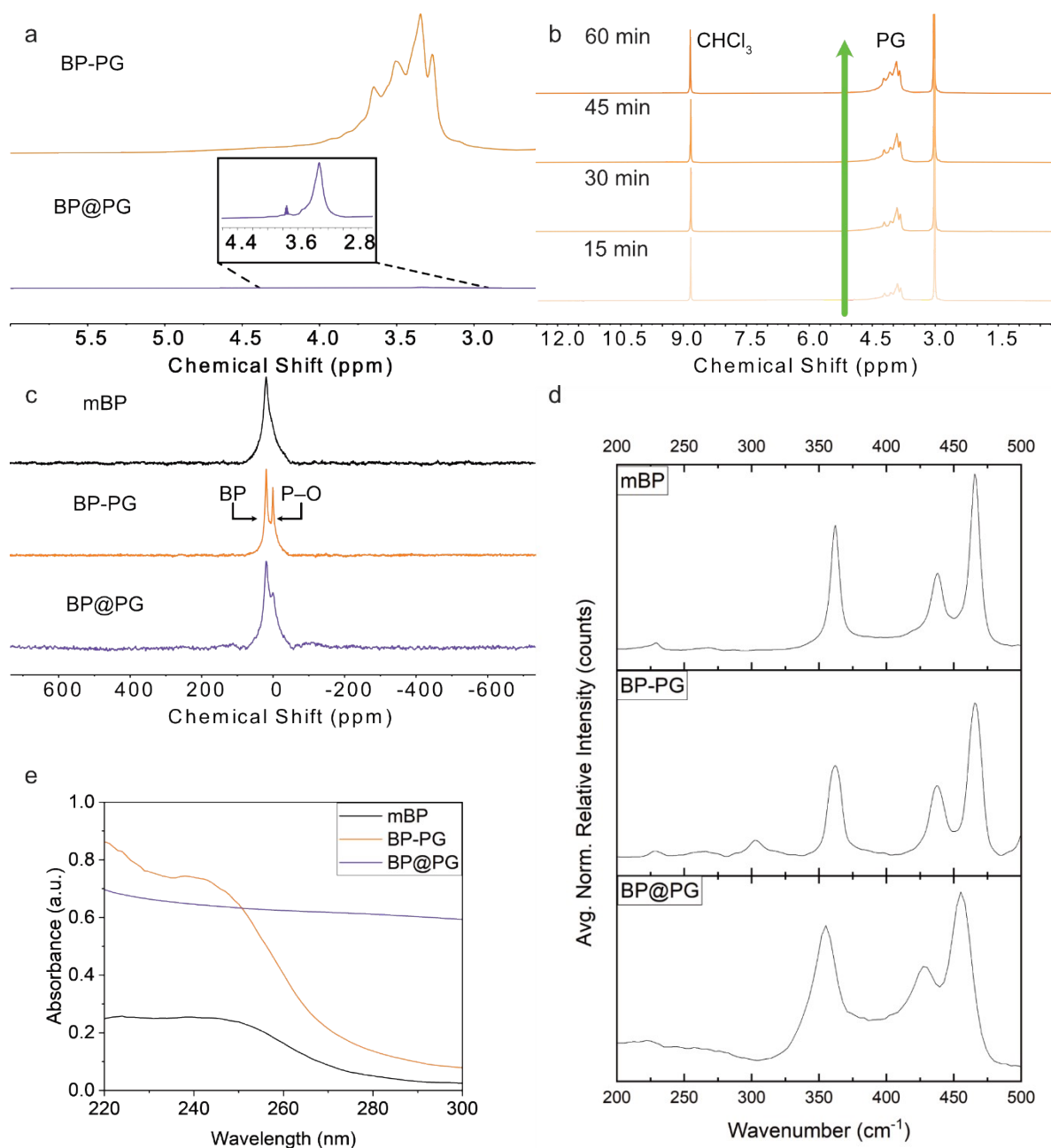
Cyclic voltammetry experiments were conducted to investigate the electrochemical properties of the BP-PG nanomaterial. A 1 mg mL^{-1} suspension of BP-PG was prepared and drop-cast on a polished glassy carbon electrode, which served as the working electrode. A platinum wire and an Ag/AgCl electrode (3.5 M KCl) were used as the counter and reference electrodes, respectively. The electrochemical measurements were performed in a standard three-electrode cell containing water. The potential sweep was conducted from 0.0 V to 1.2 V versus the Ag/AgCl reference electrode at a scan rate of 50 mV/s. The experiments were carried out at room temperature (approximately 25°C), and the data were recorded and analyzed using Echem Analyst from Gamry Instruments®, focusing on the identification of oxidation peaks to elucidate the redox behavior of the BP-PG nanomaterial.

