Supporting Information

A Combined Mechanochemical and Calcination Route to Mixed Cobalt Oxides for the Selective Catalytic Reduction of Nitrophenols

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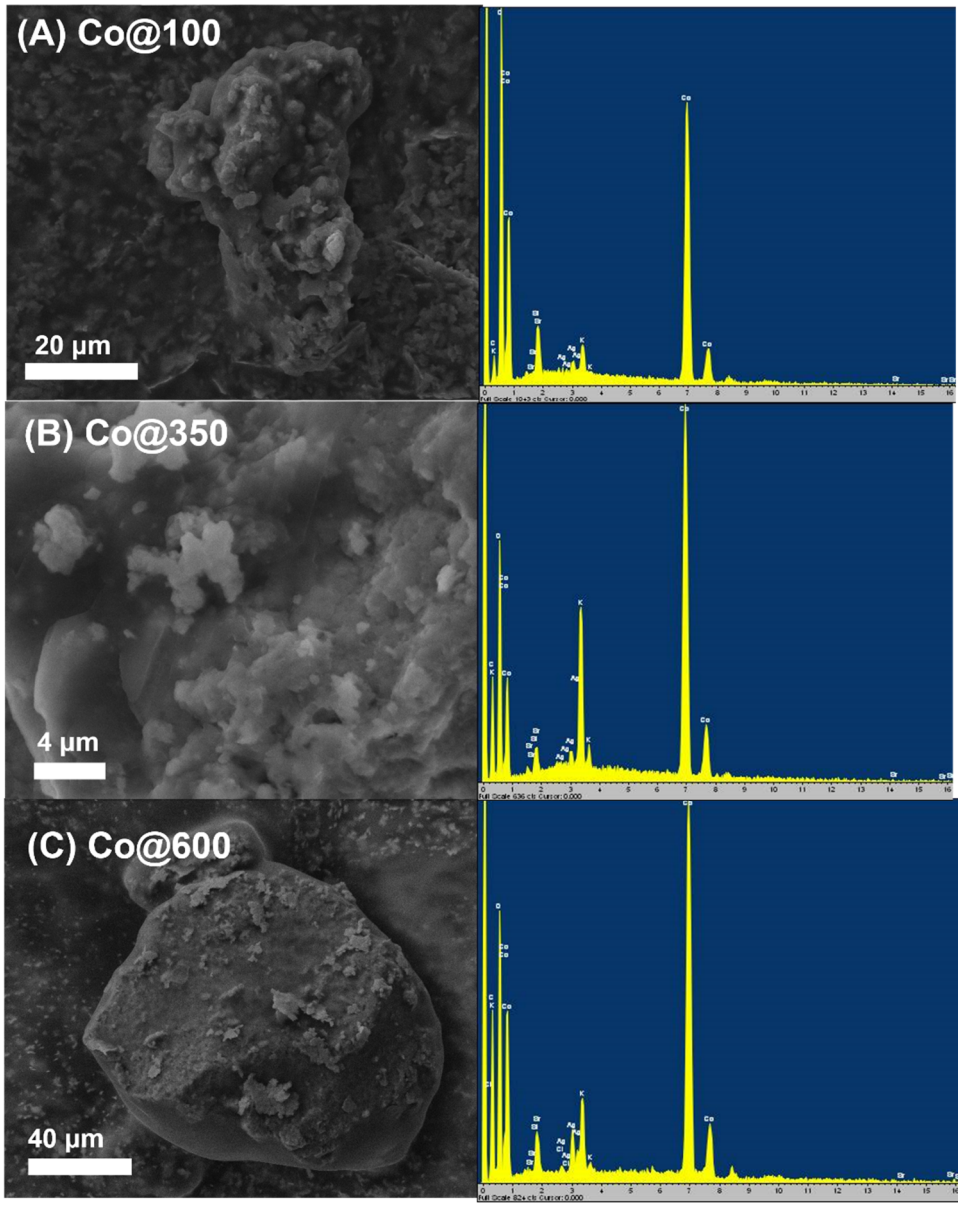

Figure S1: (*left*) Additional representative Scanning Electron Microscopy (SEM) images of (A) **Co@100**, (B) **Co@350**, and (C) **Co@600**; (*right*) representative corresponding SEM-EDX analysis.

