nature portfolio

Peer Review File

Continuous Solar-driven Recycling of Lithium-ion Battery Cathode Materials Enabled by A Stable Benzobisthiazole-linked Polymeric Photocatalyst

Corresponding Author: Professor Yanguang Li

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This work presents a solar-driven lithium-ion battery cathode recycling strategy based on hydrometallurgical leaching, but generates H_2O_2 on-site with a photocatalyst. A benzobisthiazole-linked porous organic polymer (TpTz) was synthesized to enable on-site H_2O_2 generation under visible light. The leaching process is assisted by a weak organic acid (acetic acid), allowing efficient dissolution of Li^+ and transition metals under mild conditions, followed by conventional downstream selective precipitation to recover Co and Li. Notably, the system demonstrates impressive long-term stability, achieving continuous metal recovery over a 30-day outdoor test under real sunlight without noticeable performance decay.
Comments:
1. In this work, molecular oxygen is reduced to H_2O_2, while the solvent 1-octanol is oxidized to 1-octanal as the sacrificial electron donor. The authors state that the reactor was purged with O_2 for 30 min prior to illumination. It would be helpful to clarify whether oxygen mass transport may limit the reaction under these conditions. Specifically, how much O_2 can be dissolved and retained in the organic phases after the 30 min purge, and does this supply remain sufficient throughout illumination? In addition, would continuous O_2 bubbling or flow during operation further enhance H_2O_2 productivity or long-term stability compared to a static O_2-saturated system?
2. As 1-octanol is oxidized to 1-octanal during photocatalysis, clarification on the recyclability of the solvent would strengthen the techno-economic discussion. Is there a feasible pathway to recycle or reduce 1-octanal back to 1-octanol to close the solvent loop, or is 1-octanal treated as a value-added side product? If the latter, providing a brief comparison of the market prices of 1-octanol and 1-octanal would help assess the economic impact of solvent oxidation.
3. A central claimed advantage of this work is the on-site, continuous generation of H_2O_2, which is proposed to (1) enable $LiCoO_2$ leaching under mild acidic conditions and (2) avoid the H_2O_2 decomposition in the presence of transition metals. While the second point is reasonably supported, the first is not directly demonstrated experimentally. Including a control experiment using commercial H_2O_2 at a comparable concentration with acetic acid, under identical temperature and mixing conditions, would be important to clarify whether the observed performance arises specifically from in situ H_2O_2.
4. The authors employ commercial $LiCoO_2$ powders to demonstrate the recycling process; however, real battery-derived LCO black mass typically contains additional impurities such as aluminum current-collector residues, conductive carbon, and organic binders. Demonstrating the recycling performance using actual battery black mass would further strengthen the practical relevance and robustness of the proposed approach.
5. In Figure 2e, two distinct data series are shown; however, the difference between these two sets is not specified in the figure caption.
6. In line 241, the authors state that “this design eliminates the need for external energy inputs, significantly reducing operational costs.” However, the recycling process is still operated at ~80 degree C, which requires thermal energy input (even if partially supplied by solar concentration). As written, the term “eliminates external energy inputs” may therefore be overstated. A more precise description clarifying the source of thermal energy or rephrasing this claim would improve accuracy.

Reviewer #2

(Remarks to the Author)

In this manuscript, Yu and co-workers report a thoughtfully engineered, solar-driven battery-recycling platform in which in situ photosynthesized H2O2 is utilized to mediate cathode-material leaching and transition-metal recovery. The process is enabled by a benzobisthiazole-linked polymer photocatalyst (TpTz) that appears to combine strong structural robustness with high H2O2 productivity, translating into rapid Li^+ leaching kinetics and >90% recovery of transition metals. The demonstration of sustained operation under natural sunlight, together with a techno-economic consideration, makes this work as a potentially impactful contribution at the intersection of green oxidant generation, hydrometallurgy, and circular-economy chemistry. I strongly recommend this manuscript to be published in this open access journal.
Several key points require clarification and additional experiments to the claims. Hopefully, the following comments could further refine this study.
1. The H2O2 photosynthesis performance of TpTz is reported at room temperature, whereas the cathode-recycling/leaching step is conducted at 80 °C. Please evaluate (or otherwise justify) whether TpTz maintains comparable H2O2 generation rates, selectivity, and stability at 80 °C. At minimum, provide temperature-dependent H2O2 production profiles (e.g., 25/50/80 °C) and comment on any changes in apparent quantum yield, decomposition contributions, or catalyst integrity (PXRD/FTIR/solid-state NMR as appropriate).
2. While control experiments establish H2O2 as the critical oxidant, the manuscript would benefit from a quantitative correlation between H2O2 concentration and leaching efficiency/kinetics. This will clarify whether the process is limited by oxidant availability, mass transfer across phases, or surface reaction steps.
3. The system is demonstrated with acetic acid; however, from a practical hydrometallurgy perspective, it is important to understand the acidity/ligand requirements. Please assess whether other acids (e.g., formic, citric, lactic, sulfuric, hydrochloric) can be used without sacrificing H2O2 utilization efficiency or causing excessive catalyst degradation.
4. Since an oil–water biphasic configuration is central to the design, the authors should provide evidence that TpTz exhibits stable and selective localization/dispersion in the intended phase over the full reaction duration.
5. The manuscript asserts that the biphasic system enhances H2O2 production while mitigating interference with light absorption. A rigorous control experiment under otherwise identical conditions (light intensity, catalyst loading, O2 availability, stirring, temperature) in a monophasic medium is needed to validate this claim.
6. For $LiFePO_4$, the oxidation of Fe^{2+} to Fe^{3+} is invoked, implying formation of $FePO_4$ as a solid residue. Please provide direct experimental evidence (e.g., XRD of residues, Fe 2p XPS with Fe^{2+}/Fe^{3+} deconvolution, Mössbauer where available) to confirm phase identity and oxidation state after leaching. This is important to distinguish true oxidative delithiation from partial dissolution/reprecipitation or side-phase formation.
7. The manuscript notes accelerated H2O2 decomposition in the presence of accumulated Co^{2+}. Please provide time-resolved H2O2 concentration profiles with and without added Co^{2+} (and ideally across a relevant concentration range) under typical leaching conditions (same pH, temperature, biphasic configuration, and illumination/dark).