SI 1: Raman, ^{31}P -MAS-NMR, and PXRD Analysis of BP Nanomaterials



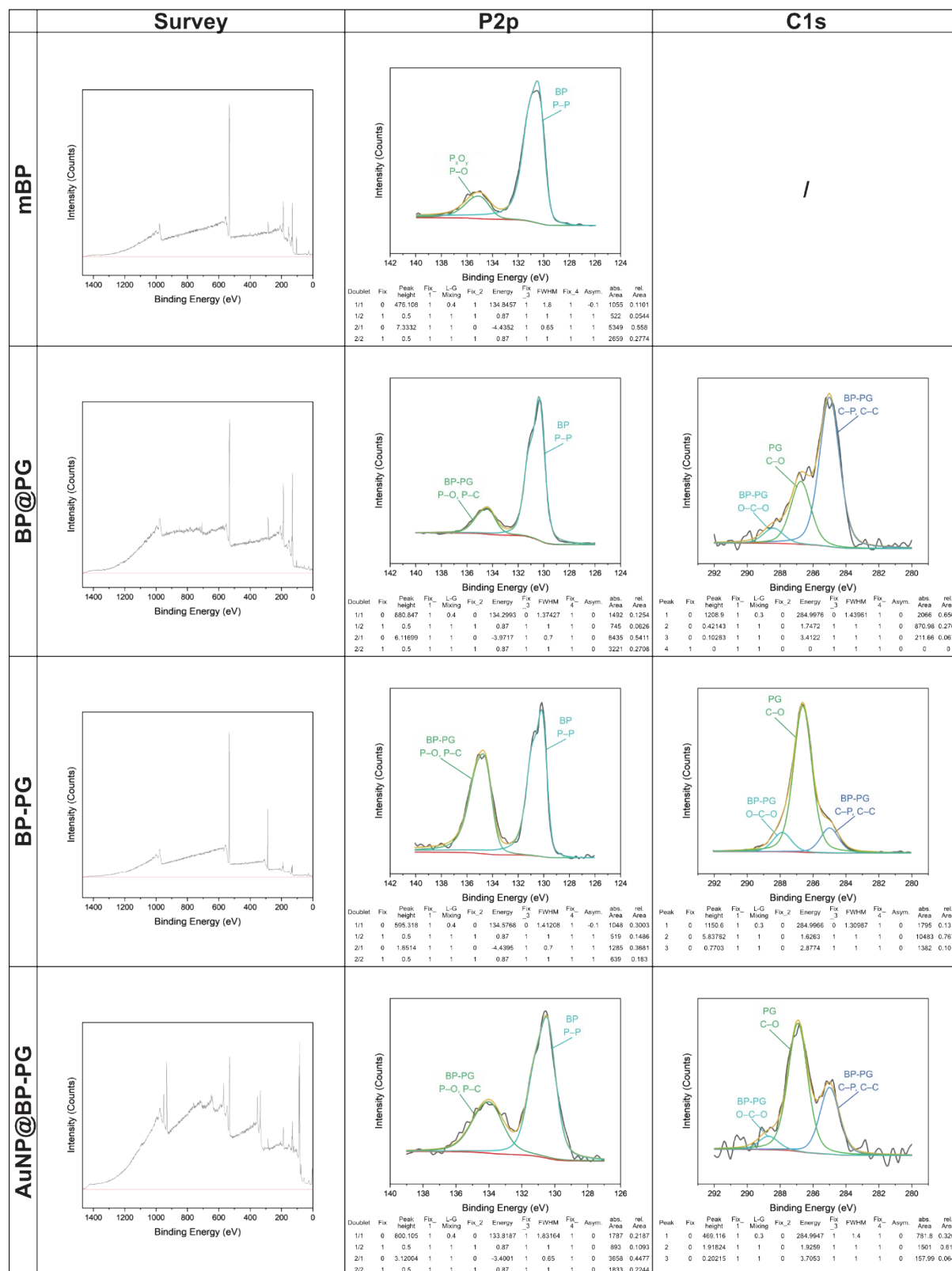
SI 1: Raman spectra obtained from map measurements, ^{31}P -MAS-NMR, and PXRD spectra of RP, mBP (100:1 BPR), mBP (25:1 BPR), cBP, and sBP. PXRD of cBP is adapted from ICSD.⁷⁶