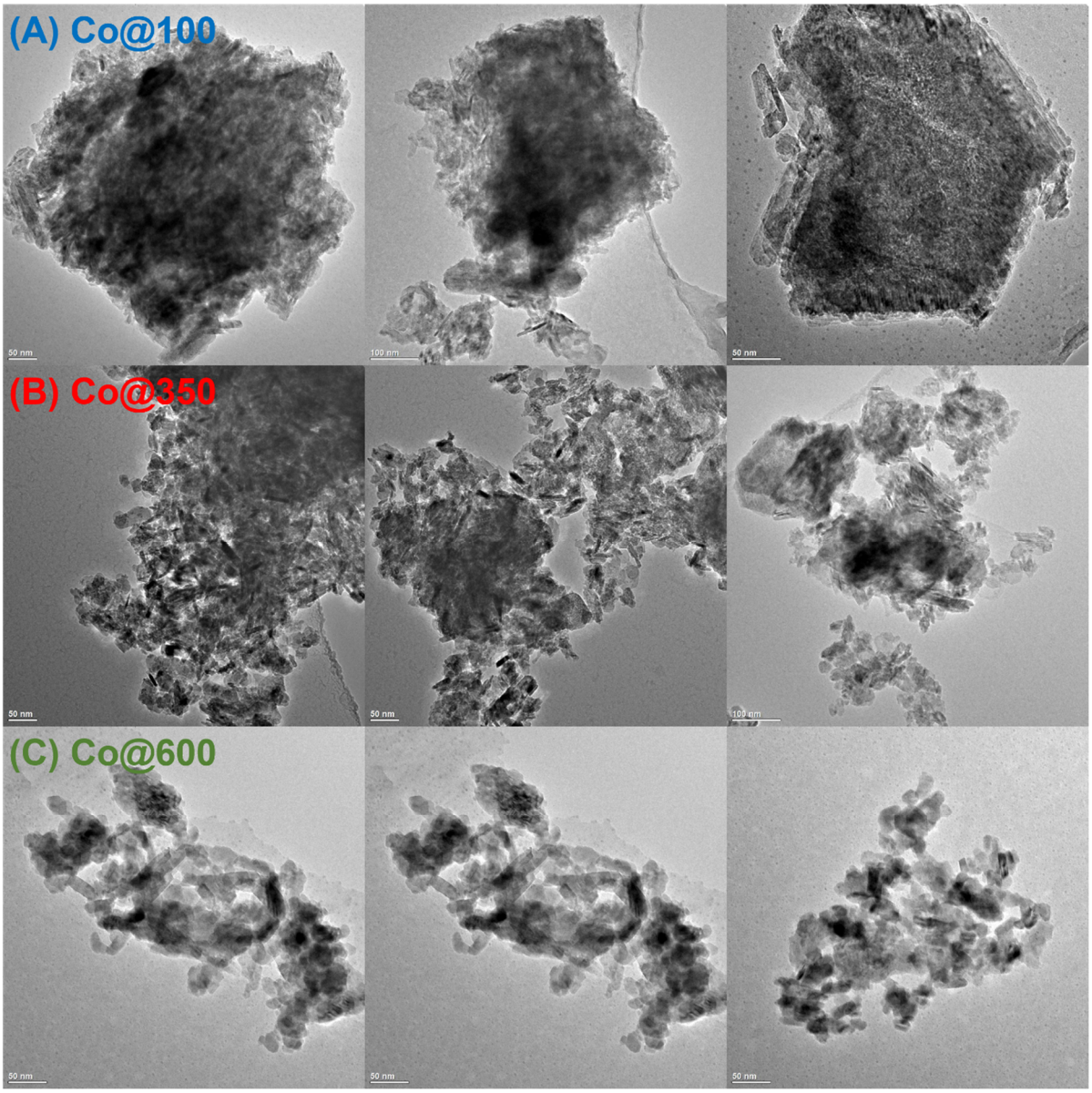

Figure S2: Additional representative Transmission Electron Microscopy (TEM) images of (A) **Co@100**, (B) **Co@350**, and (C) **Co@600**.

