

Electronic Supplementary Information

Redispersion of Transition Metal Nanoparticle Catalysts in Tetraalkylphosphonium Ionic
Liquids

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Experimental

Materials: Commercially available reagents (such as metal precursors from Sigma Aldrich) were used without purification unless noted otherwise. High purity solvents were purchased from Fischer Scientific and 100% ethanol was purchased from Commercial Alcohols. 18M Ω cm Milli-Q (Millipore, Bedford, MA) was used throughout. Ionic liquids were donated by Cytec Canada, and were used after drying under the vacuum at 60⁰C for 8 hours.

General Comments on Techniques: Unless otherwise stated, all reactions were performed using standard Schlenk techniques, with nitrogen to provide an inert atmosphere, in oven-dried Schlenk glassware. ¹H and ¹³C-NMR spectra were recorded at 500 MHz on a Bruker Avance spectrometer. NMR spectra were recorded in deuterated chloroform (CDCl₃) solutions, with residual chloroform ($\delta = 7.27$ ppm for ¹H NMR and $\delta = 77.23$ ppm for ¹³C-NMR) taken as the internal standard, and were reported in parts per million (ppm). For ambient temperature UV/Vis spectra, a Varian Cary 50 Bio UV/Visible spectrophotometer with a scan range of $\lambda=200-800$ nm and quartz cuvettes with optical path lengths of 0.4 cm were used. A Cary 6000i spectrophotometer, equipped with a sample changer and a constant temperature bath capable of holding cuvettes and stirring their contents with the aid of a magnetic stirrer while recording their spectra, was used for the etching studies. To avoid effects of oxygen depletion on etching of NPs, the contents of the cuvettes were flushed with oxygen between readings. TEM analyses of the NPs in different ILs were conducted by using a Philips 410 TEM operating at 100 kV. The TEM samples were prepared by ultrasonication of ~5% solution of the NP/IL solution in CHCl₃ followed by drop-wise addition onto a carbon-coated copper TEM grid (Electron Microscopy Sciences, Hatfield, PA). To determine particle diameters, a minimum of 100 particles from each sample from several TEM images were manually measured by using the ImageJ program. For

Cu, Fe and Co NPs, TEM sample preparation was performed using de-aerated 1,4-dioxane under nitrogen. For Ni NPs, which oxidized quickly in air while in the IL, the NPs were extracted from the ionic liquid matrix into a toluene layer containing phenylethanethiol, and this Ni-enriched layer was used for drop-coating the TEM grid under nitrogen.

Synthesis of NPs: In a representative synthesis, Pd NPs were generated in trihexyl(tetradecyl)phosphonium chloride as follows: K_2PdCl_4 (16 mg; 0.05 mmol on the basis of Pd content) was added under N_2 to a sample of the IL (10 mL) at 70°C , and vigorously stirred to give a reddish-brown solution.¹ The solution was cooled to 60°C , and a stoichiometric excess of LiBH_4 reagent (1.5 mL, 2.0M in THF) was injected drop-wise over a period of 5 min. Rapid effervescence followed, and the entire solution turned milk-brown, indicating NP formation. After the addition of LiBH_4 , volatile impurities were removed by vacuum stripping the system at 80°C . The Pd NP solution thus obtained was stored under N_2 in capped vials until use. UV-Visible spectra of the precursor in the IL, as well as the NPs, were recorded after dilution to ~ 0.5 mM with methanol, with neat methanol as the blank, and compared with the literature.² Similar spectra were recorded after the oxidative degeneration of the NPs to show that the systems reverted to their precursors under these conditions. It is to be noted that the excess reductant present in the system offers protection against accidental exposure of NPs to air, especially for the 3d transition metal NPs, which are readily oxidized upon aerial exposure. For Ag NPs, synthesis in the absence of light produced reproducible results. For all the systems, information about precursors, NP sizes, *etc.* can be found in Table 1 (below). Note that for Fe NPs, large aggregates were not taken into account while measuring particle sizes.

Table 1: Regeneration conditions for MNPs studied.

<u>Metal</u>	<u>Precursor</u>	<u>Reductant</u>	<u>NP size (nm)</u>	<u>NP size after regeneration (nm)</u>	<u>Oxidant</u>
Ag	AgNO ₃	LiBH ₄	3.5 ± 0.6	4.1 ± 0.8	Oxygen
Au	HAuCl ₄ .4H ₂ O	LiBH ₄	3.2 ± 0.8	5.5 ± 1.4	Oxygen
Cu	Cu(NO ₃) ₂ .2.5 H ₂ O	LiAlH ₄	4.2 ± 1.0	9.1 ± 3.7	Air
Co	CoCl ₂	LiAlH ₄	4.7 ± 1.3	12.5 ± 4.1	Air
Fe	FeCl ₃ .6H ₂ O	LiAlH ₄	7.4 ± 2.0	8.0 ± 3.1	Air
Ni	NiCl ₂ .6H ₂ O	LiAlH ₄ or LiBH ₄	5.9 ± 1.3	6.8 ± 2.1	Air
Pd	K ₂ PdCl ₄	LiBH ₄	4.9 ± 2.2	3.1 ± 1.1	<i>t</i> -butyl hydroperoxide
Pt	Pt(acetylacetonate) ₂	LiBH ₄	2.4 ± 0.4	2.2 ± 0.7	<i>t</i> -butyl hydroperoxide
Rh	Na ₃ RhCl ₆	LiBH ₄	9.6 ± 3.5	11.3 ± 3.9	<i>t</i> -butyl hydroperoxide
Ru	RuCl ₃ .3H ₂ O	LiBH ₄	4.5 ± 1.2	3.5 ± 1.1	<i>t</i> -butyl hydroperoxide

Hydrogenation catalysis: Hydrogenation reactions were performed in a Schlenk flask, with the stem initially connected to an H₂ gas source. In a representative reaction, 10mL of 10mM Ni NPs in P[6,6,6,14]Cl in the Schlenk flask was flushed with H₂ for 15 minutes at 65⁰C, and the reactant (cyclohexene, 2mL) was injected into the reaction vessel. The Schlenk flask was then connected to a reflux condenser, and the reaction was allowed to progress at this temperature for 8 hours under constant hydrogen supply via a hydrogen-filled balloon connected securely to the top of the reflux condenser using a Schlenk adapter. Vacuum stripping at elevated temperatures was used to recover the product and leftover substrate from the reaction mixture, and ¹H NMR spectroscopy was used to determine the ratio between the product(s) and the unreacted substrate (if any) from the areas of the signals. It was observed that after each cycle, the yield of cyclohexane went down, and the initially transparent brown Ni NP solution became cloudy (likely suspended agglomerates). For the regeneration procedure, the Ni NPs in P[6,6,6,14]Cl were exposed to air, and heated at 65⁰C with stirring, which led to the development of a greenish-blue solution. This, upon reduction by LiBH₄ under nitrogen after de-aeration, regenerated the brown Ni NPs. TEMs were taken after the regeneration to ensure that NPs were indeed being formed. These ‘re-formed’ NPs were used for another cycle of catalytic hydrogenation, and it was seen that they produced yields similar to the first cycle.

¹H NMR data for a sample extract: 5.584 (1 and 2, 2H, m), 2.021 (3 and 6, 4H, m), 1.649 (4 and 5, 4H, m) [cyclohexene], 1.348 (1, 6H, m) [cyclohexane].