SI 2: ^1H -NMR, ^{31}P -MAS-NMR, Raman, and UV-Vis Analysis of Functionalized Nanomaterials



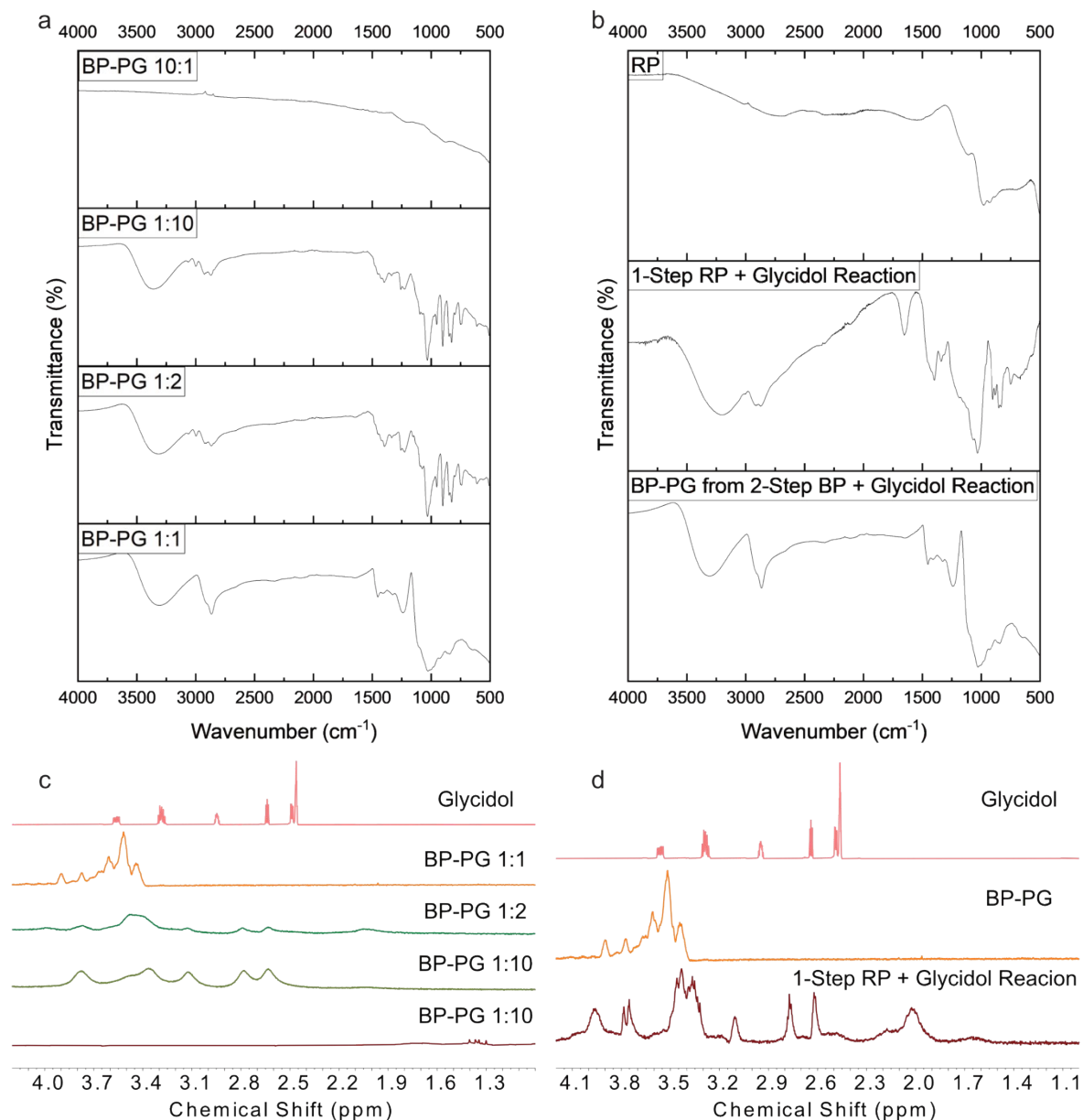
SI 2: **a** ^1H -NMR spectra of BP-PG and BP@PG in DMSO- d_6 , normalized to CHCl_3 calibrant, obtained after 1 hr of HEPBM. **b** ^1H -NMR spectra of BP-PG in DMSO- d_6 , normalized to CHCl_3 calibrant, obtained after 15 min intervals of HEPBM. **c** ^{31}P -MAS-NMR spectra of mBP, BP-PG, and BP@PG showing a high degree of functionalization of BP-PG. **d** Average normalized Raman spectra derived from Raman maps obtained from mBP, BP-PG, and BP@PG. **e** UV-Vis analysis of mBP, BP-PG, and BP@PG after 15 min from dispersing in H_2O ($100 \mu\text{g mL}^{-1}$).

