Supporting Information for

Upcycling spent Lithium-ion battery cathodes to cobaltpolyphenol network by DES dissolution and solvent-induced

crystallization†

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Section S1. Experimental

Materials

Gallic acid (GA), choline chloride (ChCl), LiCoO₂, ethylene glycol (EG), anhydrous methanol (MeOH), anhydrous ethanol (EtOH), 1-pentanol, 1-hexanol, cyclohexanol, isopropyl alcohol (IA), anhydrous cobalt chloride (CoCl₂), anhydrous cobalt nitrate (Co(NO₃)₂), cobalt oxide (CoO), cobalt hydroxide (Co(OH)₂), tricobalt tetraoxide (Co₃O₄), lithium chloride (LiCl), potassium chloride (KCl), sodium chloride (NaCl), vanillic acid (VA), isovanillic acid (IVA), methyl gallate (MG), syringic acid (SA), protocatechuic acid (PCA), pyrogallol acid (PGA), Nile red (NR), 4-nitroaniline (NA), ethylene diamine tetraacetic acid (EDTA), urea, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), Tween 20, and Triton X-100 were purchased from Innochem company. NCM523, NCM111were purchased from Shenzhen Kejing Zhida Technology Co. Spent lithiumion cell phone batteries were purchased from local waste cell phone battery market in Xi'an, Shaanxi Province.

Characterization

Ultraviolet-visible (UV-vis) absorption spectra of solutions are measured on Cary 60 (Agilent, China) spectrophotometer. Fourier transform infrared spectra (FI-IR) are obtained using Tensor 27 (Bruker, American) infrared spectrometer with KBr base and the resolution of 1 cm⁻¹. Thermogravimetric (TG) analysis is performed on TA Q500 thermogravimetric analyzer (TA, American) in N₂ atmosphere, with the test range of 25-600 °C and heating rate of 5 °C /min. SEM images are obtained on field emission scanning electron microscope SU8010 (Hitachi, Japan) operating at 5 kV, while elemental mapping is recorded using Energy dispersive X-ray spectroscopy (EDS) with the Oxford instrument. X-ray photoelectron spectroscopy (XPS) is performed using K-Alpha photoelectron spectrometer (Thermo Scientific, American), corrected with C 1s 284.8 eV binding energy. Particle size distribution and ζ -potential are measured by dynamic light scattering (DLS) on Zetasizer Nano ZS90 (Malvern, UK), and each set of measurements is repeated three times for averaging. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 715, Germany) is used to measure the content of metal ions in solution. X-ray powder diffraction is performed on the XRD-7000 (Shimadzu, Japan). Diffuse reflectance spectra of powders are obtained on UV3600 spectrophotometer (Shimadzu, Japan) with BaSO₄ as reference whiteboard. Electrospray ionization mass spectrometry (ESI-MS) experiments are carried out using highresolution gas chromatography-mass spectrometry Q Exactive Gc (Thermo Scientific, American), coupling quadrupole with high-resolution orbit trap in tandem combined mass spectrometry to the gas chromatography, with anhydrous methanol as dispersing medium for the solid particles. Raman spectroscopy (Raman) is performed on Xplora plus (Horiba, Japan) laser Raman spectrophotometer with the excitation wavelength of 532 nm, and signals with the spectral resolution of 1 cm^{-1} are acquired using 50× microscope objective, and the laser and grating are corrected with silicon wafer, with three measurements at each point. NMR spectra of liquids and solids are obtained using superconducting NMR spectrometer Ascend 600 (Bruker, Germany) with CDCl₃ as solvent. Thermogravimetric-mass spectrometry (TG-MS) experiments are performed using thermogravimetric analyzer STA 449 F3 (Netzsch, Germany) coupled to mass spectrometer QMS 403D (Netzsch, Germany) with the heating rate of 10 °C/min and N₂ atmosphere. Electrochemical tests are performed on CHI600E electrochemical workstation (CH, China) with the three-electrode system, using glassy carbon electrode as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode.

Concentration of metal ion in DES leaching solution:

Following the addition of LCO to DES for a suitable reaction period, EG (at a molar ratio of 10:1 to GA) was introduced and stirred at 0-3°C to achieve thorough mixing. The concentration of metal ions (C_{Me}) in the mixture was quantified using ICP-OES. Subsequently, the leaching efficiency (η_1) can be calculated according to equation (1):

$$\eta_1 = 1.66m_0 \times C_{Me} \times \frac{m_{DES} + m_{EG}}{m_{LCO}} \times 100\%$$
(1)

where m_{θ} represents the mass ratio of the sample solution before and after dilution for ICP-OES determination, m_{DES} denotes the mass of DES utilized, m_{EG} indicates the mass of EG added, and m_{LCO} signifies the mass of LCO. The sample solution was diluted with 1 mol/L nitric acid, and each set of results was measured three times, with the average value calculated.

