Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

for

Understanding Reaction Mechanisms of Nicotinamide Adenine Dinucleotide (NADH) with Lithium Cobalt Oxide and Other Metal Oxide Nanomaterials

Catherine E. Kruszynski Earl†, Austin H. Henke†, Elizabeth D. Laudadio†, and Robert J. Hamers†*.

†Department of Chemistry, University of Wisconsin-Madison, Madison, WI, 53706

*To whom correspondence should be addressed: rjhamers@wisc.edu

Table S1. Components of minimal medium with dextrose

	Concentration (mM)
NaCl	11.6
HEPES	10.0
Dextrose	10.0
KCl	4.0
Na_2SO_4	2.8
NH_4Cl	2.8
$MgCl_2$	1.4
Na_2HPO_4	0.088
$CaCl_2 \cdot H_2O$	0.051

X-ray diffraction analysis of starting nanomaterials

Powder x-ray diffraction (XRD) patterns were taken of each material to assess purity and crystallinity and are shown in Figure S1. The synthesized compounds $LiCoO_2$ and $Co(OH)_2$ match the expected literature patterns.[1, 2] Nanomaterials purchased with the nominal compositions of Ni_2O_3 and MnO_2 were determined in fact to be NiO and Mn_2O_3, respectively, according to XRD analysis. Each pattern agrees well with reference patterns.[3, 4] Slight broadening of XRD peaks is expected given their nanoscale size. [5]

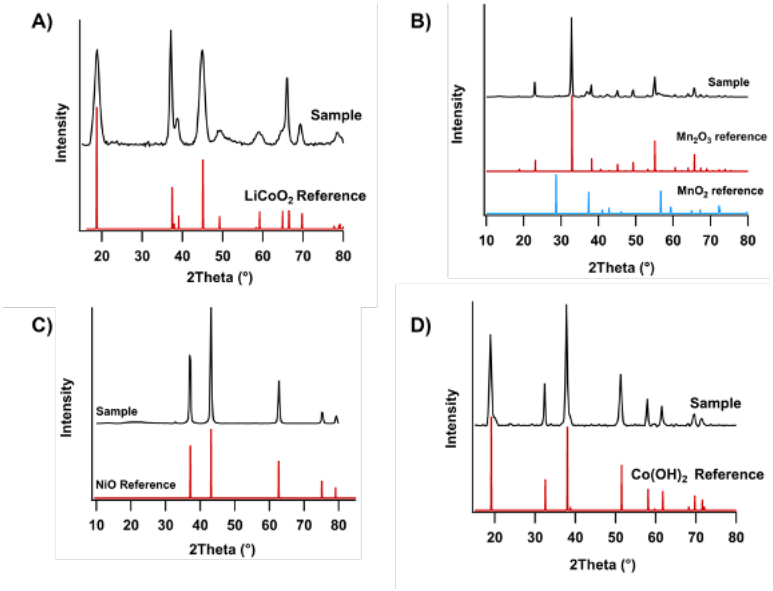

Figure S1. XRD diffraction patterns of nanomaterials used in the studies presented here, and comparison with reference spectra.

Scanning Electron Microscopy images of the starting nanomaterials

Scanning Electron Microscopy images were taken of all the starting nanomaterials. The Mn_2O_3 and the NiO materials were imaged as received and the $LiCoO_2$ nanosheets and $Co(OH)_2$ nanosheets were imaged as synthesized. Aggregates formed from drop-casting the nanoparticle suspensions onto the silicon wafers.