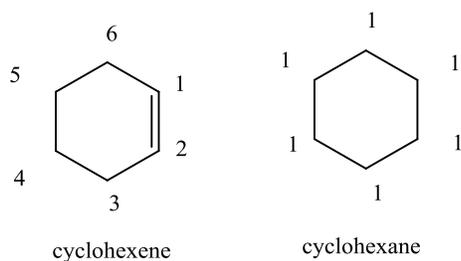
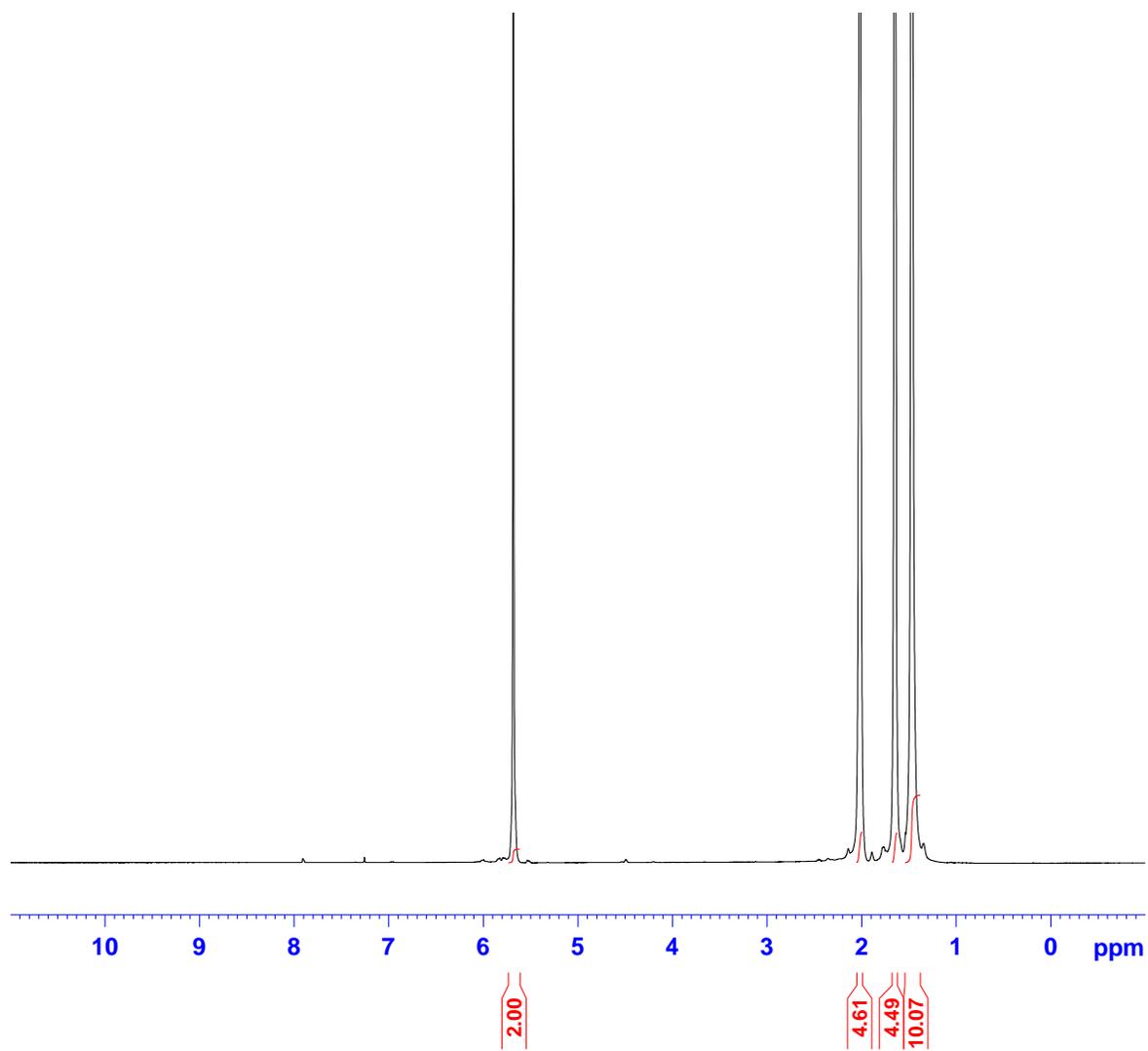
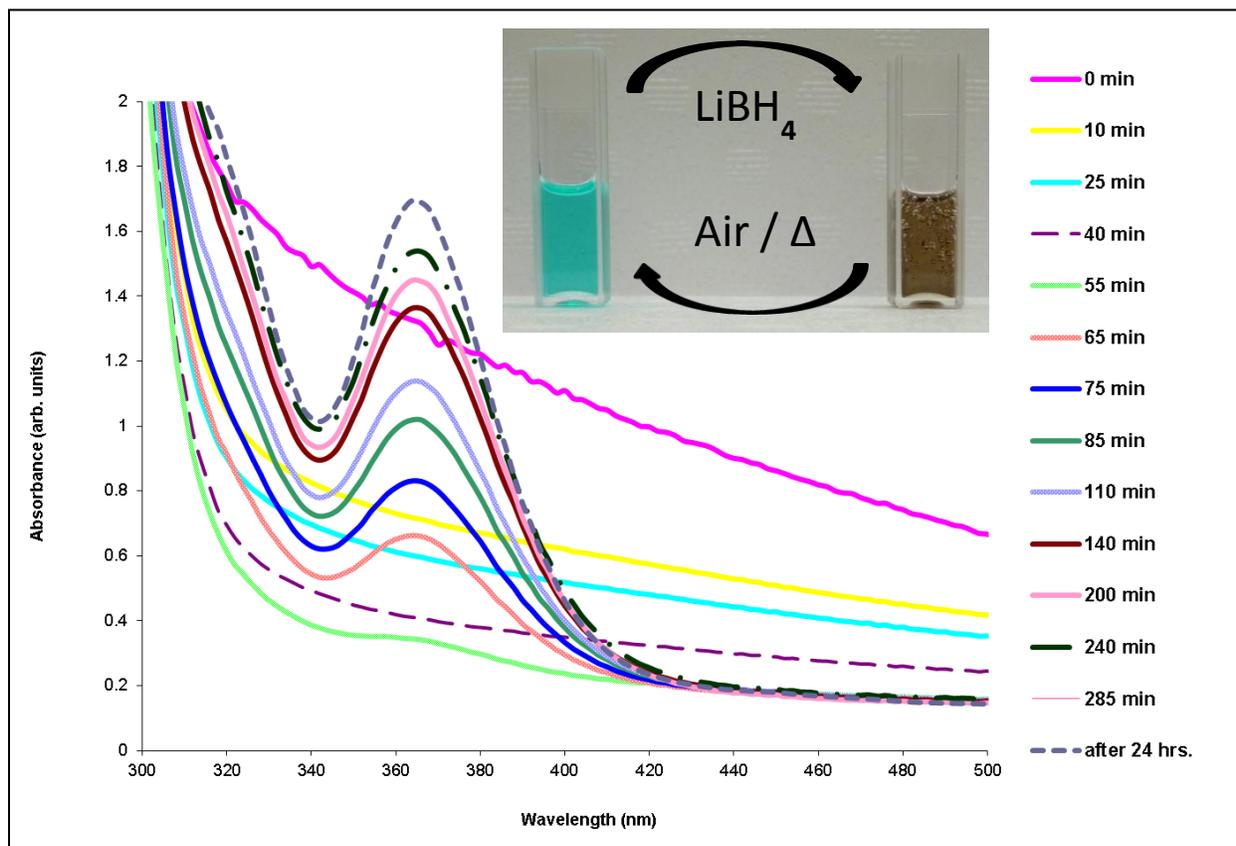


Figure S1: ^1H NMR spectrum of neat vacuum extract after NiNP/IL catalyzed hydrogenation of cyclohexene.



UV-Vis spectroscopic study of Ni NP oxidative degeneration: While Ni NPs in P[6,6,6,14]Cl can serve as powerful hydrogenation catalysts in the presence of gaseous hydrogen at temperatures well below 100°C, repeated use of the same catalyst affects the yields adversely, likely due to increase in size from 6.0 ± 1.4 nm to 19.5 ± 2.5 nm.³ To counter this, Ni NPs in the IL were heated to 65°C in air to oxidize Ni⁰ to NiCl₄²⁻, followed by re-reduction of the Ni salts. This transformation could be followed spectroscopically for a diluted Ni NP system (2.5mM Ni⁰ in P[6,6,6,14]Cl), as shown in Figure S2. Several prominent peaks appeared gradually as the dispersion changed colour upon being heated and stirred. The intense bands at ~365nm were clearly LMCT bands, while weaker bands at higher wavelengths (659nm, 710nm) could be attributed to LaPorté forbidden *d-d* transitions in the metal cation and their splitting owing to lowering of symmetry of the Ni-complexes due to the non-uniform fields of the tetraalkylphosphonium cations.^{4,5} As Ni is more susceptible to oxidation than Au, the oxidation process was significantly faster, and bubbling of oxygen through the dispersion was not necessary. The turquoise Ni(II)/IL system could then be re-reduced with a stoichiometric excess of LiAlH₄ or LiBH₄ to regenerate small NPs. In P[6,6,6,14]Cl, the regenerated Ni NPs show enhanced catalytic activity for cyclohexene hydrogenation under ambient hydrogen pressures.