Conversion of cobalt ions to MPNPs:

The concentration of cobalt ion (C_{Me}) in the supernatant of DES-EG mixture was measured by ICP-OES, and the conversion rate (η_2) was calculated according to equation (2):

$$\eta_2 = 1 - \eta_1 \tag{2}$$

The leaching conditions for LCO were: T = 110 °C, s/s = 15 mg/g, and t = 8 h, during which LCO underwent near-complete dissolution. Following the addition of EG, the mixture was maintained at 80 °C for 30 minutes to ensure the stability of the conversion process. Each group was subjected to two replications, and the average value was calculated.

Measurement of the solvation parameters of "DES + inducing agent" system:

Kamlet-Taft solvation parameters of the DES-EG hybrid system were measured, using a solvent to DES molar ratio of 10:1. Nile red (NR) and 4-nitroaniline (NA) were employed as probe molecules. They were dissolved in methanol at a concentration of 1 mM, and subsequently dried in the vacuum drying oven at 60 °C. Then 20 μ L of the dye solution was added into a quartz cuvette containing 2.0 mL of the DES-EG solution. The maximum absorption wavelength (λ_{max}) of Nile red was obtained using UV-vis spectrophotometer (Cary 60, Agilent) after thorough mixing. The similar procedure was followed when using MeOH, EtOH, and H₂O as inducing agents. The Kamlet-Taft parameters of the mixture were determined through multiple repeated tests, and the values of α , β and π^* were calculated according to **equation (3)**^{1,2} :

$$a = (19.9657 - 1.0241 \times \pi^* - v_{(NR)}) / 1.6078$$

$$\beta = 11.134 - 3580 / \lambda_{(NH_2)max} - 1.125 \times \pi^*$$

$$\pi^* = (19.893 - v_{(NR)}) / 2.9912$$

$$v_{(NR)} = 1 / \lambda_{(NR)max} \times 10^{-4}$$
(3)

where α represents the ability of system to provide hydrogen bond (hydrogen bond acidity), β denotes its capacity to accept hydrogen bond (hydrogen bond alkalinity), and π^* reflects the polarity/polarizability of the system.

Preparation of MPNPs from DES and regeneration of LCO:

Initially, the DES comprising of GA and ChCl was synthesized by mixing them in a 1:2 molar ratio and heating the mixture at 90 °C until a yellow transparent solution was formed. Subsequently, LCO was added to this solution in a prescribed mass ratio (m_{LCO} : m_{DES}), and the reaction was carried out for a duration varying between 4 to 12 hours at temperatures spanning from 80 to 120 °C. After completing the reaction, the resulting solution was transferred to a temperature-controlled heating table with settings ranging from 50 to 80 °C. Then EG was introduced into the solution at a molar ratio of EG to GA of 10:1, and the mixture was stirred at 400 rpm for 30 minutes to ensure complete homogenization of the leaching solution and EG. At this juncture, a substantial quantity of suspended MPNPs formed within the solution. After that, the mixture underwent high-speed centrifugation at 10,000 rpm for a duration of 20 minutes, and the resultant precipitate was collected, followed by multiple ethanol washes to remove adsorbed lithium ions and residual organic compounds. Following the washing steps, the particles were subjected to vacuum drying for a period of 6 hours. The identical procedure was replicated employing MeOH, EtOH, and H₂O as inducing agents. All DES solutions were freshly prepared, and a hermetic seal was maintained throughout the entire process, spanning from DES synthesis to LCO dissolution and MPNP crystallization. The obtained MPNPs were subjected to calcination in a tube furnace at 700 °C for a duration of 4 hours, with the heating rate of 10 °C/min, resulting in the formation of Co₃O₄ precursor. Then the Co₃O₄ precursor was blended with recovered Li₂CO₃ in a molar ratio of 1.05:1 (Li: Co) and underwent wet milling in ethanol for 40 minutes. The resultant slurry mixture was subsequently dried and subjected to dry milling for an additional 30 minutes duration. Finally, the mixture was placed in the tube furnace for oxidative calcination at 850 °C for 8 hours, leading to the regeneration of LiCoO₂.

Preparation of MPNPs from GA solutions and regeneration of LCO:

1 M GA solution (with EG as the solvent) was prepared at 90 °C. Subsequently, 15 mg/g (LCO to GA) of LCO was introduced, and the reaction proceeded at 300 rpm for 12 hours. The MPNPs exhibited a brownish-red color upon generation and suspension in the solution. The mixture was then subjected to high-speed centrifugation at 10,000 rpm for 15 minutes, and the resultant precipitate was collected and underwent multiple ethanol washes. Following this, the MPNPs were subjected to vacuum drying at 60 °C for a period of 4 hours. The similar procedure was employed using MeOH, EtOH, and aqueous solutions of GA. The obtained particles were calcined in the tube furnace at 700 °C for 4 hours, resulting in the formation of Co_3O_4 precursor. The LCO was regenerated using the method described previously. In the investigation of the Cl⁻ influence, a specific quantity of LiCl (0.08 M-0.83 M) was added to the EG, H₂O, MeOH and EtOH solutions before leaching. Due to variations in boiling points, the reaction temperature was maintained at 90 °C for EG and H₂O solutions, whereas it was set at 60 °C for MeOH and EtOH solutions.