SI 3: XPS Analysis of Functionalized Nanomaterials



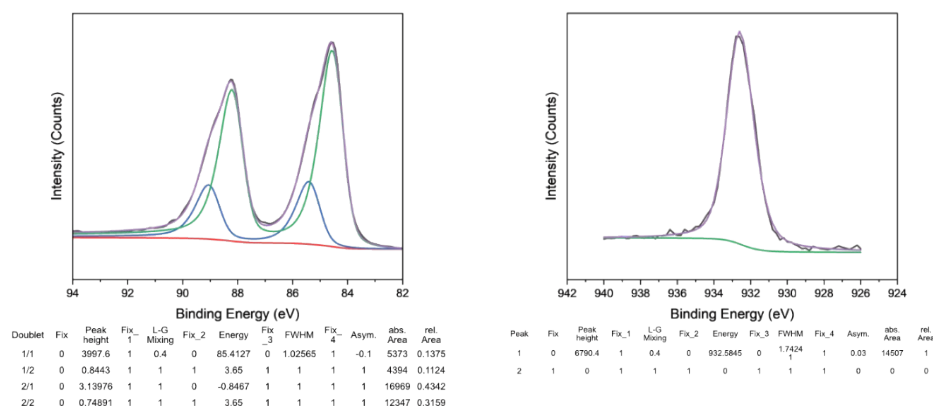
SI 3: Survey spectra, P2p, and C1s high-resolution XPS analysis of mBP, BP@PG, BP-PG, and AuNP@BP-PG, along with their fitting parameters.