Figure S2: UV-Vis spectrophotometric study of the oxidative degeneration of Ni NPs in P[6,6,6,14]Cl stirred under air at 45⁰C; inset shows appearance of the sample at t=0 (brown, on the right) and at t=24 hours (turquoise, on the left).



TEM and UV-Vis spectroscopic study of MNPs in P[6,6,6,14]Cl:

(a) TEM images:

Figure S3: TEM images of the as-synthesized metal NPs: (a) Ag(3.5 ± 0.6 nm), (b) Au(3.2 ± 0.8 nm), (c) Co(4.7 ± 1.3 nm), (d) Cu(4.2 ± 1.0 nm), (e) Fe(7.4 ± 2.0 nm), (f) Ni(5.9 ± 1.3 nm), (g) Pd(4.9 ± 2.2 nm), (h) Pt(2.4 ± 0.4 nm), (i) Rh(9.6 ± 3.5 nm) and (j) Ru(4.5 ± 1.2 nm).

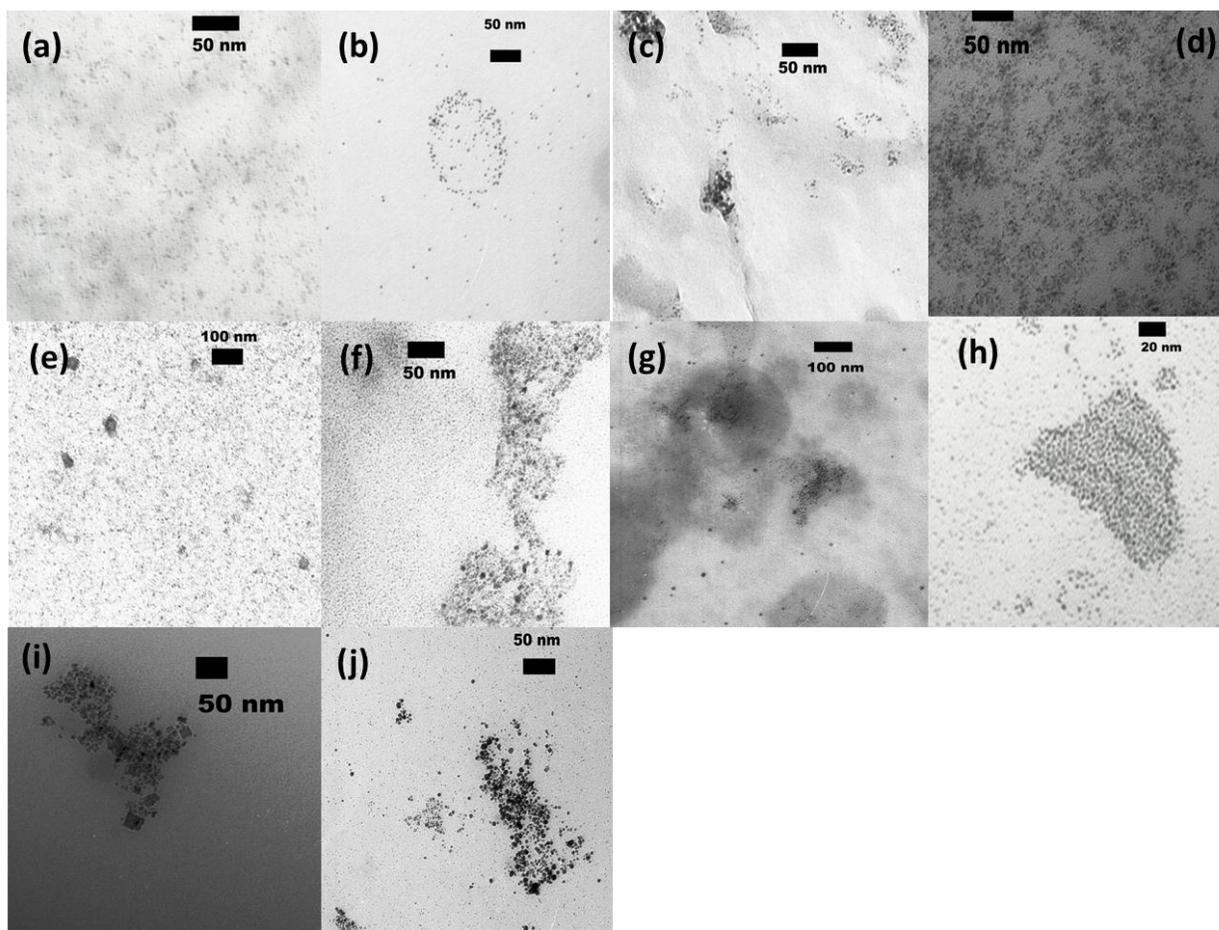
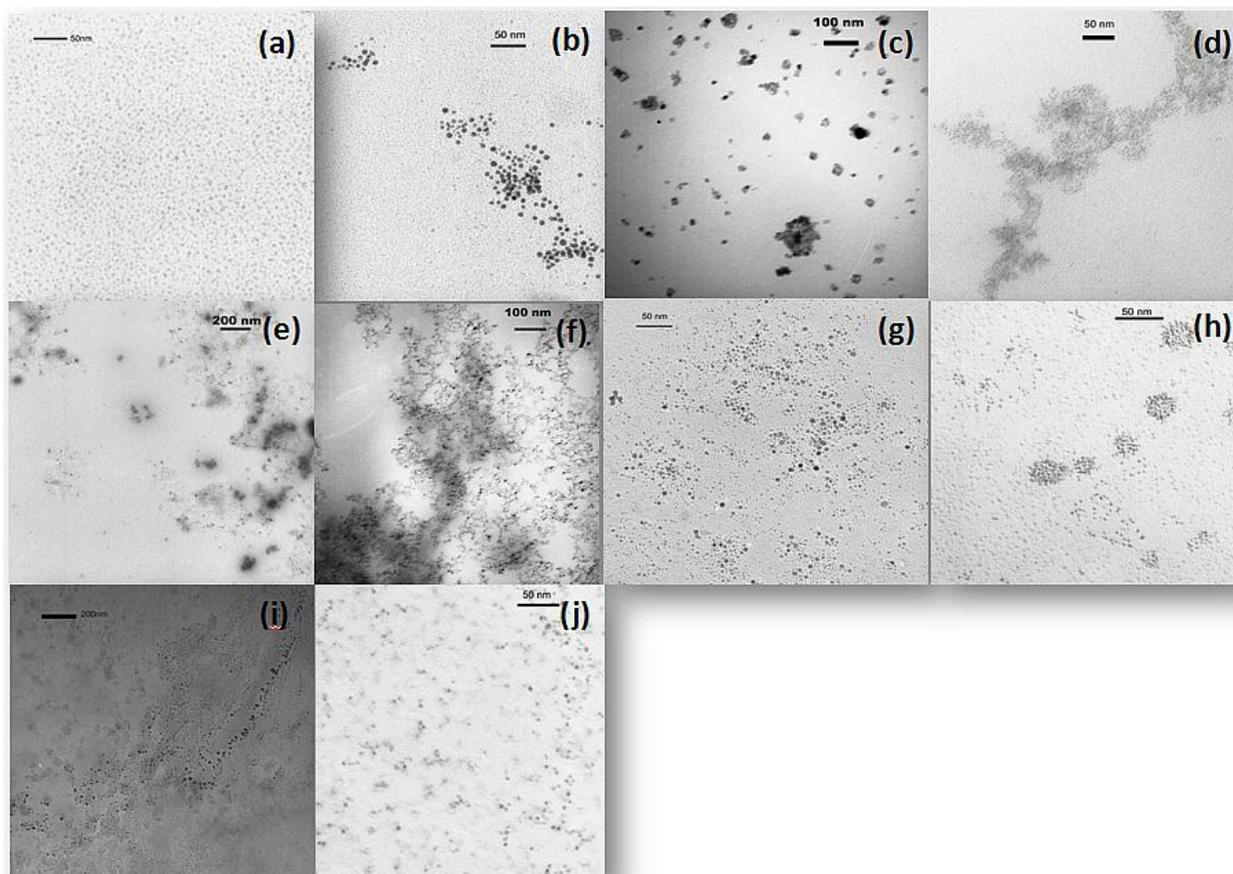
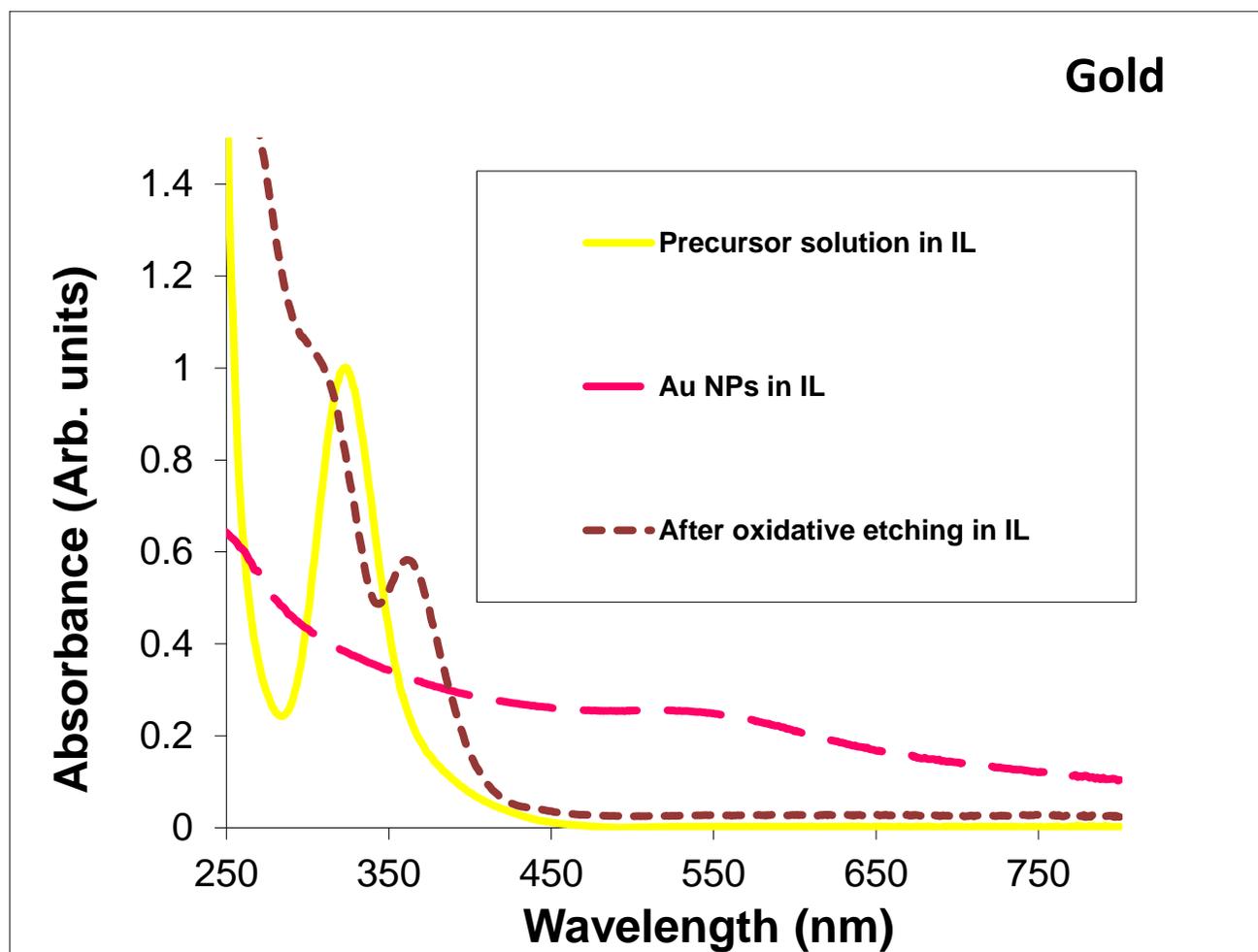
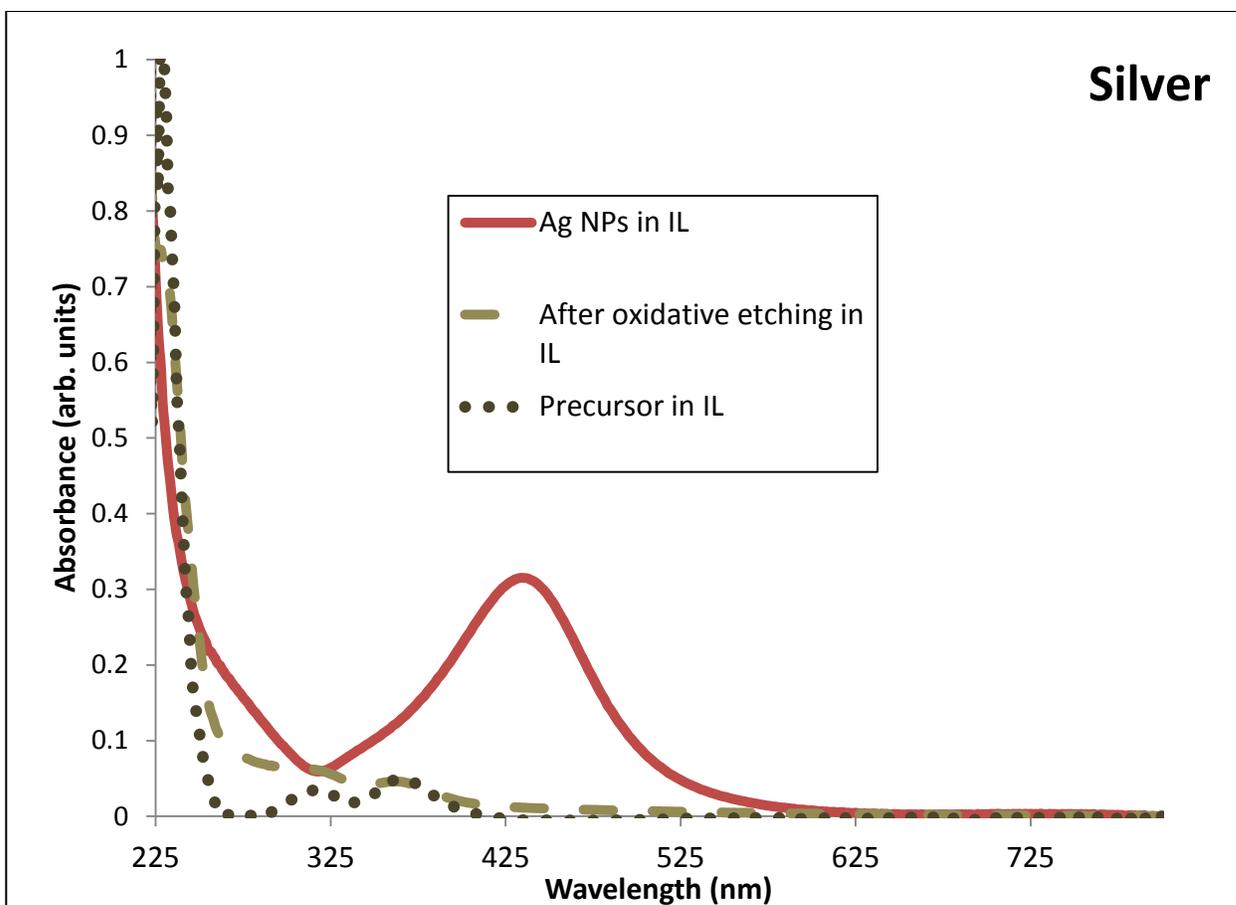


Figure S4: TEM images of the metal NPs after regeneration: (a) Ag(4.1 ± 0.8 nm), (b) Au(5.5 ± 1.4 nm), (c) Co(12.5 ± 4.1 nm), (d) Cu(9.1 ± 3.7 nm), (e) Fe(8.0 ± 3.1 nm), (f) Ni(6.8 ± 2.1 nm), (g) Pd(3.1 ± 1.1 nm), (h) Pt(2.2 ± 0.7 nm), (i) Rh(11.3 ± 3.9 nm) and (j) Ru(3.5 ± 1.1 nm).