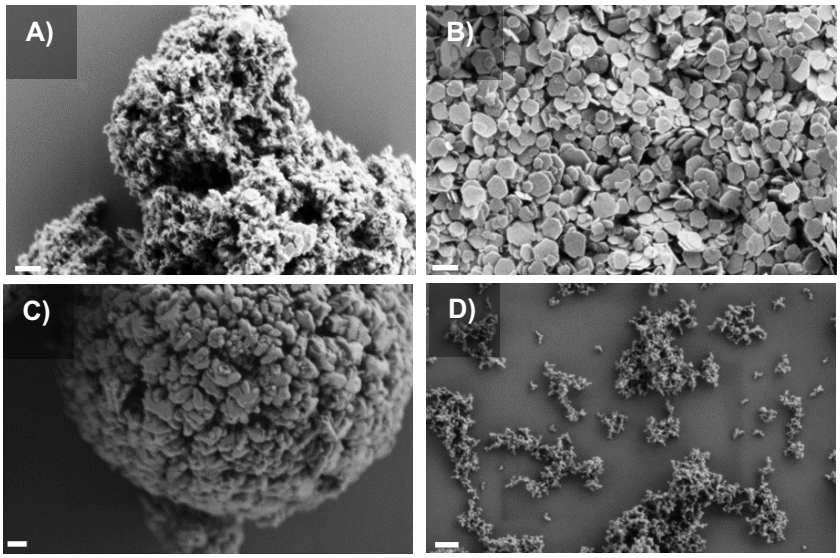

Figure S2. Representative SEM images of A) $LiCoO_2$ nanosheets, B) $Co(OH)_2$ nanosheets, C) Mn_2O_3 nanoparticles, and D) NiO nanoparticles. Scale bars= 200 nm

Quantitative Analysis of XPS data

To quantify the N coverage and P coverage on the surface of LiCoO2 nanoparticles exposed to the different biomolecules in minimal media, the following equation was used:

$$Coverage = \frac{A_{element\ of\ interest}}{A_{Co(2p)}} \times \frac{SF_{Co(2p)}}{SF_{element\ of\ interest}} \times \frac{scans_{Co(2p)}}{scans_{element\ of\ interest}} \rho_{Co} \lambda_{Co} \cos\theta$$

Where A is the area of the peaks in each region (N 1s, P 2p, and Co 2p), SF is the sensitivity factor for each peak ($SF_{N(1s)}$ =1.676146, $SF_{P(2p)}$ = 1.352941, $SF_{Co(2p)}$ = 18.23529), scans refers to the amount of scans summed to achieve the peak area (N(1s) and P(2p)= 50 scans, Co (2p) = 10), ρ_{Co} is the density of Co in the bulk material (29.09 atoms/nm^2), λ_{Co} is the inelastic mean free path of a Co electron emitted from $LiCoO_2$ (estimated to be 1.922 nm)[6], and θ refers to the angle of the analyzer relative to the surface normal (45^o). This equation treats Co as an internal standard assuming that the layer of biomolecules is small compared to the electron IMFP.

Explanation of two-dimensional spectrum and identification of optimum excitation and emission wavelengths.

Measurement made in 1 cm x 1cm fused silica cuvette with step size of 2 nm and integration time of 1 s at each point. The background at Y = X (lower right) corresponds to scattering of the excitation light.

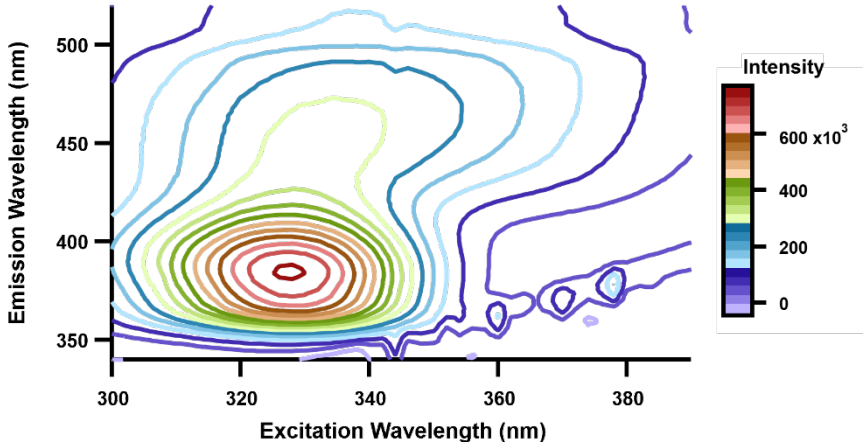

Figure S3. Excitation-emission matrix of 0.5 mM 1-methyl-1,4-dihydronicotinamide (Nico) in minimal media with dextrose

Positive Control, oxidation of Nico

One aliquot of 0.5 mM Nico was mixed with 10 mM H_2O_2 and exposed to UV light for 30 min, and another was mixed with an equal volume of water without light. The spectrum shows that this oxidation control drastically decreases Nico fluorescence, confirming that oxidation of Nico would remove fluorescence signal. The spectrum of the H_2O_2+UV Nico solution also suffers some distortion, perhaps from further molecule decomposition.