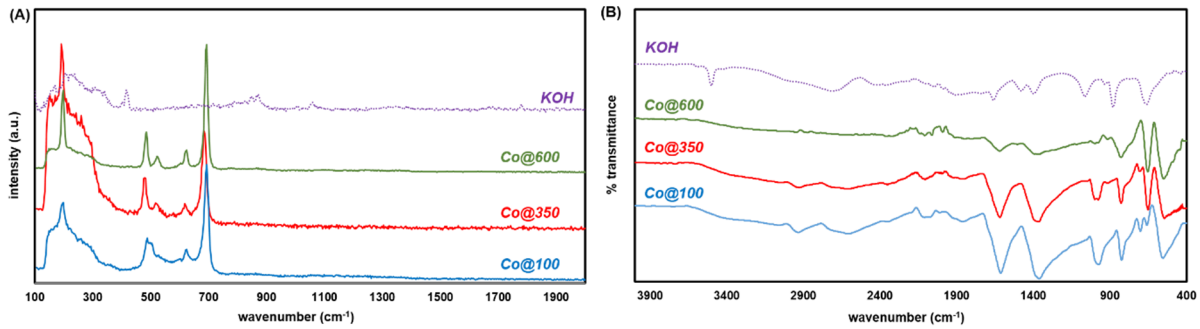

Figure S3: (*left*) Raman and (*right*) FTIR spectra of KOH, **Co@100**, **Co@350** and **Co@600**.