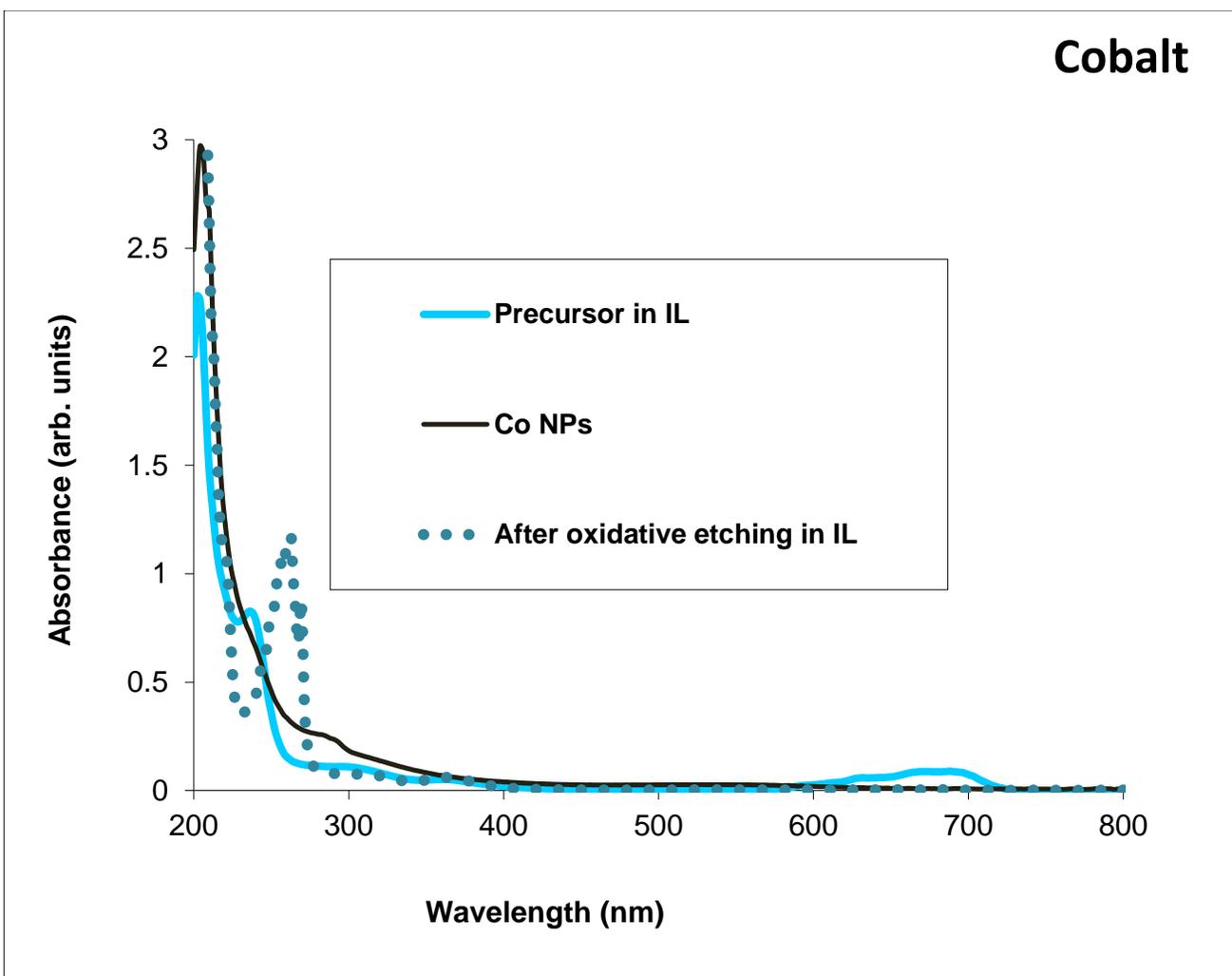


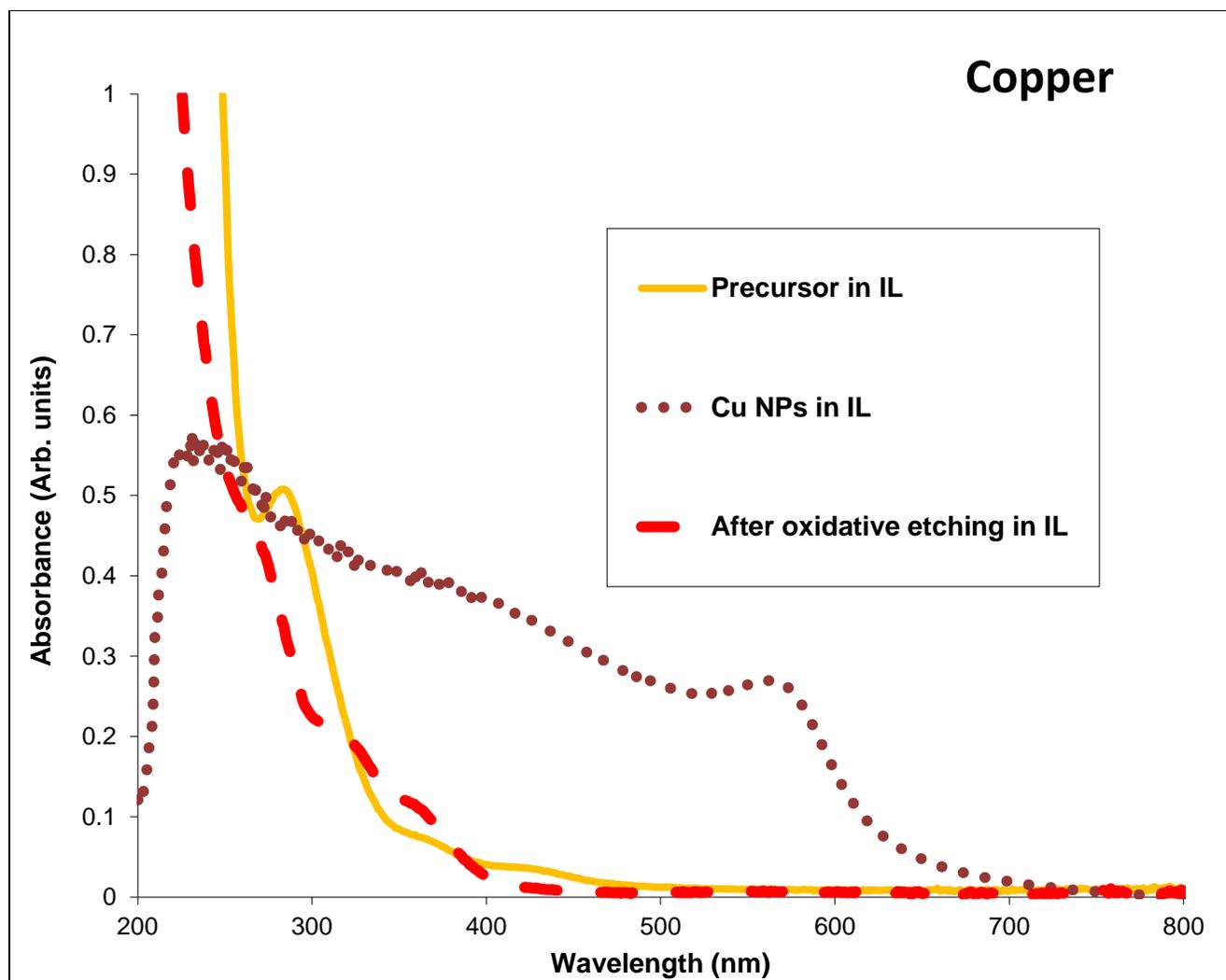
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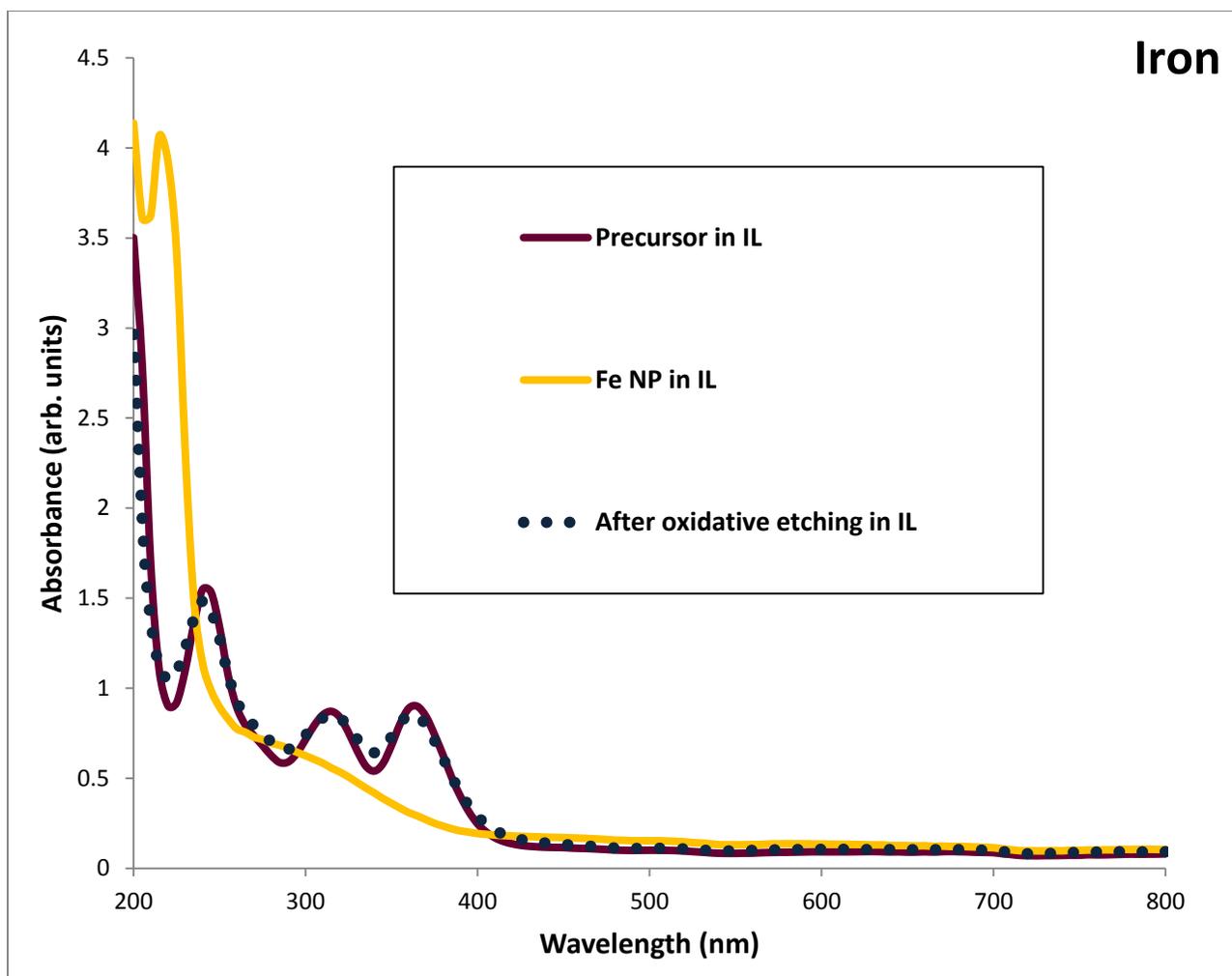