SI 4: FT-IR Analysis of Various Functionalization Reactions



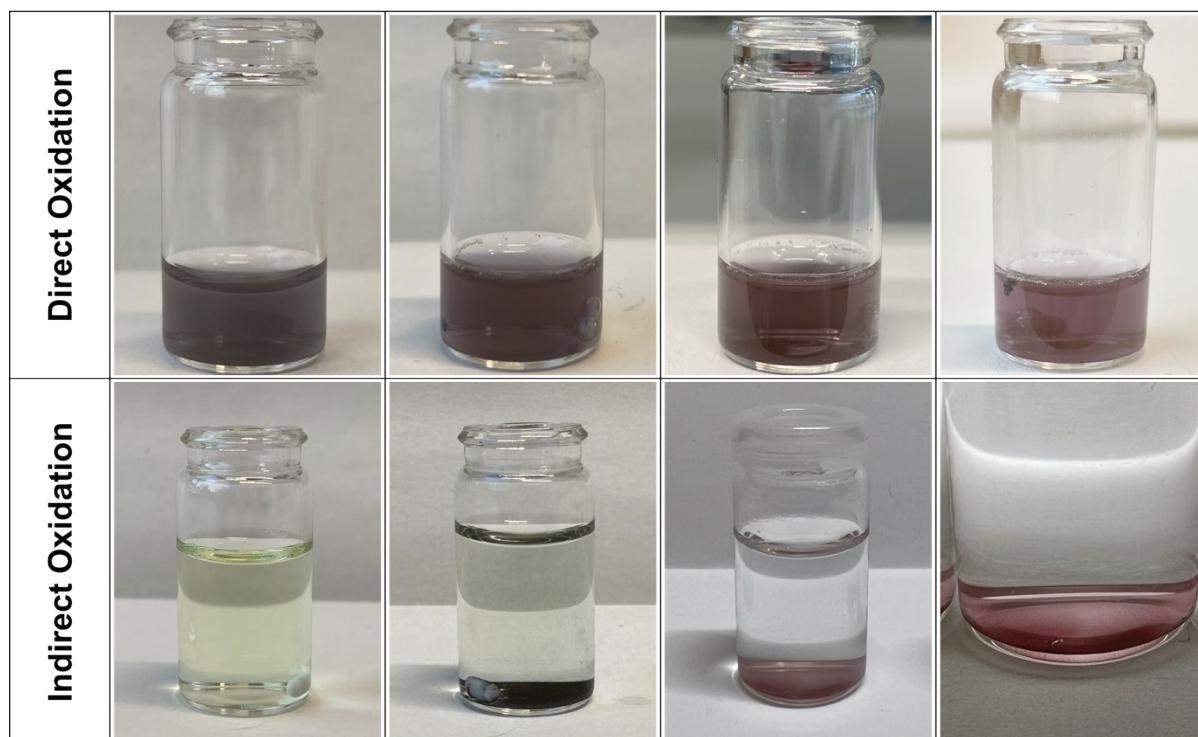
SI 4: **a** FT-IR and **c** ^1H -NMR analysis of products from various functionalization reactions between BP and glycidol with varying w/w ratios of BP-to-Glycidol. **b** FT-IR and **d** ^1H -NMR analysis of a 1-step reaction between RP and glycidol, indicating various chemical species different from that obtained by the 2-step approach.

SI 5: AuNP and Cu ion XPS Analysis of AuNP@BP-PG



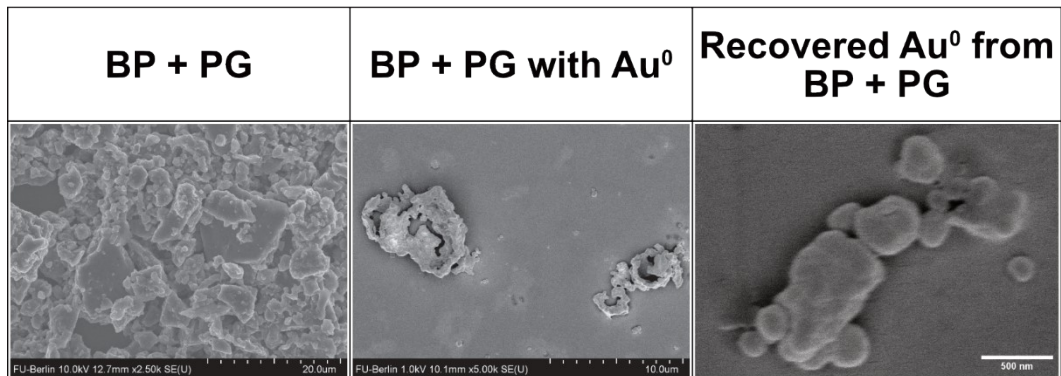
SI 5: High-resolution Au 4f and Cu 2p_{3/2} XPS analysis of AuNP@BP-PG.