Preparation of MPNPs from other phenolic acid/polyphenol solutions:

EG served as the solvent to prepare 2 M solutions of MG, PCA, and PGA, as well as 1 M solutions of IVA and VA, and 0.25 M solution of SA. LiCl was added to each of these solutions. Subsequently, 12 mg/mL of LCO was introduced into them, and the reaction were conducted at 90 °C for a duration of 12 hours. The suspensions contained MPNPs after reaction. The subsequent steps of the procedure followed the same protocol as that used for the GA solution.

Preparation of MPNPs from other cobalt oxide precursors:

CoO, Co(OH)₂, and Co₃O₄ were added to DES at concentration of 11 mg/g, 14 mg/g, and 12 mg/g, respectively. The ensuing reaction was conducted at 90 °C for a duration of 12 hours. Following this, EG (at a molar ratio to GA of 10:1) was introduced into the leaching solution at 80 °C and subjected to stirring for 30 minutes. The MPNPs exhibited a pink color upon generation and dispersion within the solution. The mixture was then subjected to centrifugation at the speed of 8000 rpm for 20 minutes, and the obtained MPNPs were washed three times with ethanol and vacuum-dried for a period of 4 hours.

Disassembly experiments of MPNPs:

The MPNP samples utilized were prepared from 1 M GA solutions, employing EG as the solvent. The option of introducing 0.5 M LiCl into the solution was available. Following this, a dispersion of 0.5 mg/ml of MPNPs was created in two different buffer solutions, denoted as pH=2.0 (hydrochloric acid-glycine buffer) and pH=4.0 (hydrochloric acid-citric acid buffer). UV-vis absorption spectra were recorded at the wavelength range of 400-550 nm after the complete disassembly.

Analysis of organic fragments of disassembled MPNPs:

150 μ L suspension of MPNPs, obtained from DES with EG as the inducing agent, was mixed with an excess of 6 M HCl and stirred at the rate of 400 rpm for 10 min. Following the complete disassembly of particles, they were diluted by adding an equivalent volume of deionized water, and the excess HCl was removed through lyophilization. The lyophilized product was resuspended in methanol, sonicated for 3 min, and analyzed via ESI- MS.

Stability of MPNPs:

To investigate the stability of MPN structure when utilizing various phenolic acids or polyphenols as ligands, as well as the potential driving forces behind their assembly, we dispersed MPNPs (prepared by reacting EG solutions of MG, VA, SA, IVA, PCA, and PGA with LCO) in solutions containing 100 mM EDTA, LiCl, urea, THF, DMF, Tween 20, Triton X-100. The dispersion was incubated for 12 hours, and the changes in size were measured using the Zetasizer Nano-ZS instrument,³ as an average of three independent measurements.

Monitoring of gaseous products of the reaction between DES and LCO:

To explore the potential reduction products of Cl⁻, we adopted the method proposed by Chang et al⁴ to simulate and in situ monitor the gases potentially generated during the reaction between DES and LCO. This was achieved by coupling thermogravimetric analysis and mass spectrometric detection. LCO was introduced into DES at a solid-solid ratio of 15 mg/g, and the reaction was sealed and prereacted at 90 °C for 2 h. After cooling and solidification at room temperature, 3 mg of the resulting solid was taken into a crucible. The reaction was monitored by coupling the STA 449 F3 thermogravimetric analyzer with the QMS 403D mass spectrometer. The heating program was set to 10 °C/min, with the temperature range from room temperature to 110 °C, and the reaction was conducted under N₂ atmosphere for 2 hours.





Figure S1. a) NMR H Spectra of ChCl and DES. In pure ChCl, the chemical shift of H atom in the α -methylene linked to the hydroxyl group is observed at 4.10 ppm, while the β -methylene and methyl group exhibit shifts at 3.57 ppm and 3.24 ppm respectively. When hydrogen bonds form with GA, the chemical shifts of these H atoms shift towards higher field values, specifically 4.05 ppm for the α -methylene, 3.51 ppm for the β -methylene, and 3.19 ppm for methyl group. b) FT-IR Spectra of GA and DES. Upon the formation of DES, the stretching vibration of the carbonyl group in GA shifts from 1667 cm⁻¹ to 1733 cm⁻¹, accompanied by the appearance of a broad absorption peak signal ranging from 2500 cm⁻¹ to 3500 cm⁻¹. These observations collectively indicate the formation of hydrogen bonds between GA molecules and ChCl.