Reviewer #3

(Remarks to the Author)
In this manuscript, the author used an organic photocatalyst TpTz to recover valuable metals from spent lithium-ion batteries by efficient and stable hydrogen peroxide (H2O2) production. This work also carried out outdoor sunlight-driven recycling of LiCoO2. However, some parts of the experiment and analysis are not comprehensive. Therefore, under current version, I think this work is not suitable for publication in Nature Communications. We suggested the author provide further analysis and data.
1. In the Techno-Economic Analysis (TEA), the cost of the photocatalyst accounts for 65.8% of the total Levelized Cost of Product (LCP), making it the largest expenditure item. It is recommended to explore more cost-effective precursor monomers or simplify the synthesis steps to reduce production costs.
2. From a practical application perspective, the long-term stability of organic photocatalysts is definitely inferior to that of inorganic photocatalysts.
3. Also, the current economic model is evaluated based on a 3-month operational lifespan for the photocatalyst dispersion. If the replacement interval of the photocatalyst can be extended from 3 months to 12 months, the total profit is projected to increase by approximately 50%.
4. The continuous consumption of 0.6 M acetic acid solution (3,000 L per month) is a major component of the operating costs. Establishing an acid recovery system after leachate treatment could minimize hazardous waste emissions and reduce the cost of purchasing chemical reagents.
5. When discussing TpIm performance degradation, should it be clarified more specifically whether imine bond breakage is caused by ROS oxidative attack, acidic hydrolysis, or a synergistic effect of both?
6. How does this design systematically address the core challenges of H_2O_2 decomposition and catalyst deactivation in traditional homogeneous recycling processes?
7. TEA is pivotal to this technology's practical viability, but several core assumptions lack robust supporting evidence. Please provide more reliable substantiation!
8. In addition to qualitative comparison, it is recommended to conduct a quantitative comparison, roughly comparing the expected energy consumption, chemical usage, and carbon emissions of this method with those of traditional pyrometallurgy and hydrometallurgy, emphasizing the environmental benefits of “solar-driven” processes and “mild conditions”.
9. The manuscript title is suggested to include the photocatalyst name and the key conclusion of the work to increase the attractiveness of the readers.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have carefully addressed all my questions and the paper should be ready for publication.

Reviewer #2

(Remarks to the Author)
Authors have addressed all the concerns in this revised manuscript. Congratulations on their excellent work!

Reviewer #3

(Remarks to the Author)
The author has revised the manuscript based on the review comments and it can be accepted.

We would like to thank three reviewers for their insightful comments about this work. The following are our point-to-point responses to the concerns raised and revisions made accordingly.

Reply to Reviewer #1:

This work presents a solar-driven lithium-ion battery cathode recycling strategy based on hydrometallurgical leaching, but generates H_2O_2 on-site with a photocatalyst. A benzobisthiazole-linked porous organic polymer (TpTz) was synthesized to enable on-site H_2O_2 generation under visible light. The leaching process is assisted by a weak organic acid (acetic acid), allowing efficient dissolution of Li^+ and transition metals under mild conditions, followed by conventional downstream selective precipitation to recover Co and Li. Notably, the system demonstrates impressive long-term stability, achieving continuous metal recovery over a 30-day outdoor test under real sunlight without noticeable performance decay.

1. In this work, molecular oxygen is reduced to H_2O_2, while the solvent 1-octanol is oxidized to 1-octanal as the sacrificial electron donor. The authors state that the reactor was purged with O_2 for 30 min prior to illumination. It would be helpful to clarify whether oxygen mass transport may limit the reaction under these conditions. Specifically, how much O_2 can be dissolved and retained in the organic phases after the 30 min purge, and does this supply remain sufficient throughout illumination? In addition, would continuous O_2 bubbling or flow during operation further enhance H_2O_2 productivity or long-term stability compared to a static O_2-saturated system?

Reply to the reviewer and revision made: We thank the reviewer for these insightful questions. To evaluate whether O_2 availability limits the reaction, we first considered the dissolved O_2 capacity of the reaction medium. According to the literature, the O_2 solubility of in 1-octanol is about 9.5 mmol L^{-1} at 25 °C and 1 atm, which is 7.3 times higher than that in water (1.3 mmol L^{-1} at 25 °C) (*J. Phys. Chem. Ref. Data*, **1983**, 12, 163-178; *J. Chem. Thermodynamics*, **1978**, 10, 817-822). Therefore, our two-phase system provides a relatively O_2-rich environment for the reduction reaction. Furthermore, an O_2 reservoir of 170 mL (7.6 mmol) was maintained in the headspace of the photoreactor to establish gas-liquid equilibrium, ensuring a steady-state supply of dissolved O_2 to offset its consumption during the reaction. Based on the initial H_2O_2 production rate (0.045 mmol h^{-1} for the first hour), the amount of O_2 in within the reaction vessel is sufficient to sustain the reaction over the test period (4 h).

To further assess potential mass transport limitations, benzotrifluoride with higher O_2 solubility (18 mmol L^{-1}) was used as the organic phase (*J. Chem. Educ.* **1996**, *73*, 143), while retaining 10 vol% 1-octanol as the sacrificial electron onor. As shown in **Fig. R1a**, no appreciable enhancement in H_2O_2 production was observed compared to the 1-octanol system. In addition, photocatalytic performance and stability were compared under continuous O_2 bubbling and a static O_2-saturated system in initial 1-octanol/H_2O system. As shown in **Fig. R1b**, both conditions exhibit nearly identical H_2O_2 production profiles, with continuous accumulation over 10 h. These results indicate that further increasing O_2 availability or supply does not further affect the catalytic activity and stability of the photocatalyst, suggesting that

O_2 mass transport is not the dominant limiting factor for our current reaction system.

For the revision, Fig. R1a was included in the Supplementary Information as Supplementary Fig. 6. In addition, we updated the related description on paragraph 10 in the manuscript as follows: "Similar activity was observed when using benzotrifluoride (with 10 vol% 1-octanol) as the oil phase, a solvent with higher O_2 solubility than 1-octanol, demonstrating that O_2 mass transport does not limit H_2O_2 production (Supplementary Fig. 6)."

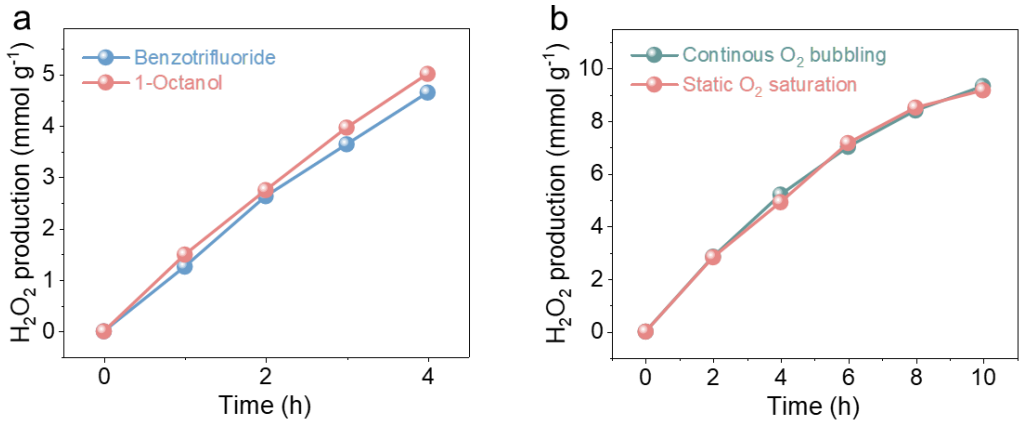

Fig. R1 | a, Photocatalytic H_2O_2 production in two-phase systems with 1-octanol and benzotrifluoride (10 vol% 1-octanol) as the organic phase. **b,** Photocatalytic H_2O_2 production in the 1-octanol/H_2O system under static O_2 saturation and continuous O_2 bubbling.

2. As 1-octanol is oxidized to 1-octanal during photocatalysis, clarification on the recyclability of the solvent would strengthen the techno-economic discussion. Is there a feasible pathway to recycle or reduce 1-octanal back to 1-octanol to close the solvent loop, or is 1-octanal treated as a value-added side product? If the latter, providing a brief comparison of the market prices of 1-octanol and 1-octanal would help assess the economic impact of solvent oxidation.