SI 6: Recovery of AuNPs from AuNP@BP-PG via Direct and Indirect Oxidation



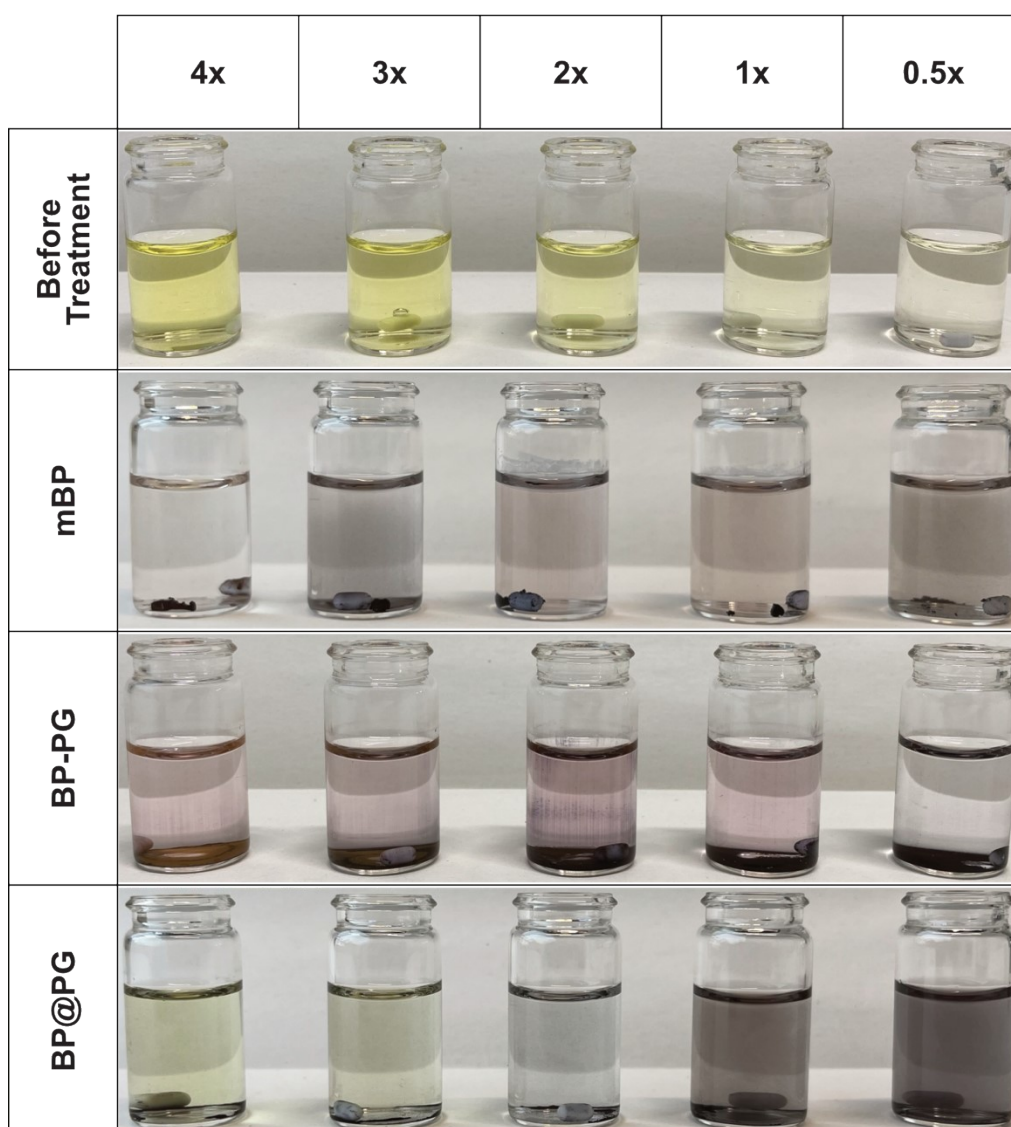
SI 6: Direct oxidation using H₂O₂ (30 % w/w in H₂O) and indirect oxidation using oxygen from atmosphere of AuNP@BP-PG. Direct oxidation occurs immediately, while degradation from ambient atmosphere can occur within a few days.