Figure S2. Thermogravimetry (TG) diagram of DES. The initial mass loss observed at approximately 97 °C can be attributed to the desorption of water of crystallization. Subsequent weight loss around 198 °C corresponds to the decarboxylation of carboxyl group in GA, potentially involving the dehydration process of esterification reaction. Finally, the mass loss observed at approximately 274 °C is attributed to the degradation of benzene ring and decomposition of ChCl.



Figure S3. a) Cyclic Voltammetry (CV) Plot of DES. The stoichiometric ratios of GA to ChCl employed were 1:2, 1:3, and 1:4. The experiment utilized a three-electrode system, including a glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode. The oxidation peak at approximately 1.0 V served as the indicator of DES reductivity. It exhibited a pattern of initial decrease followed by an increase with increasing ChCl content. Likewise, the two reduction peaks at approximately -0.49 V and -1.06 V displayed a similar trend. b) Oxidation peak potentials of DES at various GA/ChCl ratios. The graph, resembling an "n" shape, illustrates that higher concentrations of both GA and ChCl result in enhanced reduction properties of DES. The optimal condition is observed at a GA to ChCl ratio of 1:2, yielding a potential of 0.92 V.



Figure S4. a) SEM image of pure GA. It displays an inhomogeneous rod-like structure with a length of 100 μ m. b) SEM image of the LiCoO₂ used in our experiments. It reveals a polygonal structure with varying sizes and inhomogeneous shapes.



Figure S5. FT-IR spectrum of GA and MPNPs.

The MPNPs exhibit similar absorption peaks in the "fingerprint region" (1000 cm⁻¹ to 450 cm⁻¹) as GA molecules, indicating the preservation of the GA structure within the metal-polyphenol network. The stretching vibration of the phenolic hydroxyl group on the benzene ring redshifted from 3279 cm^{-1} to 3192 cm^{-1} , suggesting the formation of coordination bond between the phenolic hydroxyl group and cobalt ions. Furthermore, the absorption peak corresponding to the C=O stretching vibration in GA carboxyl functional group vanished at 1667 cm⁻¹, indicating the formation of coordination bond between the carboxyl group and cobalt ions. As a result, cobalt ions in the MPN form coordination bonds with GA molecule through interactions with both the phenolic hydroxyl group and the carboxyl group.



Figure S6. Elemental composition of MPNPs with the inset depicting the EDS testing area. The MPNPs predominantly contain carbon (C), oxygen (O), and cobalt (Co), with lower concentration of (nitrogen) N and chlorine (Cl), originating from ChCl. The presence of Au can be attributed to the gold plating applied to the sample's surface.



Figure S7. SEM image of MPNPs obtained using EtOH as the inducing agent. The particulate aggregates exhibit variations in size and non-uniform shapes.



Figure S8. X-ray Photoelectron Spectra (XPS) of cobalt within MPNPs synthesized using H₂O, MeOH, and EtOH as inducing agents. a) H₂O: binding energies at 780.66 and 796.50 eV correspond to Co $2p_{3/2}$ and $2p_{1/2}$, respectively, indicating the presence of Co (II). b) MeOH: binding energies at 780.47 and 796.82 eV indicate the presence of Co (II), whereas binding energies of 783.82 eV and 800.02 eV corresponds to Co (IV). c) EtOH: binding energies at 783.63 eV and 799.06 eV indicate Co (IV), while binding energies at 780.17 eV and 795.77 eV correspond to Co (II).



Figure S9. Elemental species in MPNPs obtained from XPS with various inducing agents. a) EG. b) EtOH. c) H_2O . d) MeOH. The N and Cl content in MPNPs exhibited slight variations when different inducing agents were employed, with exception of EG, which displayed a particularly noticeable variation.



Figure S10. Thermogravimetric (TG) analysis of MPNPs obtained with various inducing agents. a) EG. b) EtOH. c) H₂O. d) MeOH.

In summary, the weight loss of MPNPs can be attributed to three distinct processes.

DES-EG-MPNPs: Process I took place within the range of 25-182 °C; Process II was observed in the range of 183-210 °C, leading to a decrease in mass fraction to 58.13%. This process was related to the decarboxylation reaction of GA⁵ as well as the removal of EG (boiling point of EG is approximately at 198 °C); Process III occurred in the range of 276-387 °C, with the mass fraction decreasing to 24.37%. This process encompasses the degradation of aromatic ring and decomposition of ChCl.

DES-EtOH-MPNPs: Process I took place in the range of 25-96 °C; Process II occurred within the range of 103-362 °C, and the mass fraction decreased to 40.11%; Process III-IV was observed in the range of 367-496 °C, leading to a decrease in mass fraction to 22.23%, corresponding to the degradation of aromatic ring. Process V corresponded to the complete decomposition of residual organic compounds, which was observed at 512-590 °C, with the mass fraction decreased to 17.26%.