Reply to the reviewer and revision made: We thank the reviewer for this important question. In our system, the selective oxidation of 1-octanol to 1-octanal should be regarded as a valorization process rather than mere solvent consumption. At present, the market price of 1-octanol is approximately 1.0 USD kg^{-1}, whereas that of 1-octanal is about 5.4 USD kg^{-1} (https://www.chempricehub.com/product/summary-noctyl-alcohol-3cw.html; https://www.pharmacompass.com/price/octanal). This over 5-fold increase in value underscores the potential for high-value chemical upgrading alongside metal recovery. Given the remarkable difference in boiling points between 1-octanol (196 °C) and 1-octanal (163 °C), fractional distillation offers a potential route for product recovery. Moreover, increasing the conversion of 1-octanol through prolonged reaction time would further enrich 1-octanal in the organic phase, thereby improving separation efficiency and overall process economics.

For the revision, the related description on paragraph 22 was updated as follows: "Further opportunities for cost optimization include the efficient recovery of acetic acid through membrane separation technology or the extraction of value-added byproducts *i.e.* 1-octanal — which has a 5-fold value premium over 1-octanol — through fractional condensation systems."

3. A central claimed advantage of this work is the on-site, continuous generation of H_2O_2, which is proposed to (1) enable $LiCoO_2$ leaching under mild acidic conditions and (2) avoid the H_2O_2 decomposition in the presence of transition metals. While the second point is reasonably supported, the first is not directly demonstrated experimentally. Including a control experiment using commercial H_2O_2 at a comparable concentration with acetic acid, under identical temperature and mixing conditions, would be important to clarify whether the observed performance arises specifically from in situ H_2O_2.

Reply to the reviewer and revision made: We thank the reviewer for this valuable suggestion. H_2O_2 has been demonstrated as a key role in our recycling system for promoting metal leaching under mild acidic conditions. Our previous control experiments showed that negligible metal leaching occurred in the absence of light, O_2 or catalyst, indicating that the leaching process critically depends on the photocatalytic H_2O_2 generation process. To directly verify the role of H_2O_2 in enabling $LiCoO_2$ leaching, additional experiments were conducted through directly adding comparable commercial H_2O_2 to the recycling system. To simulate photocatalytic conditions, a biphasic configuration was maintained using a 1:1 ratio of 1-octanol (oil phase) and 0.2 M acetic acid (aqueous phase with 50 mg $LiCoO_2$). Considering the gradual accumulation of photogenerated H_2O_2, varying H_2O_2 concentrations (0 - 50 mM) were prepared from a 30 wt% stock and added to the reaction mixture at 80°C. Our results indicate that the leaching amount increases progressively with H_2O_2 concentration up to 30 mM, confirming that H_2O_2 availability is essential for triggering $LiCoO_2$ leaching under mild acidic conditions (**Fig. R2**). Moreover, metal leaching concentrations at 30 mM H_2O_2 is similar to that achieved in photocatalytic system. When H_2O_2 concentration exceeds 30 mM, the leaching efficiency reaches a plateau, likely due to the accelerated decomposition of H_2O_2 induced by released Co^{2+}. Notably, this 30 mM threshold aligns well with the photocatalytic H_2O_2 yield over 4 h at 80°C. This result demonstrates that the photocatalytic system can continuously provide a sufficient amount of H_2O_2 to achieve the maximum leaching efficiency observed in the control experiments.

For the revision, Fig. R2 was placed in the Supplementary Information as Supplementary Fig. 13. The following discussion was also included on paragraph 14 in the manuscript: "Direct addition of an equivalent amount of commercial H_2O_2 (~ 30 mM) leads to a metal leaching efficiency similar to that achieved in photocatalytic system (Supplementary Fig. 13). These observations confirm the indispensable role of photogenerated H_2O_2 in initiating the metal leaching reaction."

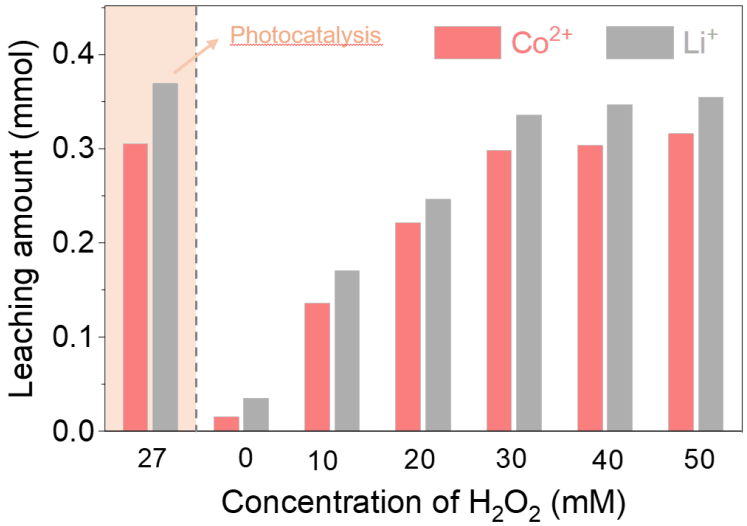

Fig. R2 | Comparison of $LiCoO_2$ leaching performance between *in-situ* photogenerated H_2O_2 versus direct addition of commercial H_2O_2 solution with varying concentrations (0-50 mM).

4. The authors employ commercial $LiCoO_2$ powders to demonstrate the recycling process; however, real battery-derived LCO black mass typically contains additional impurities such as aluminum current-collector residues, conductive carbon, and organic binders. Demonstrating the recycling performance using actual battery black mass would further strengthen the practical relevance and robustness of the proposed approach.

Reply to the reviewer and revision made: We thank the reviewer for this constructive suggestion. To evaluate the practical applicability of our recycling strategy, additional experiments were performed using actual battery-derived black mass from spent commercial LIBs. To this end, the LIBs were fully discharged by immersion in 10 wt% NaCl aqueous solution for 12 h (*Nat. Energy* **2023**, *8*, 1137-1144), followed by rinsing with water and dried at 60 °C (As shown in **Fig. R3a**). Subsequently, the battery was manually disassembled to separate the cathode film. The black mass was then carefully stripped from the aluminum foil, ground into a fine powder. Photocatalytic recycling of the real black mass was performed under identical conditions with those for pure $LiCoO_2$. As shown in **Fig. R3b**, continuous metal leaching is observed over 4 h, with an average leaching rate of 2.96 mmol g^{-1} h^{-1} for Li^+ and 2.49 mmol g^{-1} h^{-1} for Co^{2+}. The leaching performance of the battery-derived black mass is comparable to that of commercial $LiCoO_2$ powder (3.08 mmol g^{-1} h^{-1} for Li^+ and 2.55 mmol g^{-1} h^{-1} for Co^{2+}) (**Fig. R3c)**. These results indicate that the presence of common impurities in the actual cathode materials does not inhibit the leaching reaction, further demonstrating the robustness and high practical relevance of our strategy for recycling cathode materials from spent LIBs.

For the revision, Fig. R3a,b were placed in the manuscript as Fig. 3g and h, respectively. Related description was added on paragraph 13 in the manuscript as follows: “To evaluate practical applicability, real cathode materials were recovered from spent commercial LIBs through discharging, disassembly, and stripping from the current collectors (**Fig. 3g**). The collected black mass was directly subjected to photocatalytic recycling under conditions identical to those used for pure $LiCoO_2$. As shown in **Fig. 3h**, continuous metal leaching is

sustained over 4 h, affording an average leaching rate of 2.96 mmol g^{-1} h^{-1} for Li^+ and 2.49 mmol g^{-1} h^{-1} for Co^{2+}, comparable to those obtained with commercial $LiCoO_2$ powder."