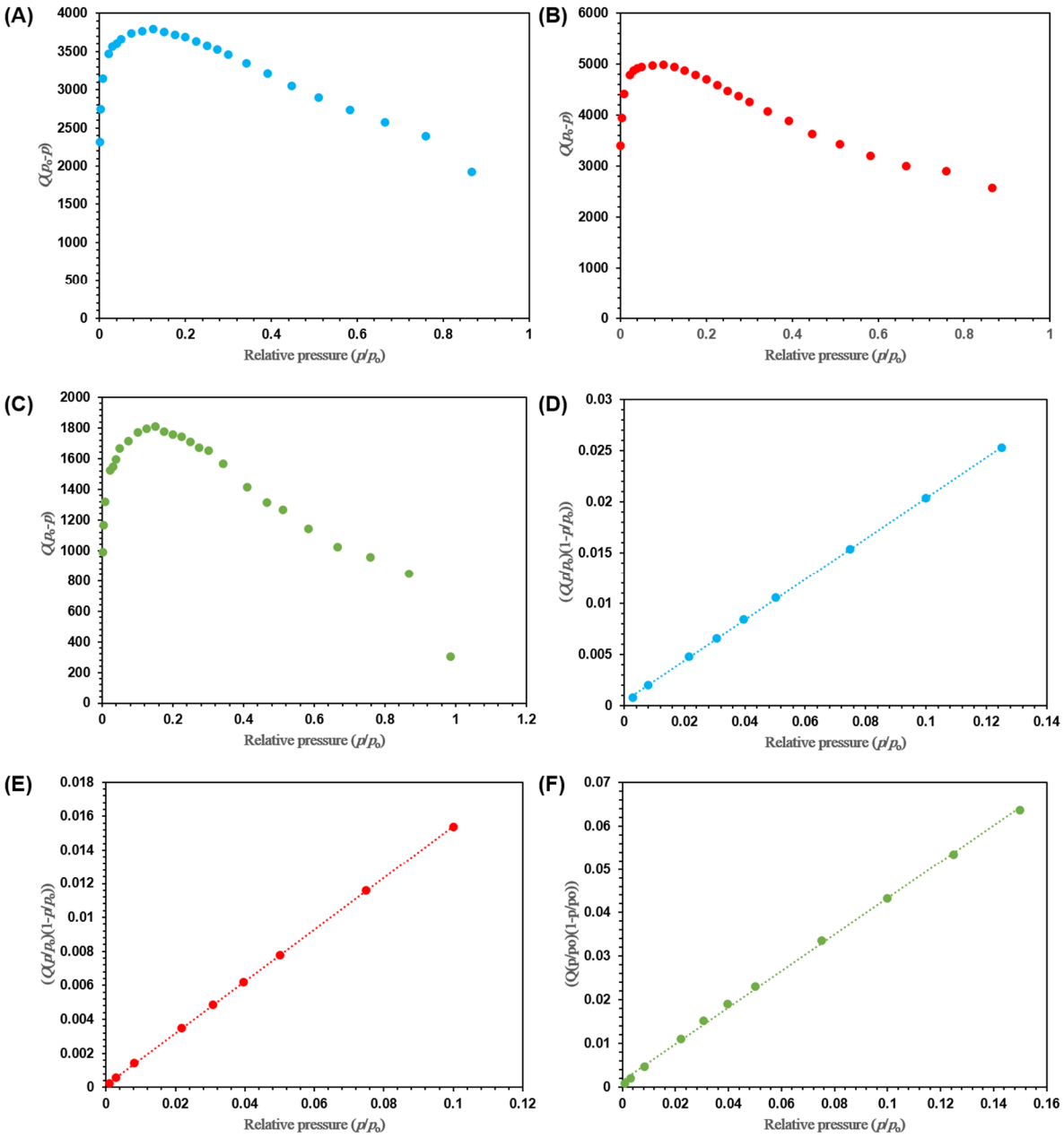

Figure S4: Roquerol plot of (A) **Co@100**, (B) **Co@350**, and (C) **Co@600**; BET plot of (D) **Co@100**, (E) **Co@350**, and (F) **Co@600**.

Table S1. BET parameters, volume of monolayer, surface area and C-parameters of the prepared cobalt oxide particles including the standard deviations.

Sample	Co@100	Co@350	Co@600
BET slope	1.99×10^{-1}	1.53×10^{-1}	4.18×10^{-1}
$\sigma_{\text{BET slope}}$	8.43×10^{-4}	3.46×10^{-4}	4.64×10^{-3}
BET intercept	4.07×10^{-4}	1.32×10^{-4}	1.57×10^{-3}
$\sigma_{\text{BET intercept}}$	5.39×10^{-5}	1.68×10^{-5}	3.41×10^{-4}
V_m (cm^3(STP) g^{-1})	5.00	6.55	2.39
σ_{Vm}	0.02	0.02	0.03
S_{BET} (m^2 g^{-1})	21.75	28.48	10.38
σ_{S_BET}	0.10	0.07	0.12
C_{BET}	491	1121	268
σ_{C_BET}	65	138	58

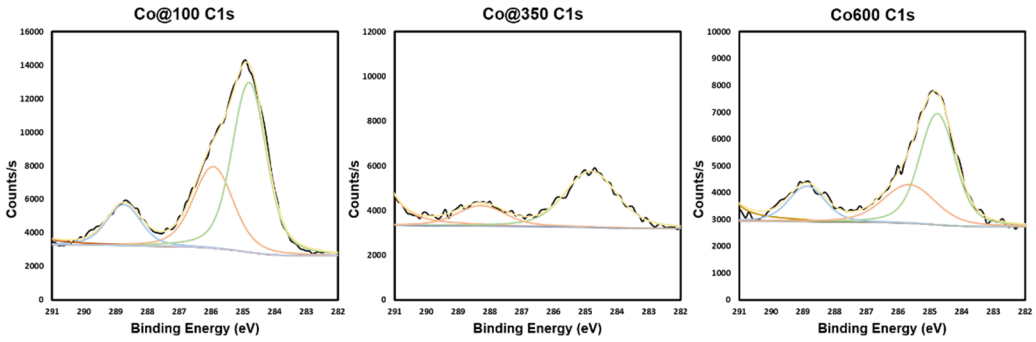

Figure S5:

XPS spectra for the C 1s region for **Co@100**, **Co@350** and **Co@600**.