DES-H₂O-MPNPs: Process I occurred in the range of 74-147 °C; Process II took place within the range of 189-355 °C, leading to a decrease in mass fraction by 25.37%; Process III was observed within the range of 451-547 °C, resulting in a reduction of mass fraction from 58.06% to 29.61%.

DES-MeOH-MPNPs: Process I occurred in the range of 25-131°C; Process II took place within the range of 173-348°C, with a decrease in mass fraction of 35.37%; Process III was observed in the range of 432-564°C, leading to a decrease in mass fraction to 20.09%.



Figure S11. Variations of LCO leaching efficiency in DES as the function of time (t), temperature (T), and solid-solid ratio (s/s). a) Time (with additional conditions: T=110 °C, s/s = 15 mg/g). b) Temperature (with additional conditions: t=8 h, s/s = 15 mg/g). c) Solid-solid ratio (with additional conditions: t=8 h, T=110 °C).

Figure S11a: As the reaction time remains below 8 hours, the leaching efficiency of metal ions progressively rises, reaching its zenith at 8 hours with 99.87% for Co and 98.04% for Li. Prolonging the leaching time beyond 8 hours results in a reduction in leaching efficiency, with Co and Li declining to 92.61% and 83.7% after 12 hours, respectively.

Figure S11b: The reaction rate displays an upward trend with increasing temperatures, culminating at 110°C, where the extraction of cobalt and lithium attains peak values of 99.87% and 98.04%, respectively. However, further temperature increments lead to a decline in efficiency, resulting in values of 90.19% for Co and 89.71% for Li. This phenomenon can be attributed to side reactions involving organic molecules. More specifically, prolonged reaction times, which accumulate over time, and higher reaction temperatures, which accelerate the reaction rate, have the potential to enhance the leaching efficiency of LCO. Nevertheless, excessively prolonged reaction times and elevated temperatures serve to exacerbate side reactions involving GA molecules, which encompass processes such as oxidation to quinone due to dissolved oxygen, intermolecular esterification, and dehydration. As a result, system degradation intensifies, leading to a reduction in the leaching efficiency of DES on LCO.

Figure S11c: The highest leaching efficiency of LCO to DES is observed at a solid-to-solid ratio of 15 mg/g, where cobalt and lithium exhibit efficiencies of 99.87% and 98.04%, respectively. Beyond this ratio, the leaching efficiency progressively diminishes, reaching a minimum of 90.93% for cobalt and 82.2% for lithium at 30 mg/g.



Figure S12. Conversion efficiency of MPNPs impacted by the type of inducing agents, crystallization temperature, the molar ratio of $[GA]/[Co^{2+}]$ and $[Cl^{-}]/[Co^{2+}]$ within the DES. The leaching conditions were: s/s=15 mg/g, t=8 h, T=110 °C, and the loading of 140% inducing agents. In the graph, blue dots represent a decrease in DES quantity, while violet dots signify an increase in the mass. Specific experimental conditions for each variable are detailed as follows: a) Type of inducing agents. The other conditions were crystallization at 80°C, a $[GA]/[Co^{2+}]$ ratio of 15, and a $[Cl^{-}]/[Co^{2+}]$ ratio of 29. b) Crystallization temperature. In this scenario, the inducing agent is EG, with a $[GA]/[Co^{2+}]$ molar ratio of 15 and $[Cl^{-}]/[Co^{2+}]$ ratio of 29. c) $[GA]/[Co^{2+}]$ molar ratio in DES. Crystallization is conducted at 80°C, with 140% loading of EG, while the $[GA]/[Co^{2+}]$ molar ratio is 15.

Figure S12a: When isopropanol, 1-pentanol, 1-hexanol, and cyclohexanol were utilized as inducing agents, it was observed that these inducers exhibited insolubility in DES. A portion of these inducing agents permeated into the DES phase, resulting in an increase in the mass of DES after reaction, as depicted by the violet dots. During the experiment, it was observed that the utilization of these alcohols resulted in the formation of a viscous substance at the bottom of the container post-reaction, predominantly comprising cobalt and lithium. This phenomenon is likely associated with the solidification of DES at room temperature.

Figure S12b: MPNPs were not observed within the range of 0-20 °C. While the conversion rate rose to 88.66% as the temperature reached 50 °C, reaching its peak at 80 °C of 95.63%.