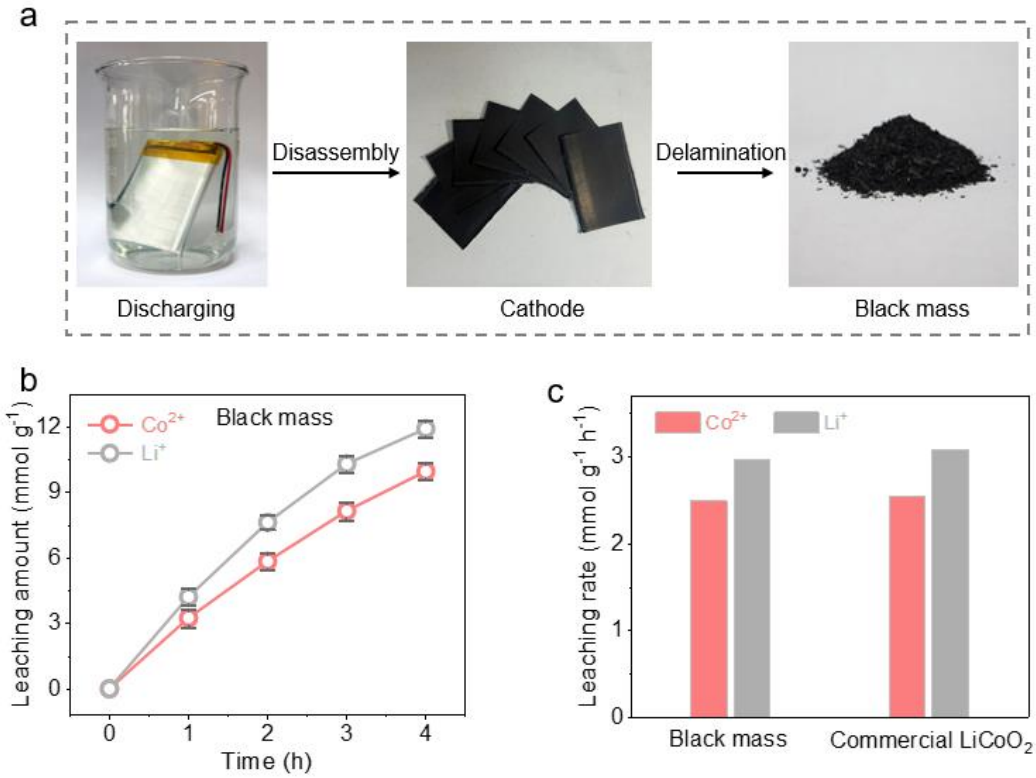

Fig. R3 | a, Treatment of spent commercial LIBs to yield cathode black mass. **b,** Time-dependent leaching profiles of Li^+ and Co^{2+} from black mass at 80 °C. **c,** Comparison of leaching performance between real battery-derived black mass and commercial $LiCoO_2$.

5. In Figure 2e, two distinct data series are shown; however, the difference between these two sets is not specified in the figure caption.

Reply to the reviewer and revision made: We thank the reviewer for this kind reminder. In the revised manuscript, the two distinct datasets (adsorption and desorption curves) have been clearly specified in the corresponding figure (**Fig. R4**). During the revision, the corresponding figure was updated.

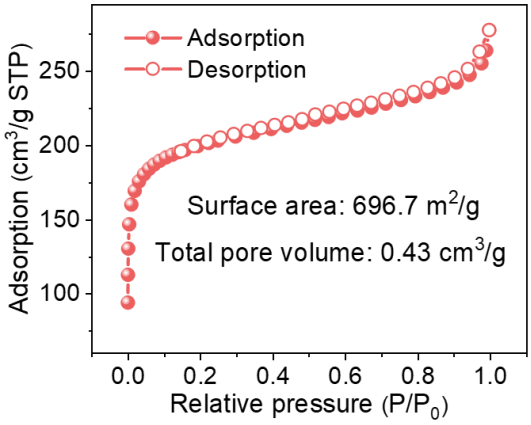

Fig. R4 | N_2 sorption isotherm curve of TpTz.

6. In line 241, the authors state that "this design eliminates the need for external energy inputs, significantly reducing operational costs." However, the recycling process is still operated at ~80 degree C, which requires thermal energy input (even if partially supplied by solar concentration). As written, the term "eliminates external energy inputs" may therefore be overstated. A more precise description clarifying the source of thermal energy or rephrasing this claim would improve accuracy.

Reply to the reviewer and revision made: We thank the reviewer for this kind reminder. An elevated temperature is indeed necessary in our photocatalytic recycling system to facilitate metal leaching process. Here, we would like to clarify that we employed a Fresnel lens in our outdoor photocatalytic tests to concentrate the incident solar irradiation. This setup not only increases the photon flux to enhance the photocatalytic reaction, but also generates a significant thermal effect that effectively raises and maintains the reaction temperature at ~80 °C. This is sufficient to meet the requirements of the leaching process. As a result, no additional heating facilities were used during our outdoor tests, although external energy input was still required for stirring and pumping.

To avoid the ambiguity, the related statement on paragraph 16 was updated during the revision: "This design reduces the demand for external energy inputs, significantly lowering operational costs."

Reply to Reviewer #2:

In this manuscript, Yu and co-workers report a thoughtfully engineered, solar-driven battery-recycling platform in which in situ photosynthesized H_2O_2 is utilized to mediate cathode-material leaching and transition-metal recovery. The process is enabled by a benzobisthiazole-linked polymer photocatalyst (TpTz) that appears to combine strong structural robustness with high H_2O_2 productivity, translating into rapid Li^+ leaching kinetics and >90% recovery of transition metals. The demonstration of sustained operation under natural sunlight, together with a techno-economic consideration, makes this work as a potentially impactful contribution at the intersection of green oxidant generation, hydrometallurgy, and circular-economy chemistry. I strongly recommend this manuscript to be published in this open access journal. Several key points require clarification and additional experiments to the claims. Hopefully, the following comments could further refine this study.

1. The H_2O_2 photosynthesis performance of TpTz is reported at room temperature, whereas the cathode-recycling/leaching step is conducted at 80 °C. Please evaluate (or otherwise justify) whether TpTz maintains comparable H_2O_2 generation rates, selectivity, and stability at 80 °C. At minimum, provide temperature-dependent H_2O_2 production profiles (e.g., 25/50/80 °C) and comment on any changes in apparent quantum yield, decomposition contributions, or catalyst integrity (PXRD/FTIR/solid-state NMR as appropriate).

Reply to the reviewer and revision made: We thank the reviewer for this insightful suggestion. To evaluate the photocatalytic performance of TpTz under recycling conditions, we conducted photocatalytic H_2O_2 production at 80 °C with otherwise identical conditions. As displayed in **Fig. R5a**, TpTz exhibits a continuous and nearly linear H_2O_2 accumulation over 4 h of irradiation, reaching a total yield of 13.1 mmol g^{-1} and a final concentration of 27 mM, approximately 2.7 times higher than that at room temperature. Moreover, no significant morphological and structural changes were observed for the recycled TpTz after the photocatalytic test at 80 ℃ (**Fig. R5b,c**). These results collectively demonstrate that TpTz maintains excellent photocatalytic activity and operational stability even at elevated temperature. This improvement can be attributed to accelerated reaction kinetics and reduced activation barriers at higher temperature, which facilitate both charge transfer and surface redox processes (*ACS Catal*. **2024**, 14, 16543-16550; *Nano Research*, **2026**, 19, 94908130).