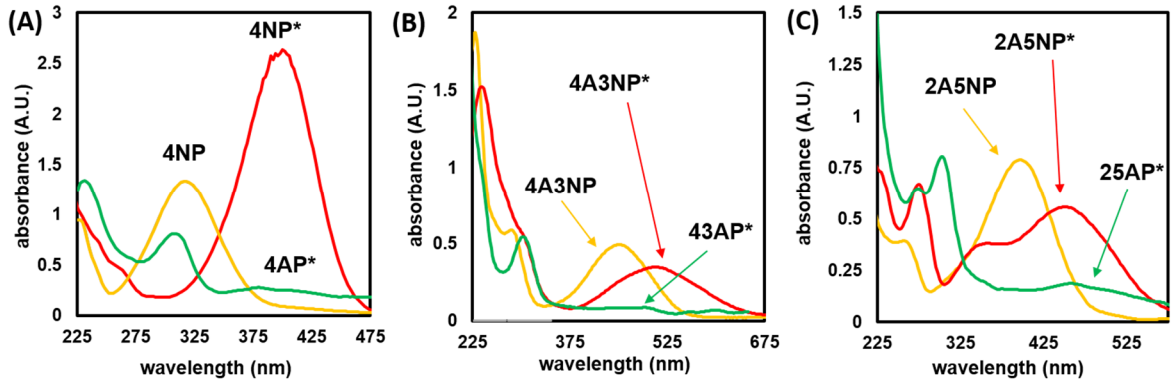

Figure S6: Reference UV-Vis spectra for parent nitrophenol (A-C) (*yellow line*), resulting product from interaction with BH_4^- in solution (*red line*), and respective reduced product/products after catalytic reaction (*green line*).

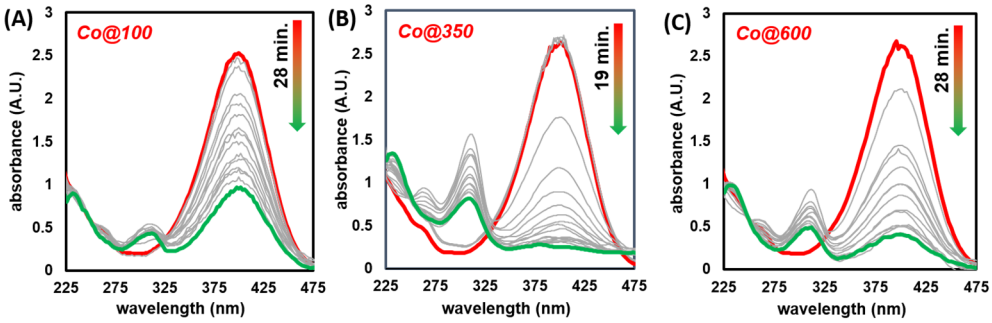

Figure S7: UV-Vis spectra for the reduction of **4NP** by (A) **Co@100**, (B) **Co@350**, and (C) **Co@600**.