Figure S12c: In the formation of MPN, an increase in organic linker loading enhances formation of coordination network, thereby increasing the conversion of dissolved cobalt ions into MPNPs. With an increase in the $[GA]/[Co^{2+}]$ molar ratio from 5 to 15, the conversion rate of cobalt

ions to MPNPs increased significantly, rising from 57.19% to 95.37%. This observation highlights the pivotal role of an increased relative content of GA molecules in promoting MPN formation. Subsequently, at ratios of 20 and 25, the conversion rates for cobalt ions reached 93.15% and 95.91%, respectively, with minimal variation. This phenomenon arises from the relative content of GA within the system exceeding its saturation point, indicating the near-complete conversion of most cobalt ions. Consequently, the optimal [GA]/[Co²⁺] molar ratio is 15.

Figure S12d: In the formation of MPN, an increase in Cl⁻ leads to the formation of negatively charged soluble cobalt-chloride complexes and diminishes the assembly process. As the [Cl⁻]/[Co²⁺] molar ratio increased from 20 to 29, the conversion of cobalt ions rose from 82.78% to 95.37%. However, when the ratio surpassed 29, the conversion gradually decreased to 89.44% at 35 and 87.02% at 40. This decline can be attributed to the excess Cl⁻ breaking coordination bonds between cobalt ions and [GA]⁻ due to concentration factor, resulting in localized degradation of the MPN structure. It is evident that a low concentration of Cl⁻ fosters the conversion process, whereas a high concentration inhibits the formation of MPN structure.

The highest conversion rate is achieved at $[GA]/[Co^{2+}]=15$ and $[Cl^{-}]/[Co^{2+}]=29$. This corresponds to the scenario where pure EG is utilized as inducing agent without the necessity of adding GA or Cl⁻ to it.



Figure S13. Potential binding sites for Li ions within the MPN Structure. Li ion binding is likely driven by electron-donating interactions involving the oxygen atoms in the carboxyl and phenolic hydroxyl groups, as well as the benzene ring within the metal-polyphenol network. Derived from literatures.^{6,7}



Figure S14. Exploring the assembly object of $[Co(EG)_6]^{2+}$. The $[Co(EG)_6]^{2+}$ solution is prepared by dissolving anhydrous $CoCl_2$ in an EG solution. Both H₄L and H₃L⁻ solutions are prepared by dissolving GA in EG, with the distinction being the addition or omission of NaOH for deprotonation. Two assembly objects are studied: (a) the molecular form of GA, (b) the ionic form of GA.

The molecular form of GA is represented as H₄L, while the ionic form of GA (with one or more H⁺ ions removed) is denoted as H₃L⁻. Mixing H₄L with the $[Co(EG)_6]^{2+}$ solution resulted in a clear mixture with no observable assembly products. H₃L⁻ solution was obtained by adding a small amount of NaOH to the H₄L solution. When H₃L⁻ solution was mixed with the $[Co(EG)_6]^{2+}$ solution, it led to a rapid transformation into a purple suspension. After centrifugation, MPNPs were obtained, and the lighter yellow color in the supernatant indicated the nearly depletion of H₃L⁻ and the complete conversion of $[Co(EG)_6]^{2+}$ ions into MPNPs. These observations suggest that the ionic form of GA, rather than the molecular form, is likely the binding object for $[Co(EG)_6]^{2+}$.



Figure S15. Electrospray ionization-mass spectra (ESI-MS) of MPNPs in positive mode. The signal at m/z=104.10 corresponds to $[Ch]^+$. The prominent $[Ch]^+$ signal suggests the presence of coordination bonds between the choline ion and cobalt ion within MPNPs. The hydroxyl functional group in choline serves as a potential binding site and is susceptible break under acidic conditions.



Figure S16. Relationships among polarity/polarizability (π^*), hydrogen bond alkalinity (β), and metal ion conversion rate in "DES-Inducing agent" system. a) polarity/polarizability (π^*). As the polarity of the system increases, the conversion rate of cobalt ions to MPNPs initially rises and then declines. The EG demonstrates the highest conversion rate at 95.96%, while EtOH exhibits the lowest at 22.21%. The co-precipitation rate of lithium ions remains within the range of 10.38% to 20.41%. The formation of "n"-shaped curve may be attributed to the effect of solvent polarity on activity of cobalt complex ions.⁸ b) Hydrogen bond basicity (β). There is no significant correlation between the conversion rate to MPNPs and the β value.



Figure S17. SEM images of MPNPs formed in GA solutions. a) EG, the particles exhibit a rod-like structure with an average length of a few micrometers. b) H_2O , these particles exhibit a "leaf" shape with an average size of 9 μ m.



Figure S18. Figures depicting MPNPs formation with and without the addition of LiCl to the GA-MeOH and GA-EG systems. a) MeOH. In the case of MeOH, depicted without the addition of LiCl on the right, a significant portion of LCO remains unconverted. However, when LiCl is added (depicted on the left), a greater number of MPNPs assembly products are obtained. b) EG. In the case of EG, LCO conversion to MPNPs occurs in both scenarios, whether with or without the addition of LiCl.