For the revision, Fig. R5a was added in Supplementary Information as Supplementary Fig. 7. Related description was also updated on paragraph 10 in the manuscript as follows: "Raising the reaction temperature to 80°C to match subsequent leaching conditions boosted H_2O_2 production 2.7-fold, achieving a total H_2O_2 yield of 13.1 mmol g^{-1} and a final H_2O_2 concentration of 27 mM after 4 h (Supplementary Fig. 7). This improvement was attributed to accelerated reaction kinetics and reduced activation barriers at elevated temperature."

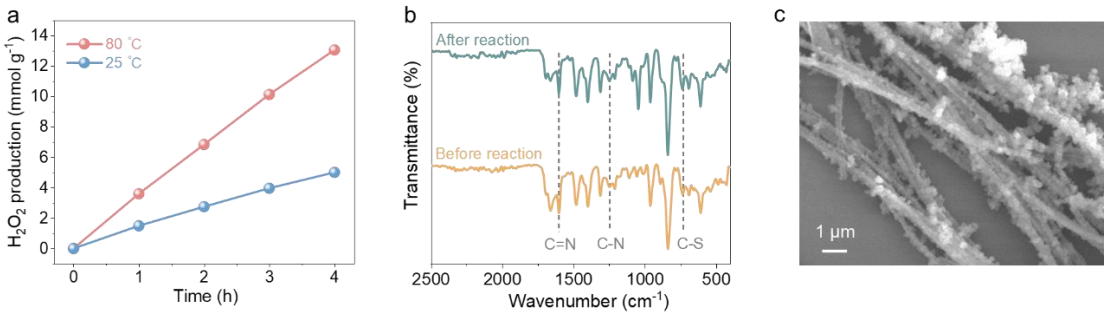

Fig. R5 | a, Photocatalytic H_2O_2 production on TpTz at 25°C and 80 °C in the biphasic system under visible light irradiation (λ >420 nm, 300 mW/cm^2). **b,** FT-IR spectra of TpTz before and after photocatalysis at 80 °C. **c,** SEM image of TpTz after photocatalysis at 80 °C.

2. While control experiments establish H_2O_2 as the critical oxidant, the manuscript would benefit from a quantitative correlation between H_2O_2 concentration and leaching efficiency/kinetics. This will clarify whether the process is limited by oxidant availability, mass transfer across phases, or surface reaction steps.

Reply to the reviewer and revision made: We thank the reviewer for this insightful suggestion. To evaluate the effect of H_2O_2 concentration on metal leaching efficiency, we conducted a series of control experiments during the revision. H_2O_2 concentration varies within the range of 0 to 50 mM, and the results are presented in **Fig. R6**. Our findings show that the leaching rate gradually increases with H_2O_2 concentration up to 30 mM, suggesting that H_2O_2 availability is crucial for the leaching process. As the concentration exceeds 30 mM, the leaching efficiency plateaus. This is probably attributed to the fast decomposition of H_2O_2 triggered by the accumulated Co^{2+} in the solution. Notably, the observed 30 mM threshold aligns well with the H_2O_2 production performance of our TpTz catalyst at 80 ℃ (27 mM over 4 hours), demonstrating that the photocatalytic system is capable of suppling an adequate amount of H_2O_2 to achieving the maximum leaching efficiency.

For the revision, Fig. R6 was added in Supplementary Information as Supplementary Fig. 13. Related description was also updated on paragraph 12 in the manuscript as follows: "The average leaching rates, normalized to the mass of TpTz, are derived to be 3.08 ± 0.08 mmol h^{-1} g^{-1} for Li^+ and 2.55 ± 0.11 mmol h^{-1} g^{-1} for Co^{2+}. This corresponds to an optimal efficiency obtained by directly adding equivalent or even more commercial H_2O_2 stock (Supplementary Fig. 13)."

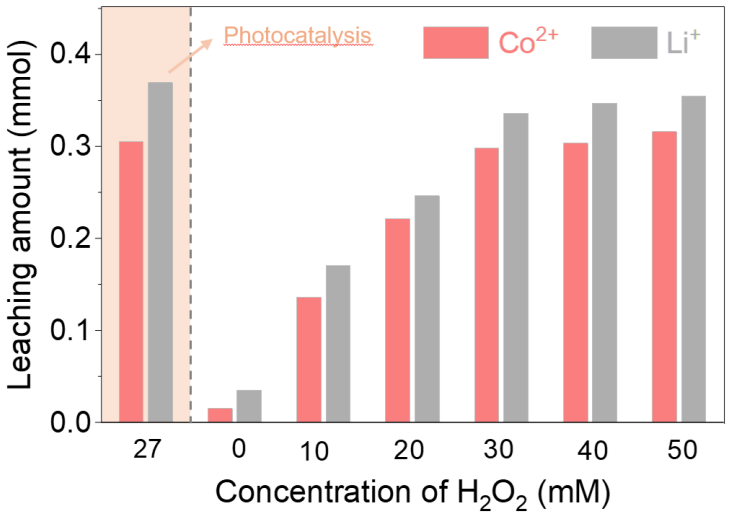

Fig. R2 | Comparison of $LiCoO_2$ leaching performance between *in-situ* photogenerated H_2O_2 versus direct addition of commercial H_2O_2 solution with varying concentrations (0-50 mM).

3. The system is demonstrated with acetic acid; however, from a practical hydrometallurgy perspective, it is important to understand the acidity/ligand requirements. Please assess whether other acids (e.g., formic, citric, lactic, sulfuric, hydrochloric) can be used without sacrificing H_2O_2 utilization efficiency or causing excessive catalyst degradation.

Reply to the reviewer and revision made: We thank the reviewer for this suggest. Per the reviewer's suggestion, we evaluated several alternative acids, including formic, citric, lactic, sulfuric, and hydrochloric acids, to elucidate their impact on leaching performance in our photocatalytic system. All experiments were conducted using 0.2 M of each acid under otherwise identical conditions to those used for acetic acid. As show in **Fig. R6**, all tested acids exhibit comparable metal leaching rates of approximately 3 mmol g^{-1} h^{-1} under visible light irradiation; however, significant differences are observed under dark conditions, where no H_2O_2 is produced. Specifically, all acids except acetic acid demonstrate notable leaching activity in the dark, likely due to their strong acidity or reducing nature (*Energy Environ. Sci.* **2022**, 15, 2732). These background effects inevitably obscure the specific role of H_2O_2 in the leaching process. In contrast, acetic acid provides negligible dark leaching, enabling the observed activity to be primarily attributed to *in-situ* photogenerated H_2O_2. Consequently, acetic acid was selected as the optimal medium, as it allows for clear assessment of H_2O_2-mediated leaching while offering distinct advantages in terms of operational safety, sustainability, and cost-effectiveness.