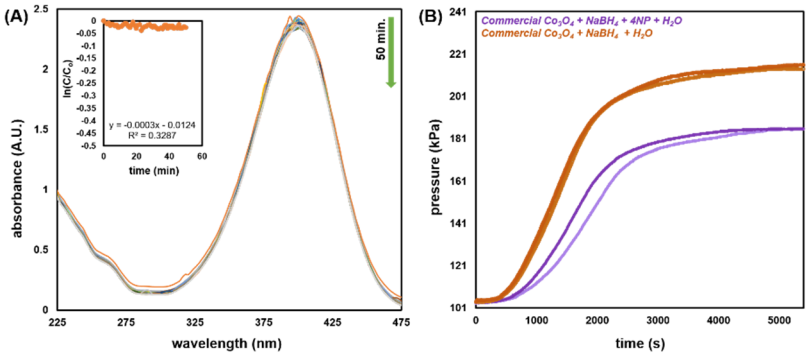

Figure S8: (A) UV-Vis spectrum for the reduction of **4NP** by commercial Co_3O_4 (inset plot of ln(C/Co) as a function of time). (B) Pressure *vs* time for 1 mg Co_3O_4 in 3 mL of DIW; 0.2 mmol of $NaBH_4$, and 1 mg Co_3O_4 in 3 mL of DIW mmol of $NaBH_4$ and 0.39 µmol of **4NP**.

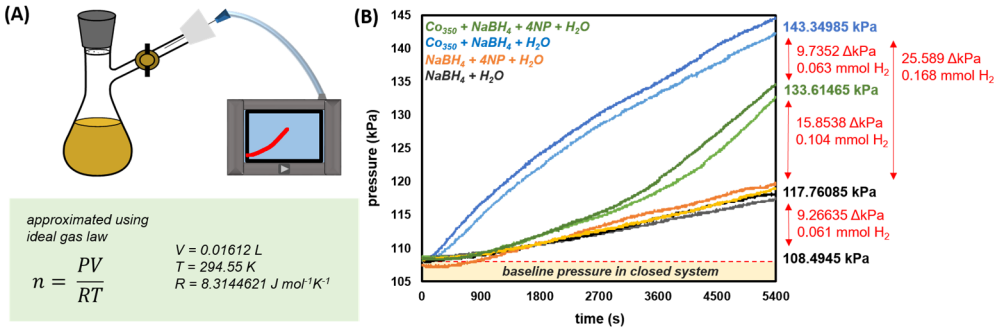

Figure S9: (A) Measurement set-up in a closed system monitored by a Vernier PS400-BTA sensor. (B) A series of measurements resulting from (**grey/black**) 0.2 mmol of $NaBH_4$ in 3 mL of DIW; (**orange/yellow**) 0.2 mmol of $NaBH_4$ and 0.39 µmol of **4NP** in 3 mL of DIW; (**green**) 0.2 mmol of $NaBH_4$, 0.39 µmol of **4NP** and 1 mg **Co@350** in 3 mL of DIW; (**blue**) 0.2 mmol of $NaBH_4$, and 1 mg **Co@350** in 3 mL of DIW. # of mol H_2 evolved approximated with the ideal gas law from the resulting pressure change.

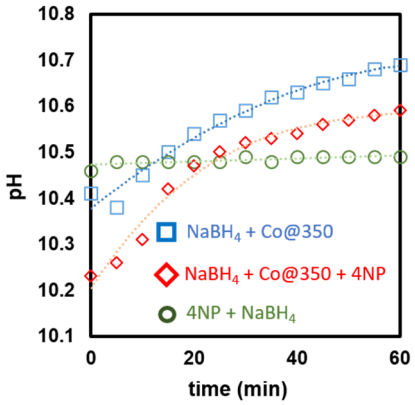

Figure S10: pH measurements for **4NP** + $NaBH_4$; $NaBH_4$ + **Co@350**; **4NP** + $NaBH_4$ + **Co@350**.