Note: These figures serve to indicate the feasibility of the conversion process but do not allow for direct comparison of MPNP yields between different systems.



Figure S19. XPS spectra of cobalt in MPNPs acquired from EG solutions. In the uppermost condition, LiCl was included, whereas in the lower condition, LiCl was omitted. In both cases, the Co $2p_{3/2}$ binding energy was occurred at 781.74 eV, and the $2p_{1/2}$ binding energy at 797.71 eV, signifying the successful completion of the conversion process from LCO to MPNPs.



Figure S20. XPS spectra of the elements in MPNPs obtained from EG solutions under two conditions: a) with the inclusion of LiCl and b) without it. No signal corresponding to the 2p orbital of Cl at the binding energy of 197.15 eV was observed, as illustrated in **Figure S9**. This observation

implies the absence of Cl in the resulting products.



Figure S21. The apparent generation time (*t*) for MPNPs with varying LiCl concentrations in the EG solution at 90°C. The transition from a black to brownish-red solution is marked by a red dashed box in the figures. The specific time for each LiCl concentration were as follows: a) 0.08 M, t=5 min. b) 0.17 M, t=13 min. c) 0.50 M, t=15 min. d) 0.83 M, t=90 min.

In EG solution, *t* extended beyond 8 hours in the absence of LiCl. Nevertheless, it reduced to mere 5 minutes with the inclusion of 0.08 M LiCl. As the concentration of Cl⁻ increased, *t* exhibited a progressive increase, ultimately reaching the maximum of approximately 90 minutes with the loading of 0.83 M. With increasing Cl⁻ concentration, the apparent generation time (*t*) delayed, indicating that higher Cl⁻ concentrations inhibited the assembly of MPNPs. The delay is likely attributed to the competition between Cl⁻ and [GA]⁻ for binding to cobalt ions, resulting in the formation of the soluble complex [CoCl₄]²⁻. When 0.83 M LiCl is present, the apparent generation time is notably delayed to 90 minutes, indicating an elevated level of inhibition.



Figure S22. The apparent generation time (*t*) for MPNPs in solutions of EtOH, MeOH, and H₂O, each containing 0.83 M LiCl. The transition from a black to brownish-red solution is marked by a red dashed box in the figures. a) EtOH. 60 °C, t > 180 min. b) MeOH. 60 °C, t = 120 min. c) H₂O. 90 °C, t = 15 min. The comparison reveals that the reaction rate is faster in MeOH than in EtOH and reaches its maximum in H₂O. This variation is attributed to the presence form of cobalt complex ions in various solutions.



Figure S23. XRD diagrams of products obtained from GA solutions with varying CF concentrations. a) EtOH, b) MeOH, c) EG, d) H₂O. The reaction was conducted at 60 °C and lasted of 3 hours. LCO content in the products was quantified by the diffraction intensity of the (1 0 4) plane at 20=45.19 °, while the crystalline MPNP content was assessed by evaluating the intensity of the corresponding crystalline plane at $2\theta = 11.60$ °, indicating the relative conversion rate by $I_{2\theta=11.60}/I_{2\theta=45.19}$.

Crystalline MPNP generation was not observed within 180 minutes when EtOH served as the inducing agent, primarily attributed to its comparatively slower reaction kinetics (**Figure S23a**). In contrast, MeOH exhibited faster reaction kinetics compared to EtOH. Additionally, the introduction of 0.17 M LiCl resulted in an enhanced generation of MPNPs compared to its absence, and the intensity ratio $I_{2\theta=11.60} / I_{2\theta=45.19}$ steadily increased as the loading reached 0.83 M (**Figure S23b**). This observation suggests a progressive conversion of LCO to MPNPs. In the EG solution (**Figure S23c**), owing to its swifter reaction rate in comparison to the previous two, the generation of crystalline MPNPs was detected at $2\theta = 11.60^{\circ}$ even in the absence of LiCl. The intensity ratio $I_{2\theta=11.60} / I_{2\theta=45.19}$ gradually increased with the increase in LiCl loading, signifying the continuous generation of MPNPs. At LiCl loadings of 0.50 M and 0.83 M, the $I_{2\theta=11.60} / I_{2\theta=45.19}$ ratios were nearly identical, indicating the attainment of maximum MPNP yield. In the H₂O solution (**Figure S23d**), large number of crystalline MPNPs were detected even without the addition of LiCl due to its rapid reaction kinetics. The diffraction peak of LCO (1 0 4) plane was not detected at $2\theta = 45.19^{\circ}$, suggesting the near-complete transformation of LCO.

In summary, the addition of Cl⁻ ions significantly enhances the rate of dissolution and conversion of LCO into crystalline MPNPs within GA solution.



Figure S24. UV-Vis absorption spectra of MPNPs after disassembled in acidic buffer solutions, both with the inclusion and exclusion of LiCl in EG solutions.