For the revision, Fig. R6 was included in Supplementary Information as Supplementary Fig. 15. Related discussion was also added in the manuscript on paragraph 14 as follows: "Although other acids can also promote metal dissolution, they exhibit high background contributions due to their strong acidity or intrinsic reducing capability, which obscures the specific role of photogenerated H_2O_2 (Supplementary Fig. 15)."

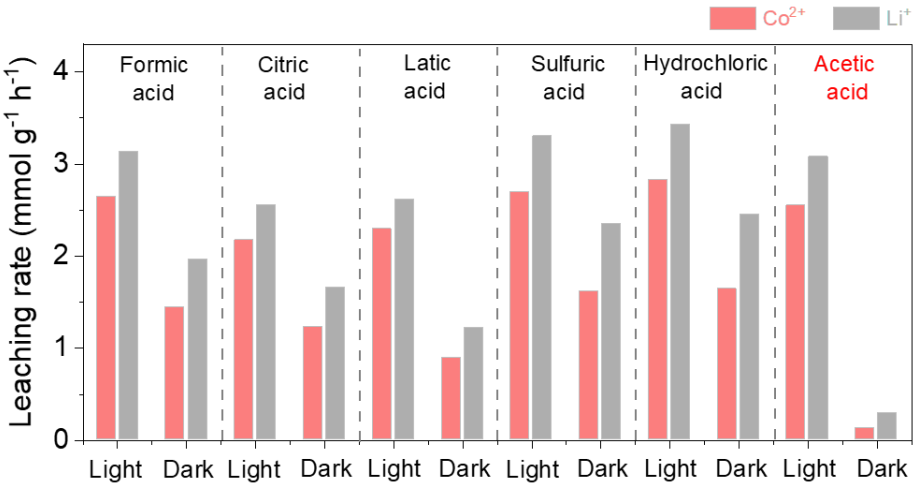

Fig. R6 | Metal leaching rates in different acidic solutions (0.2 M) over TpTz under light and dark conditions in a 1-octanol/H_2O biphasic system under O_2 atmosphere.

4. Since an oil–water biphasic configuration is central to the design, the authors should provide evidence that TpTz exhibits stable and selective localization/dispersion in the intended phase over the full reaction duration.

Reply to the reviewer and revision made: We thank the reviewer for this suggestion. To demonstrate the stable dispersion of TpTz in the oil phase throughout the reaction, we provide the following experimental evidence. First, the surface wettability of TpTz was characterized via water contact angle measurements. As shown in **Fig. R7a**, TpTz exhibits a high contact angle of over 136°, indicating its strong hydrophobicity. This ensures that TpTz prefers to remain in the organic phase rather than the aqueous phase. Second, experimental observations before and after the reaction confirm that TpTz remains selectively dispersed in the upper oil phase (**Fig. 3d** and Fig. R7b). These results validate the stable and selective localization of TpTz in the intended phase over the full reaction duration.

For the revision, Fig. R7a was placed in Supplementary Information (Supplementary Fig. 12). Relevant description on paragraph 12 in the manuscript was also updated as follows: "the aqueous phase gradually changes color from colorless to pink, and a concurrent decrease in solid residue is observed. TpTz remains in the upper oil phase throughout the process (Supplementary Fig. 12)."

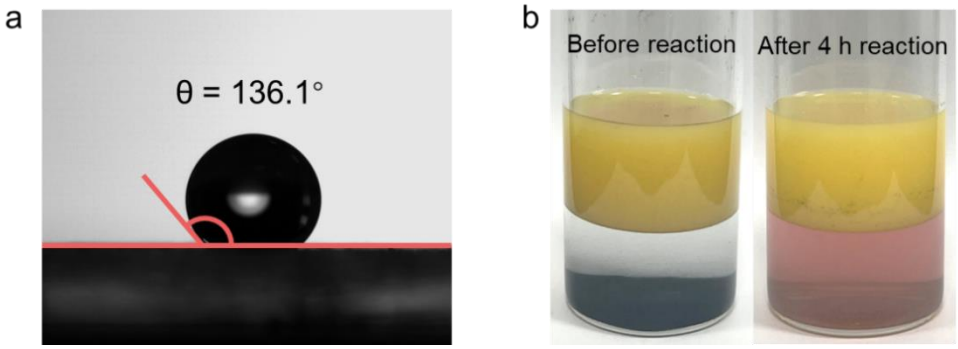

Fig. R7 | a, Water contact angle of TpTz. **b,** Photographs of the reaction mixture before and after 4 h photoreaction.

5. The manuscript asserts that the biphasic system enhances H_2O_2 production while mitigating interference with light absorption. A rigorous control experiment under otherwise identical conditions (light intensity, catalyst loading, O_2 availability, stirring, temperature) in a monophasic medium is needed to validate this claim.

Reply to the reviewer and revision made: We thank the reviewer for this important suggestion. To validate the advantages of our biphasic system, we conducted a control experiment in a monophasic medium. Specifically, the monophasic system was prepared by reducing the concentration of 1-octanol to its solubility limit in 0.2 M acetic acid solution, eliminating the phase interface. As illustrated in **Fig. R8a,b**, under otherwise identical conditions, the leaching rates of Co and Li were measured at only 1.06 and 1.22 mmol h^{-1} g^{-1}, respectively, which are 2.5 times lower than those in the biphasic system. We think that this performance decline can be attributed to two factors: (1) competitive light absorption by the black $LiCoO_2$ powder in the monophasic system, which creates a black suspension under stirring, severely limiting light penetration and thereby reducing photocatalytic activity (**Fig. R8c**); (2) the lower concentration of sacrificial agent 1-octanol and limited O_2 solubility in acidic aqueous solution than in 1-octanol stock, both of which hinder the photocatalytic H_2O_2 production.

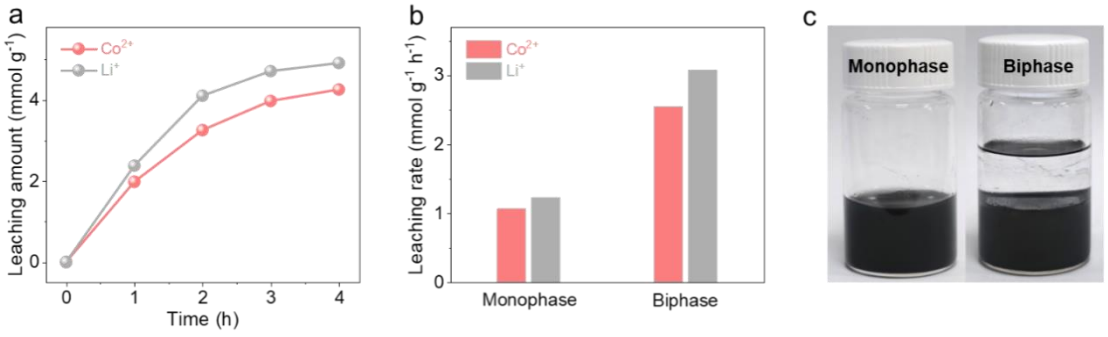

Fig. R8 | a, Time-dependent leaching profiles of Li^+ and Co^{2+} in monophase system. **b,** Comparison of leaching performance between monophase and biphase system. **c,** Photographs of the reaction mixture in monophase or biphase system. Photocatalyst was not added for clear comparison.