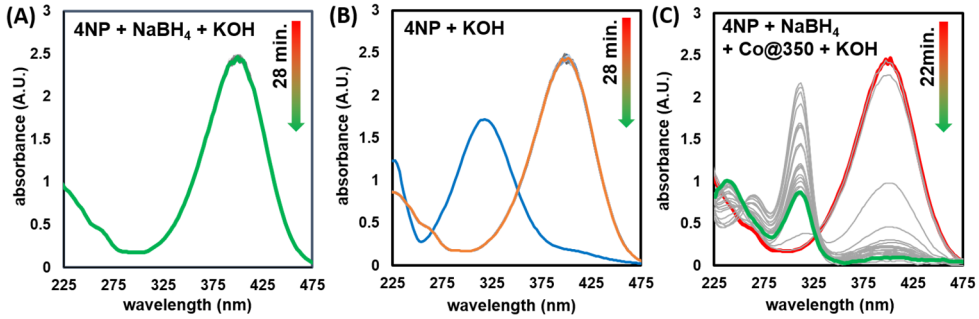

Fig. S11. UV-Vis spectra for the attempted reduction of **4NP** by KOH with (A) and without (B) $NaBH_4$; reduction of **4NP** and $NaBH_4$ with **Co@350** and 1 mg KOH (C).

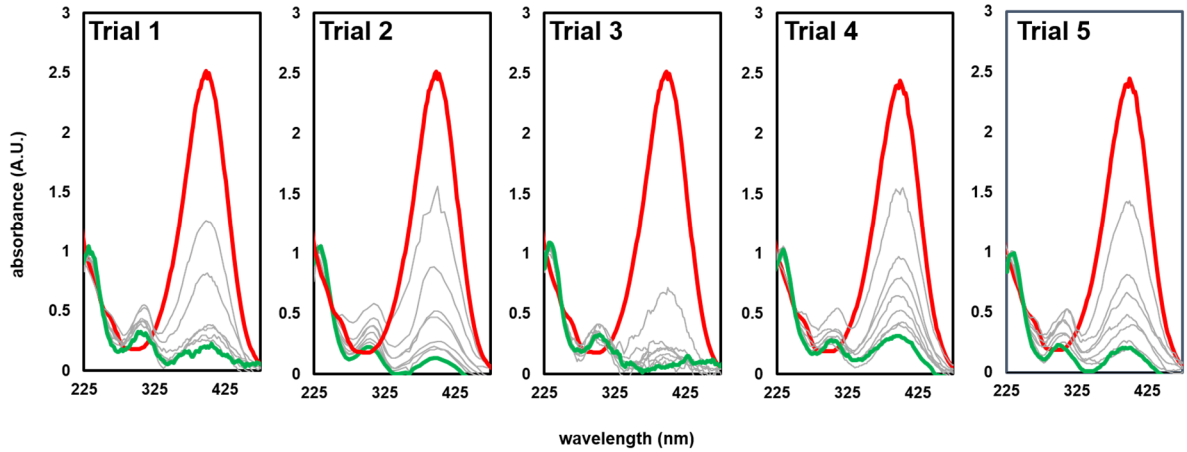

Figure S12: UV-Vis spectra for the reduction of **4NP** by **Co@350** over five successive trials with isolation after each trial.

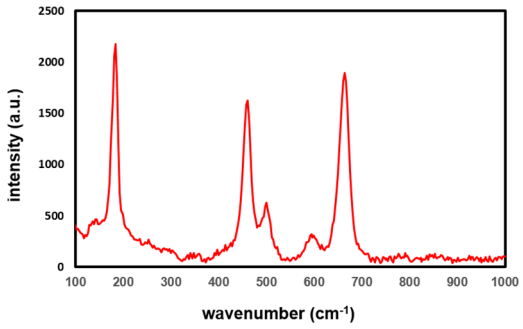

Figure S13: Raman spectra of "spent" **Co@350** after five successive reductions of **4NP** with isolation after each catalytic trial (*i.e. catalyst isolated after completion of Trial 5 in Figure S9*).