The increased absorption intensity of MPNPs in the pH=2.0 buffer solution, in contrast to that at pH=4.0, indicates that an acidic environment promotes MPNP disassembly. This phenomenon can be attributed to the H⁺ ions, which serve as more effective oxygen-binding agents, leading to the disruption of Co-O bonds and subsequent degradation of the MPN structure. The emergence of broad, asymmetric peaks in the 400-550 nm range is linked to the generation of p-benzoquinones, the product resulting from the oxidation of GA while it acts as the reducing agent.^{9,10} As a result of its interaction with the benzene ring within the supramolecular structure of MPN, the generated p-benzoquinone undergoes adsorption and subsequent release during the disassembly process. It forms highly colored charge-transfer complexes upon interaction with free GA molecules. The figure demonstrates that the absorption intensity of the charge transfer complex within the 400-550 nm range is greater in the absence of Cl⁻ compared to its presence. This observation suggests that GA molecule functions as reducing agent, akin to Cl⁻.

Moreover, the transition in color of the reaction solution from light yellow to brown (Figure 1c; Figure 3a) was attributed to the generation of GA oxidation products. A comparative experiment illustrating this transition is presented in **Figure S25**.



Figure S25. Experimental flowcharts depicting the synthesis of MPNPs via SICM employing a) CoO, b) $Co(OH)_2$, and c) Co_3O_4 as cobalt sources.

In the case of CoO and Co(OH)₂, the supernatant, observed after centrifugation, exhibited a pale blue hue, signifying the presence of the $[CoCl_4]^{2-}$ complex. Since both CoO and Co(OH)₂ contain divalent cobalt ions, no redox reactions occurred during their dissolution. The oxidation of GA by dissolved O₂ in solution during the reaction remained minimal, resulting in the negligible presence of quinone. In contrast, when Co₃O₄ was employed as cobalt source, the trivalent cobalt ions underwent reduction by GA molecules during the dissolution process. Concurrently, quinone, the oxidation product, was generated, leading to the formation of highly colored charge-transfer complexes. These complexes gave rise to a dark coloration in the supernatant.

The experiments above also demonstrated the versatility of our designed solvent-induced crystallization method in treating cobalt oxides and hydroxides, culminating in the production of MPNPs through the assembly between cobalt ions and polyphenols.



Figure S26. FT-IR spectra of MPNPs obtained from GA-based DES and GA-based EG solutions. Within the "fingerprint region" spanning from 1000 cm⁻¹ to 400 cm⁻¹, identical absorption peak positions and intensities were observed, signifying a structural resemblance among the MPNPs.



Figure S27. a) Images of suspension resulting from the reaction between phenolic acid/polyphenol-EG-LiCl system and LCO. (i) the solution of the three-component system before reaction; the postreaction solutions for (ii) vanillic acid, (iii) isovanillic acid, (iv) methyl gallate, (v) gallic acid, (vi) Syringic acid, (vii) protocatechuic acid (viii) pyrogallol acid. b) Images depicting the MPNPs generated, with the chemical structures corresponding to the phenolic acids and polyphenols utilized positioned at the top of each image.



Figure S28. SEM images of the MPNPs generated within the phenolic acid/polyphenol-EG-LiCl system. a) syringic acid (SA), b) vanillic acid (VA), c) protocatechuic acid (PCA), d) pyrogallol acid (PGA).



Recycled directly

Figure S29. Schematic diagram of the dismantling process of spent lithium-ion batteries. Briefly, the batteries underwent initial immersion in a 0.5 M NaCl solution and were subsequently disassembled into cathodes, anodes, separators, and metal shells. After that, these components were subjected to sieving, resulting in the extraction of copper foils and aluminum foils, both of which were directly recycled. The cathode electrodes underwent calcination in a tube furnace to remove residual organic compounds. Then they were employed in the experiments.



Figure S30. XRD plots of electrode materials obtained from used cell phone batteries: pre-discharge (green line), and discharged (blue line). The obtained data exhibit consistency with the standard diffraction peak of LiCoO₂, indicating that the electrode material corresponds to lithium cobaltate.



Figure S31. SEM image of recovered Co₃O₄.



Figure S32. FT-IR Spectra of recycled MeOH and EtOH.

Section S3. Supporting Tables

| and 4-introlamine as proof molecules. | | | |
|---------------------------------------|-------|-------|---------|
| System | α | β | π^* |
| DES-H ₂ O | 1.420 | 0.221 | 1.123 |
| DES-EG | 1.287 | 0.199 | 1.015 |
| DES-MeOH | 1.149 | 0.207 | 0.903 |
| DES-EtOH | 1.136 | 0.033 | 0.892 |

 Table S1. Kamlet-Taft parameters for the "DES + Inducing agent" system measured by Nile red and 4-nitroaniline as probe molecules:

Section S4. Supporting References

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