SI 7: SEM Analysis of BP + PG Pre- and Post-Treatment of EWL



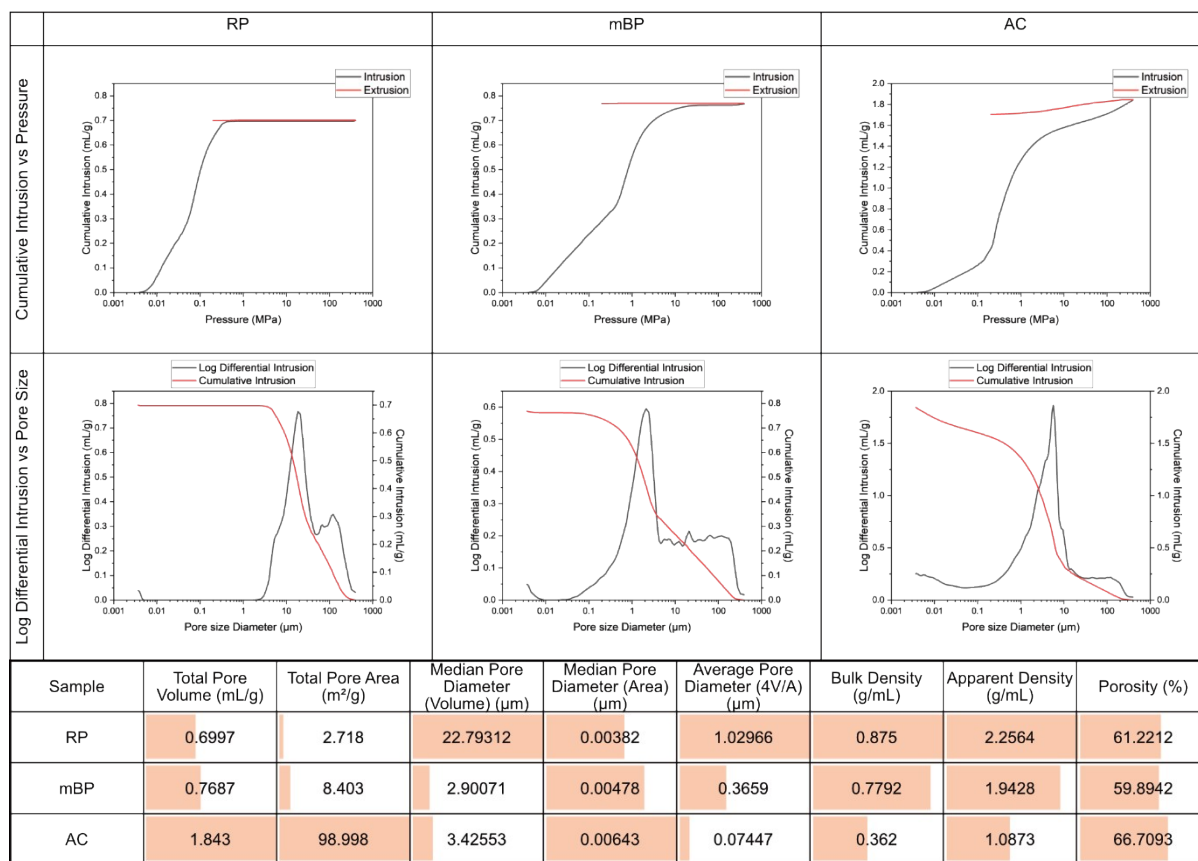
SI 7: SEM micrographs of BP + PG pre- and post-treatment of EWL.