6. For $LiFePO_4$, the oxidation of Fe^{2+} to Fe^{3+} is invoked, implying formation of $FePO_4$ as a solid residue. Please provide direct experimental evidence (e.g., XRD of residues, Fe 2p XPS with Fe^{2+}/Fe^{3+} deconvolution, Mössbauer where available) to confirm phase identity and oxidation state after leaching. This is important to distinguish true oxidative delithiation from partial dissolution/reprecipitation or side-phase formation.

Reply to the reviewer and revision made: We thank the reviewer for this important suggestion. To confirm the formation of pure-phase $FePO_4$, we collected the solid residues from the aqueous phase after the leaching reaction. The residues were thoroughly washed with deionized water, dried, and characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). As displayed in **Fig. R9a**, the XRD pattern of the solid residue shows characteristic diffraction peaks consistent with the standard reference for $FePO_4$, indicating its high purity. Moreover, the Fe 2p XPS spectrum of pristine $LiFePO_4$ exhibits two characteristic peaks at

725.8 eV (Fe $2p^{3/2}$) and 712.3 eV (Fe $2p^{1/2}$), corresponding to the Fe^{2+} state (*J. Am. Chem. Soc.* **2022**, *144*, 17097-17109) (**Fig. R9b**). In contrast, the Fe 2p XPS spectrum of the residue shows a significant shift to higher binding energies, with the Fe $2p_{3/2}$ and $2p_{1/2}$ peaks at 723.8 eV and 710.7 eV, respectively, indicating the formation of Fe^{3+} state (*Angew. Chem., Int. Ed.* **2021**, *60*, 9546-9552.). These results collectively provide direct experimental evidence supporting the oxidative delithiation mechanism. In this pathway, H_2O_2 acts as an oxidant, converting Fe^{2+} to Fe^{3+} via a Fenton-like process, driving the extraction of Li^+ while leaving $FePO_4$ as the solid residue. This mechanism stands contrast to the reductive leaching observed for $LiCoO_2$. In the latter case, H_2O_2 acts as a reductant to reduce Co^{3+} to soluble Co^{2+}, followed by acid-assisted deintercalation of Li^+ and Co^{2+} dissolution.

For the revision, Fig. R10 was added into Supplementary Information as Supplementary Fig. 18. Related discussion was also updated in the manuscript on paragraph 15 as follows: "For $LiFePO_4$, the recycling process involves H_2O_2-mediated oxidation of Fe^{2+} to Fe^{3+}, followed by selective Li^+ leaching by acetic acid, leaving behind the residual $FePO_4$, as indicated by XRD and X-ray photoelectron spectroscopy measurements (Supplementary Fig. 18)."

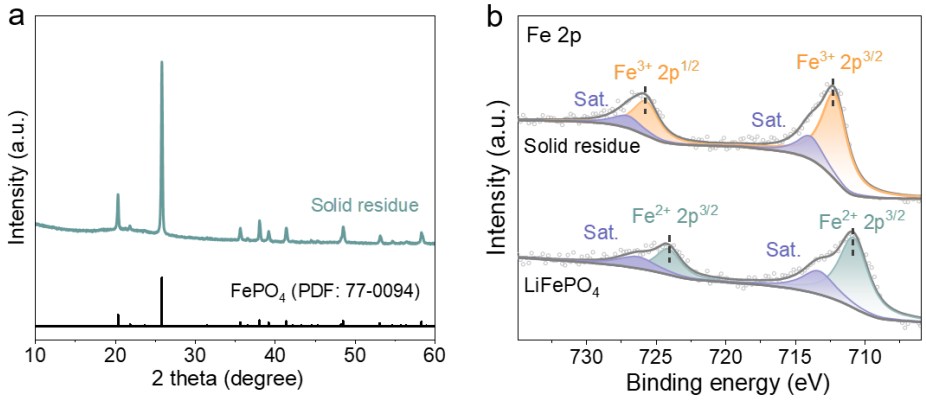

Fig. R9 | a, XRD pattern of solid residue collected after photocatalytic recycling of Li^+. b, Fe 2p XPS spectra of $LiFePO_4$ and solid residue.

7. The manuscript notes accelerated H_2O_2 decomposition in the presence of accumulated Co^{2+}. Please provide time-resolved H_2O_2 concentration profiles with and without added Co^{2+} (and ideally across a relevant concentration range) under typical leaching conditions (same pH, temperature, biphasic configuration, and illumination/dark).

Reply to the reviewer and revision made: We thank the reviewer for this valuable suggestion. To investigate the effect of Co^{2+} on H_2O_2 stability in the photocatalytic system, control experiments were conducted under conditions representative of the leaching environment. A biphasic reaction consisting of an aqueous phase (15 mL) containing 30 mM H_2O_2 and 20 mM cobalt acetate, together with 15 mL of 1-octanol as the organic phase, was prepared in the absence of photocatalyst. These concentrations are comparable to those reached during the 4 h photocatalytic recycling reaction. For comparison, a Co^{2+}-free control was prepared under otherwise identical conditions without cobalt acetate. Both systems were maintained at 80 °C under visible-light irradiation ($\lambda > 420$ nm, 300 mW cm^{-2}), and the H_2O_2 concentration in the aqueous phase was monitored over time. As shown above, in the absence of Co^{2+}, H_2O_2 remains

highly stable, with negligible decomposition (< 10%) over 4 h. In contrast, in the presence of Co^{2+}, fast H_2O_2 decomposition occurs, with approximately 50% of the initial H_2O_2 consumed within the first 30 min, and nearly complete decomposition after 4 h. These results demonstrate that Co^{2+} strongly promotes H_2O_2 decomposition, supporting the conclusion that accumulated Co^{2+} accelerates this process during leaching.

For the revision, Fig. R10 was added in the Supplementary Information as Supplementary Fig. 21. The following statements on paragraph 17 was also updated: "The metal concentrations then approached a plateau, which is attributed to accelerated H_2O_2 decomposition as Co^{2+} ions accumulate in the system (Supplementary Fig. 21)."

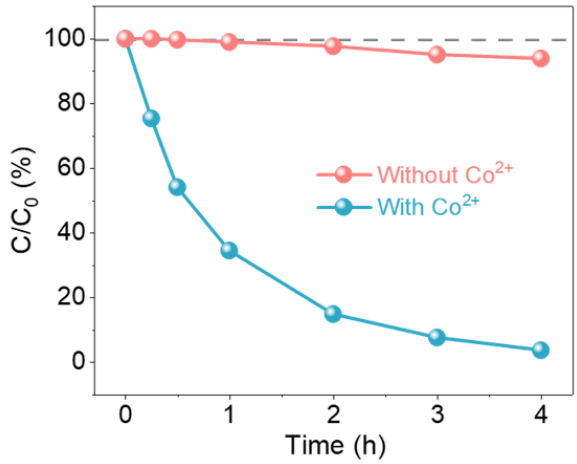

Fig. R10 | H_2O_2 decomposition with and without Co^{2+} under conditions mimicking the leaching environment.

Reply to Reviewer #3:

In this manuscript, the author used an organic photocatalyst TpTz to recover valuable metals from spent lithium-ion batteries by efficient and stable hydrogen peroxide (H_2O_2) production. This work also carried out outdoor sunlight-driven recycling of $LiCoO_2$. However, some parts of the experiment and analysis are not comprehensive. Therefore, under current version, I think this work is not suitable for publication in Nature Communications. We suggested the author provide further analysis and data.