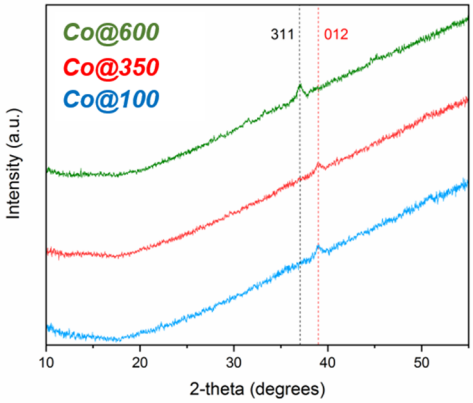

Figure S14: Powder XRD patterns of spent **Co@100**, **Co@350**, and **Co@600**. Indexed by the (311) peak of Co3O4 and (012) peak of CoO(OH).

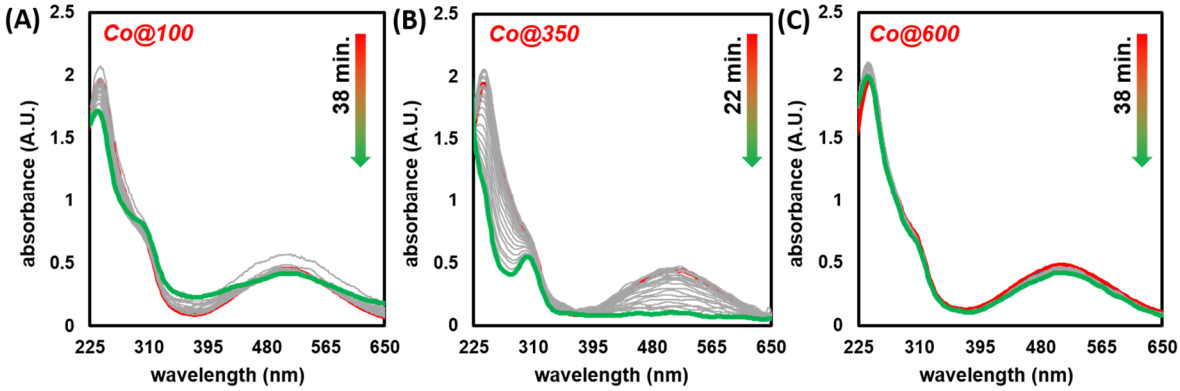

Figure S15: UV-Vis spectra for the reduction of **4A3NP** by (A) **Co@100**, (B) **Co@350**, and (C) **Co@600**.

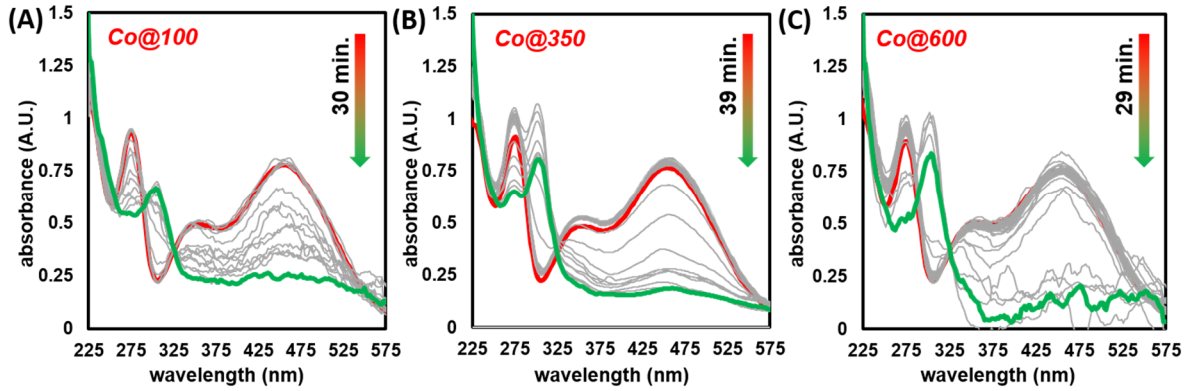

Figure S16: UV-Vis spectra for the reduction of **2A5NP** by (A) **Co@100**, (B) **Co@350**, and (C) **Co@600**.