SI 8: Gold Reduction Using Produced Nanomaterials



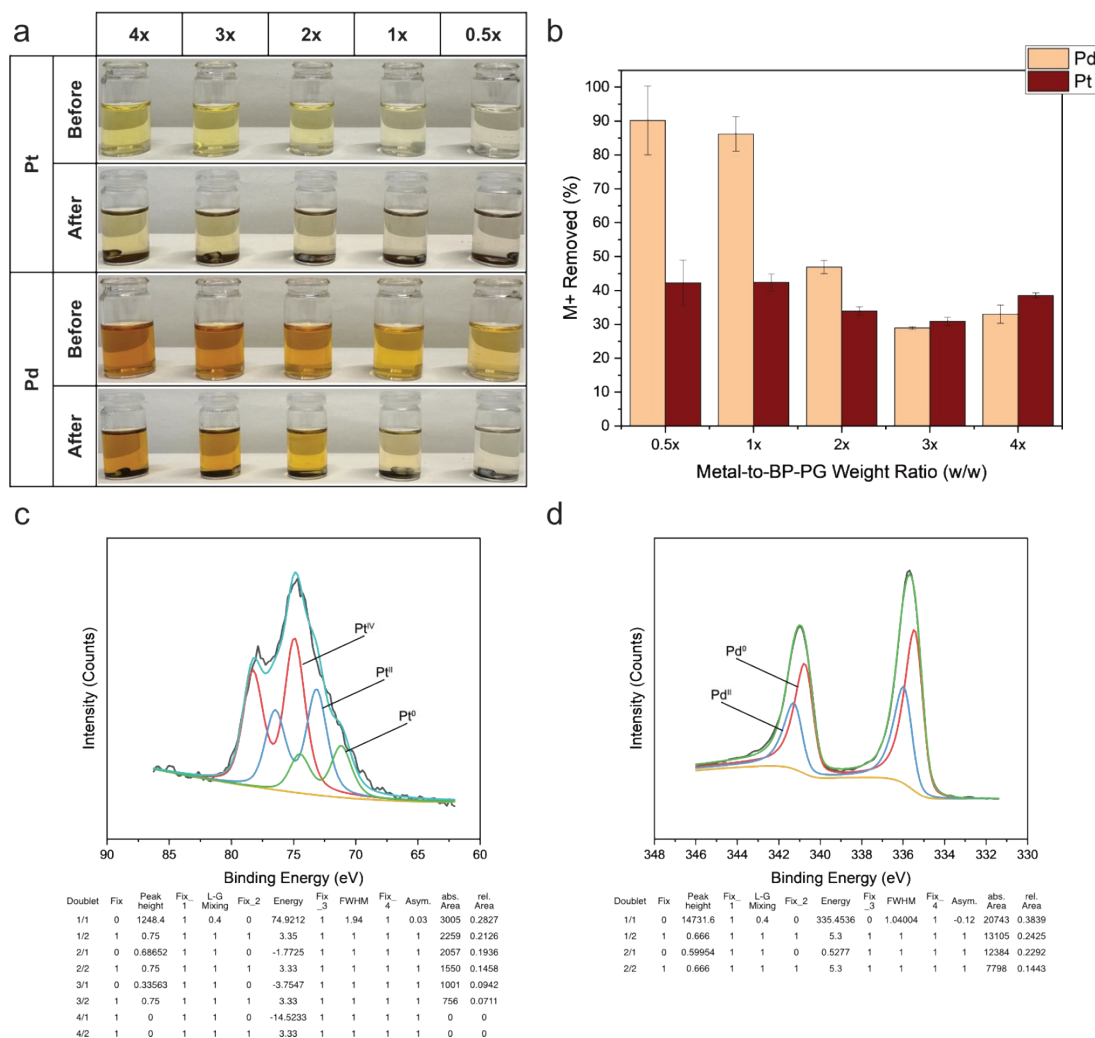
SI 8: Gold recovery test of mBP, BP-PG, and BP@PG against Au^{3+} solutions at different concentrations over 1 hour ($\text{Au}^{3+} = 125, 250, 500, 750, \text{ and } 1000 \mu\text{g mL}^{-1}$ against $250 \mu\text{g mL}^{-1}$ of BP-PG, pH 1). As clearly shown, mBP particles tend to agglomerate and requires extra efforts to disperse them in aqueous environments (i.e. sonication), whereas BP-PG is easily dispersed.

SI 9: Hg Porosimetry of RP, mBP, and AC



SI 9: Hg porosimetry of RP, mBP, and AC.

SI 10: Pt and Pd Recovery Using BP-PG



SI 10: **a** Images and **b** UV-Vis analysis of Pd²⁺ and Pt⁴⁺ removal test of BP-PG against solutions at different concentrations ($[M]^+ = 125, 250, 500, 750, \text{ and } 1000 \mu\text{g mL}^{-1}$ against $250 \mu\text{g mL}^{-1}$ of BP-PG, pH 1). **c** Pt 4f XPS and **d** Pd 3d XPS of adsorbed Pt and Pd species, respectively, after treatment of Pt^{IV} and Pd^{II} solutions ($[M]^+ = 250 \mu\text{g mL}^{-1}$) with BP-PG ($250 \mu\text{g mL}^{-1}$, pH 1).