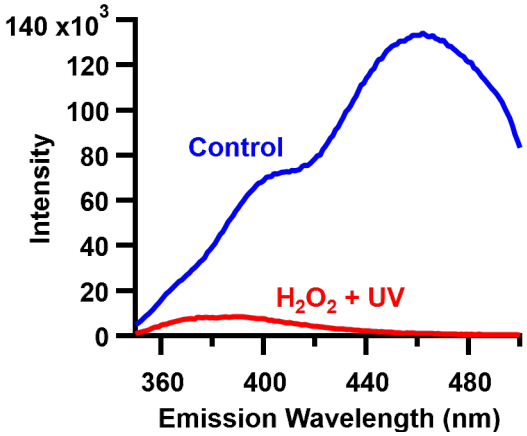

Figure S4. Fluorescence spectra of 0.5 mM Nico solution diluted 2:1 in water (blue, control), or 10 mM H_2O_2 with 30 min of UV exposure (red, intentional oxidation).

Co release over time in minimal media and minimal media plus NADH

Co release from LiCoO2 nanoparticles was measured over different time points (4h, 8h, 16h, and 24h) to show that the dissolution is still in the kinetic regime. Each exposure was conducted, and the solutions were separated from the nanoparticles using the same procedure outlined in the main text, but at each indicated time point. Each time point was measured in triplicate using ICP-MS.

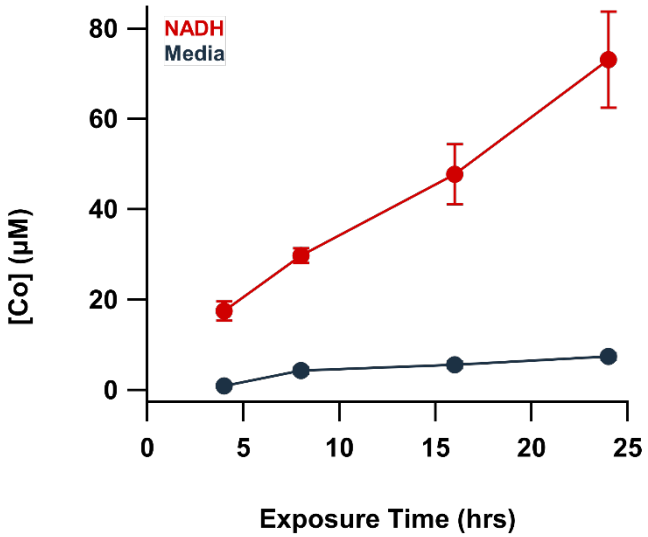

Figure S5. Time course Co release data from $LiCoO_2$ particles exposed to NADH in minimal media and media alone at 4h, 8h, 16h, and 24h as measured by ICP-MS.

References:

1. Y. Takahashi; N. Kijima; K. Dokko; M. Nishizawa; I. Uchida; J. Akimoto, Structure and electron density analysis of electrochemically and chemically delithiated $LiCoO_2$ single crystals, *Journal of Solid State Chemistry* 2007, **180**, 313-321.
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3. A. Bolzan; C. Fong; B. Kennedy; C. Howard, Powder Neutron Diffraction Study of Pyrolusite, β-MnO_2, *Australian Journal of Chemistry* 1993, **46**, 939-944.
4. W. Milligan; L. M. Watt, X-ray diffraction studies in the system NiO-Cr_2O_3-ZrO_2 *The Journal of Physical and Colloid Chemistry* 1948, **52**, 230-235.
5. D. G. Lamas; M. de Oliveira Neto; G. Kellermann; A. F. Craievich, X-ray diffraction and scattering by nanomaterials. In *Nanocharacterization techniques*, Elsevier Inc.: 2017; pp 111-182.
6. E. D. Laudadio; J. W. Bennett; C. M. Green; S. E. Mason; R. J. Hamers, Impact of phosphate adsorption on complex cobalt oxide nanoparticle dispersibility in aqueous media, *Environ Sci Technol* 2018, **52**, 10186-10195.