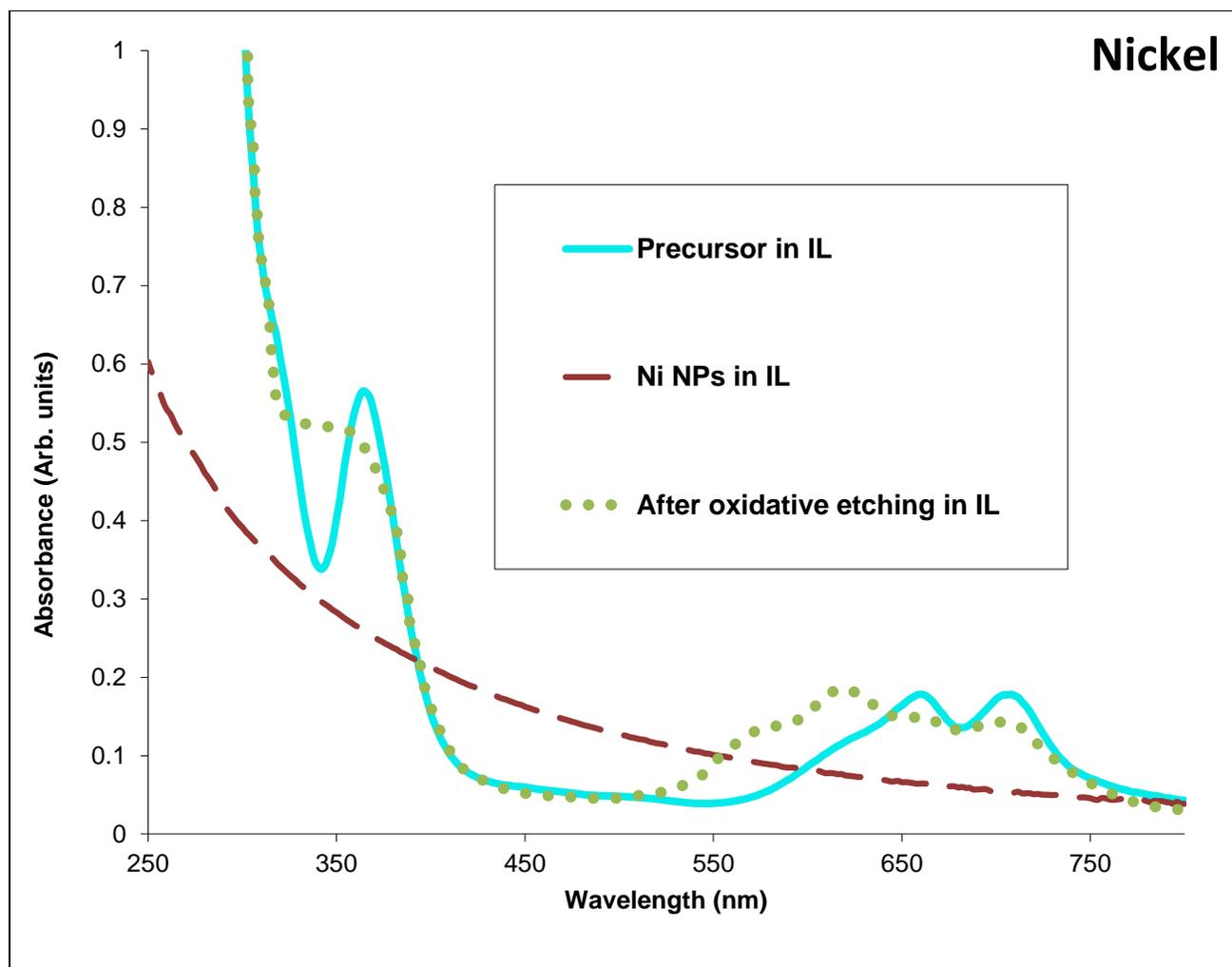


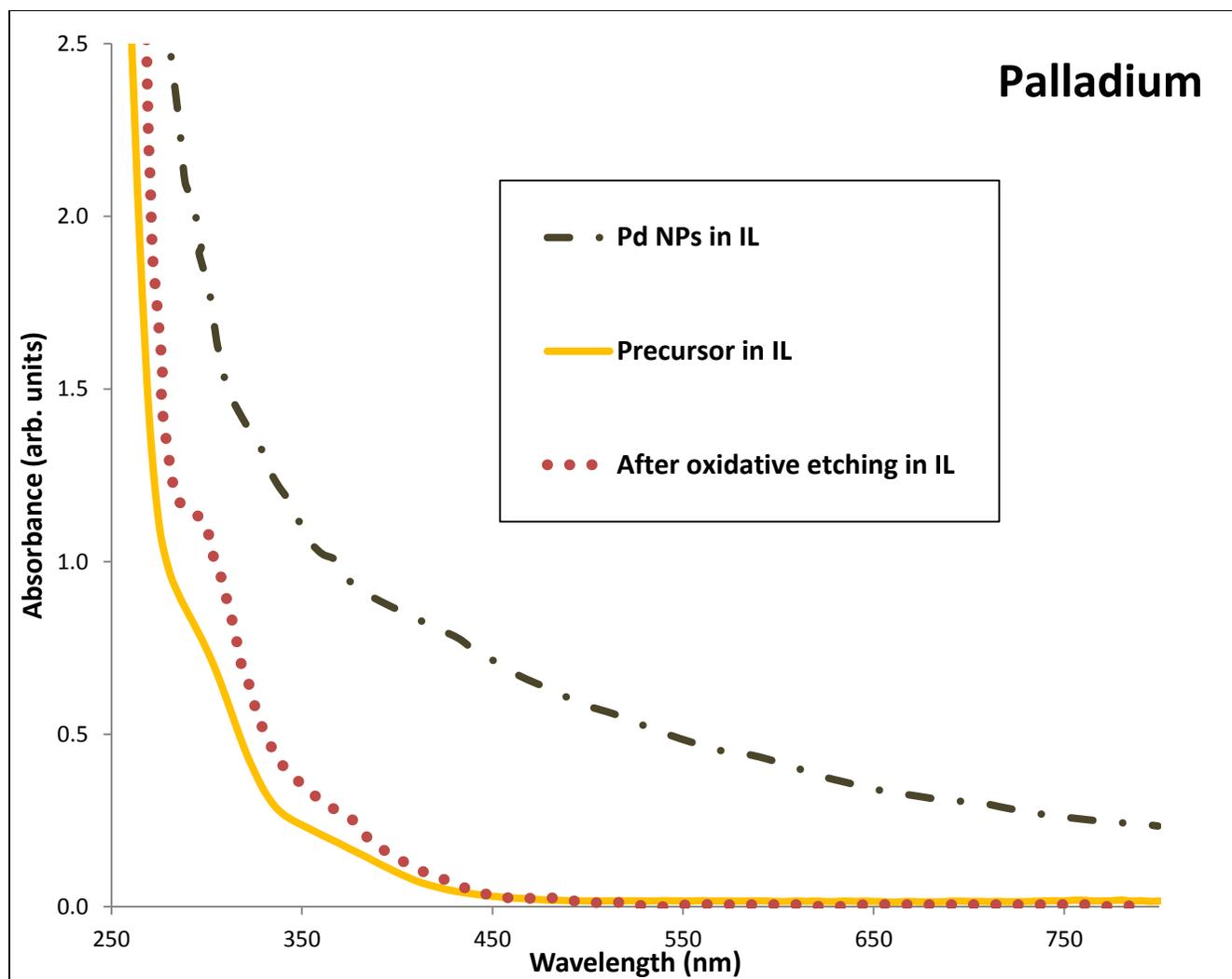
Cobalt

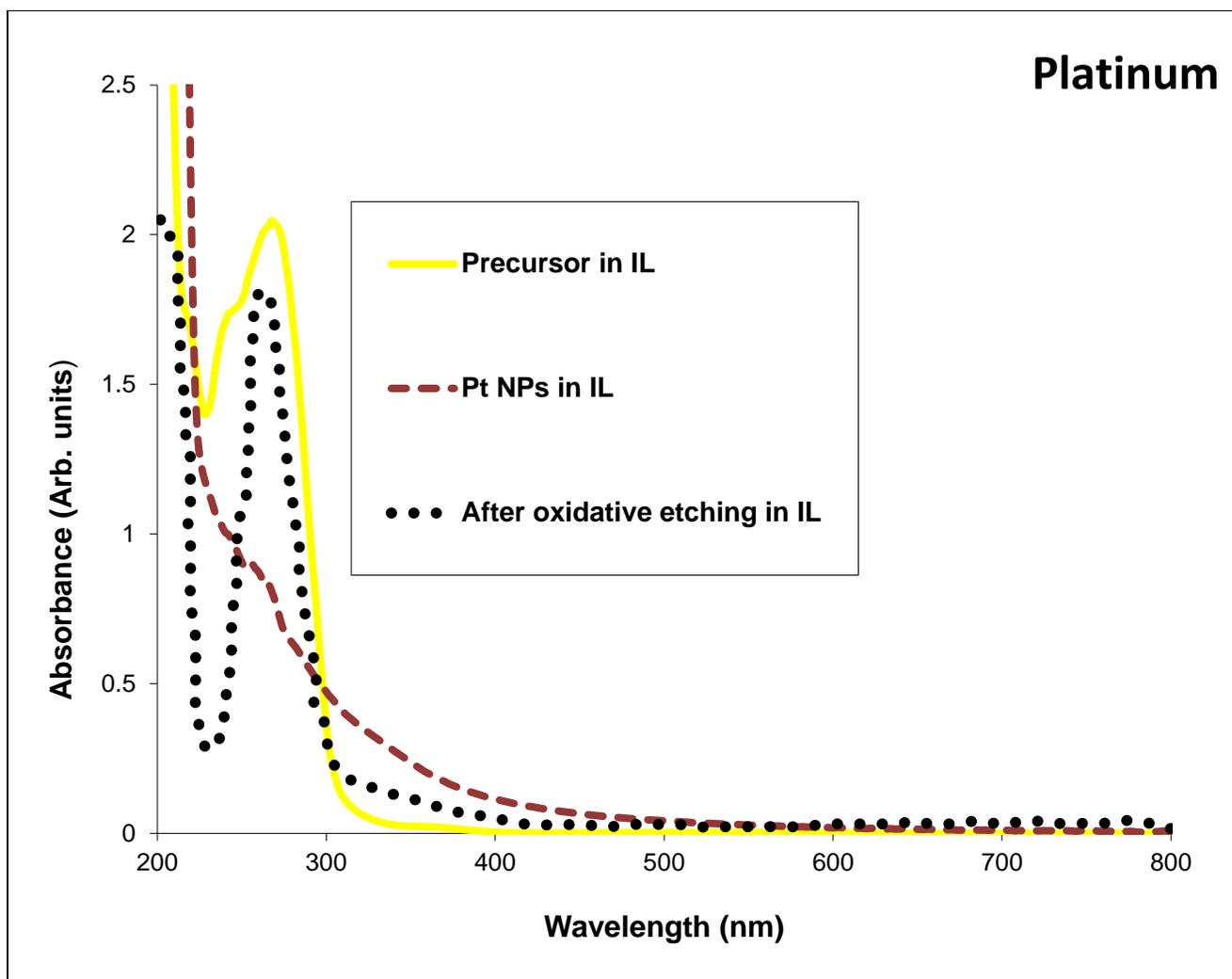


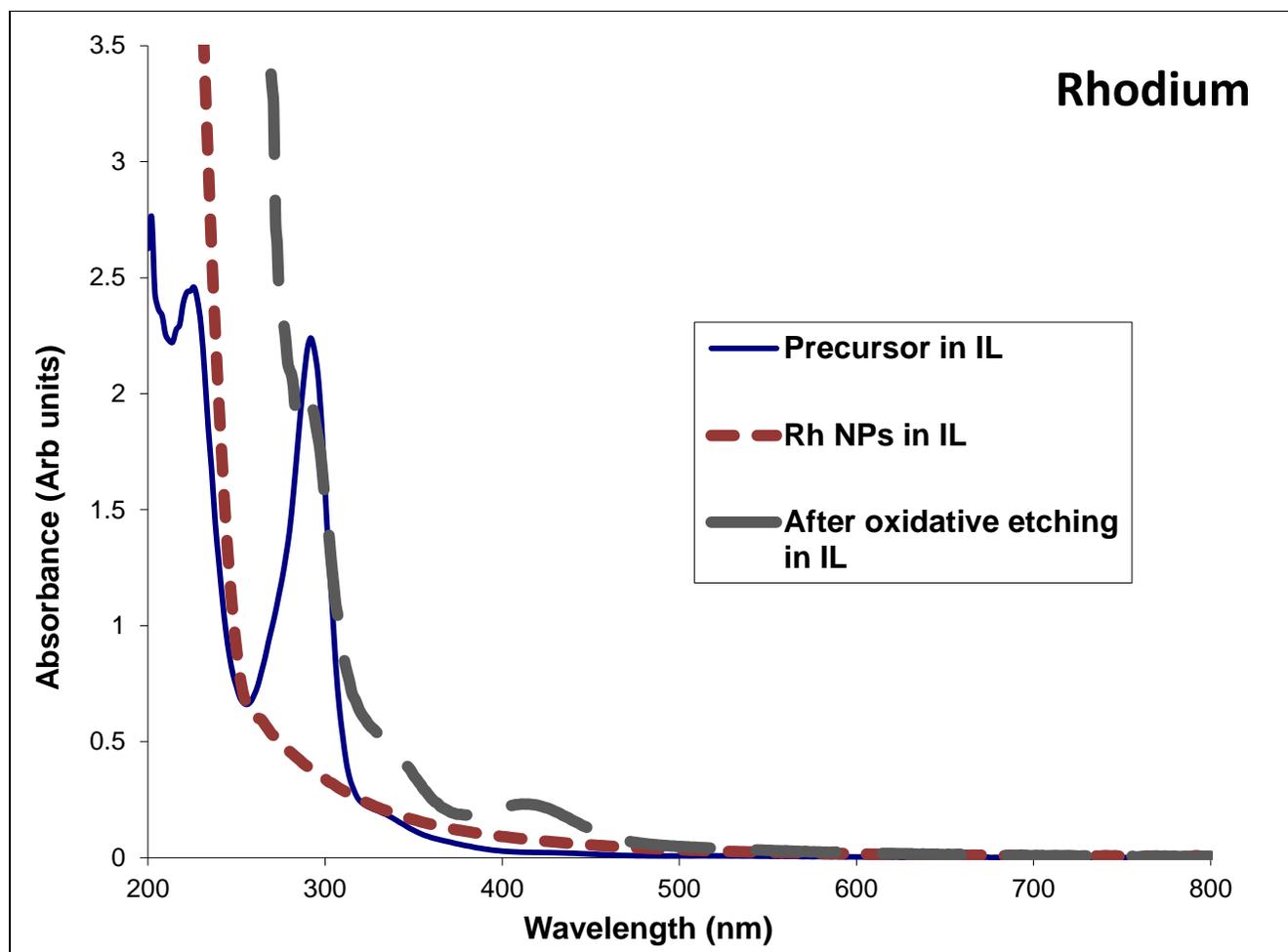


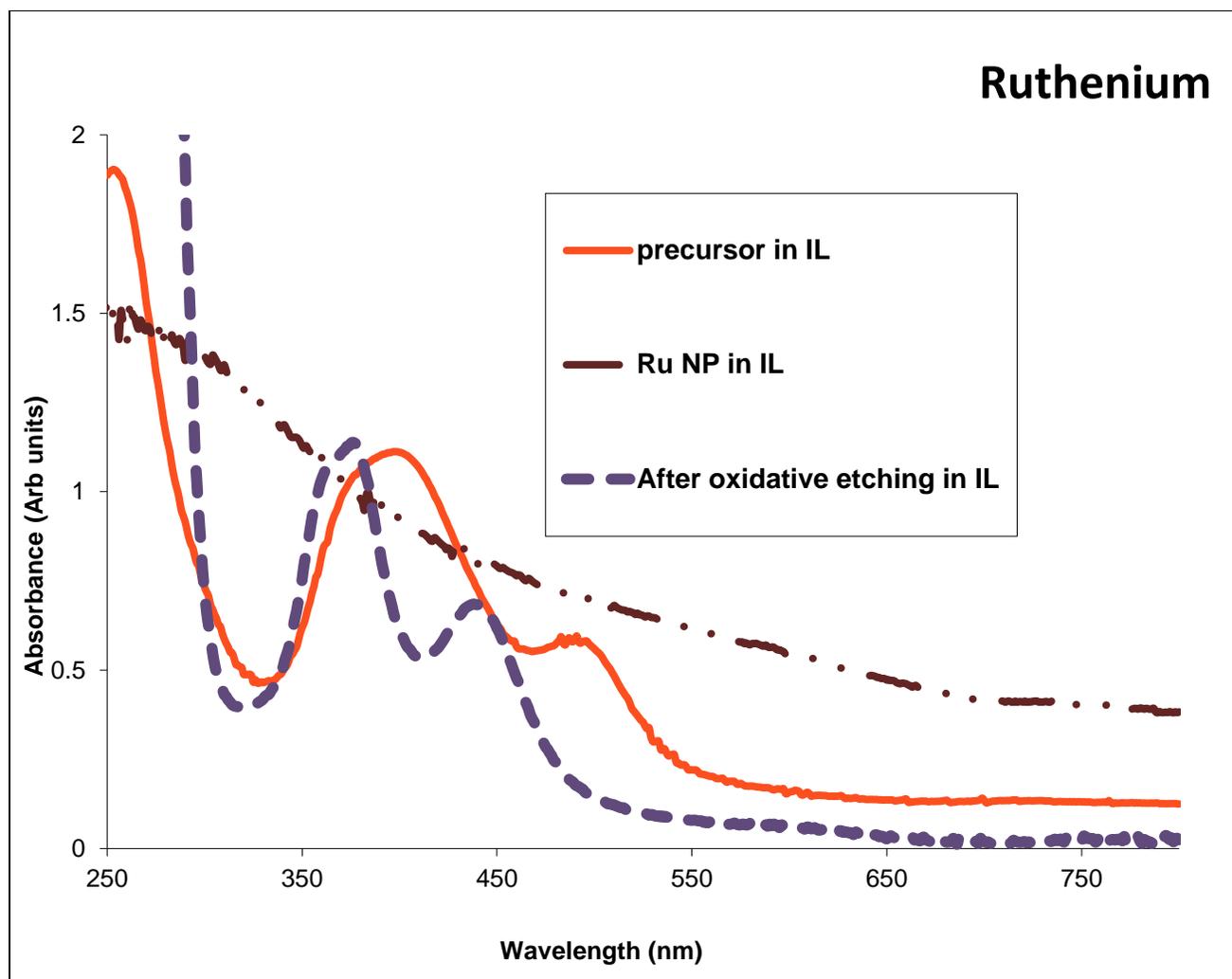












References:

1. A. Banerjee, R. Theron and R. W. J. Scott, *ChemSusChem*, 2012, **5**, 109-116.
2. J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3881-3891.
3. P. Migowski, G. Machado, S. R. Texeira, M. C. M. Alves, J. Morais, A. Traverse and J. Dupont, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4814-4821.
4. A. Khokhryakov, M. Mikhaleva and A. Paivin, *Russ. J. Inorg. Chem.*, 2006, **51**, 1311-1314.
5. C. R. Boston, J. Brynestad and G. P. Smith, *J. Chem. Phys.*, 1967, **47**, 3193-3197.