1. In the Techno-Economic Analysis (TEA), the cost of the photocatalyst accounts for 65.8% of the total Levelized Cost of Product (LCP), making it the largest expenditure item. It is recommended to explore more cost-effective precursor monomers or simplify the synthesis steps to reduce production costs.

Reply to the reviewer and revision made: We thank the reviewer for this valuable suggestion. We fully agree that current photocatalyst cost is a major expense and understand the importance to reduce it for better economic feasibility. To this end, we have explored several possible low-cost alternatives during the revision, including graphitic carbon nitride (*g*-C_3N_4), potassium doped *g*-C_3N_4 (K@C_3N_4), gold nanoparticle modified TiO_2 (Au@TiO_2) and molecular porphyrins (TCPP). These photocatalysts were synthesized according to previously reported procedures. Specifically, pristine *g*-C_3N_4 was prepared by direct thermal polymerization of melamine at 550 °C for 4 h under an argon atmosphere (*Adv. Funct. Mater.* **2022**, 32, 2205119). K@C_3N_4 was synthesized by grinding 2 g of pristine *g*-C_3N_4 with 1 g of KSCN, followed by annealing at 500 °C for 5 h under argon (*Adv. Funct. Mater.* **2022**, 32, 2205119). Au@TiO_2 was fabricated via a deposition-precipitation method. $HAuCl_4$ (40 mg) and TiO_2 (1.0 g) were stirred in deionized water at 65 °C. The pH was adjusted to 6-7 using 0.05 M NaOH aqueous solution and stirred for an additional 1 h (*Angew. Chem. Int. Ed.* **2021**, 60, 12074-12081). TCPP photocatalyst was synthesized through a pH-controlled self-assembly process (*Nat. Energy* **2023**, 8, 361-371), in which a TCPP aqueous solution in 0.5 M KOH was acidified to pH 4 with 0.1 M HCl, and stirred at 80 °C for 72 h.

As illustrated in **Fig. R11**, although pristine *g*-C_3N_4 exhibits good stability, its photocatalytic H_2O_2 production efficiency is significantly lower than that of TpTz, resulting in a negligible $LiCoO_2$ recovery rate. Chemical modification through potassium doping improves the activity of *g*-*C3N4* to some extent, but at the expense of durability, leading to noticeable degradation during reaction. Other tested alternatives, including TCPP and Au@TiO_2, failed to meet either the performance benchmarks or the necessary stability requirements. Therefore, satisfying the rigorous requirements of the metal leaching process, particularly in acidic environments at elevated temperatures, proves challenging for these materials. Consequently, based on our current experimental results, TpTz remains the optimal choice as it provides the superior trade-off between catalytic efficiency, structural robustness, and overall system performance. We hope the reviewer understands that while cost reduction is an important goal for our future work, the use of TpTz is scientifically justified at this stage to ensure the reliability of the recovery process.

For the revision, Fig. R11 was added into Supplementary Information as Supplementary

Fig. 23. The related discussion was also updated on paragraph 22 in the manuscript as follows: "Despite our efforts to explore low-cost candidates (Supplementary Fig. 23), TpTz currently offers the best balance of catalytic activity, stability, and economic viability. Furthermore, current material costs are expected to decrease with economics of scale."

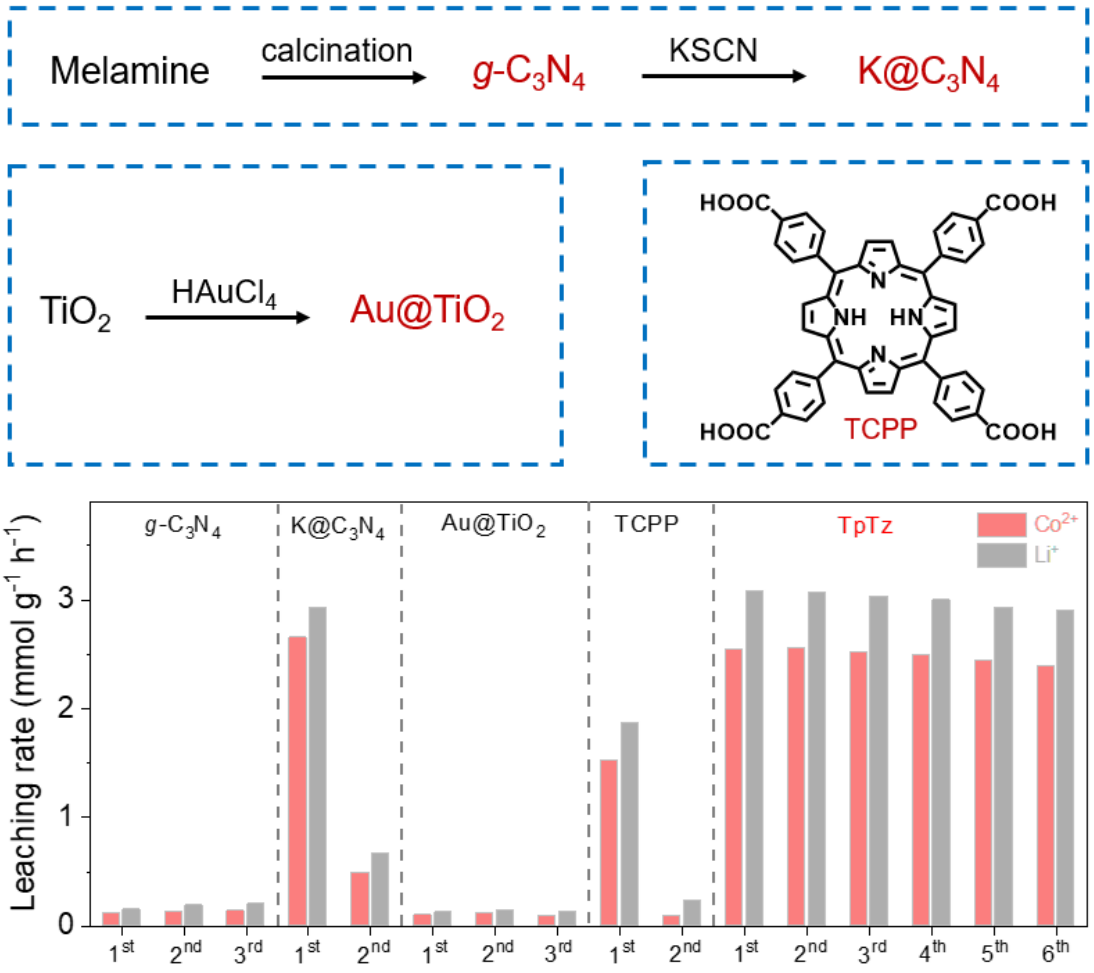

Fig. R11 | Comparison of leaching rate and stability of *g*-C_3N_4, K@C_3N_4, TCPP, and TpTz under identical conditions.

2. From a practical application perspective, the long-term stability of organic photocatalysts is definitely inferior to that of inorganic photocatalysts.

Reply to the reviewer and revision made: We thank the reviewer for this important comment. We acknowledge that while organic photocatalysts often demonstrate superior photocatalytic H_2O_2 production efficiency, compared to inorganic counterparts, their long-term stability remains a significant challenge. As previously reported, this instability primarily stems from the reactive oxygen species (ROS) generated during the reaction, which can attack and degrade the organic backbones (*J. Am. Chem. Soc.* **2021**, *143*, 19287-19293). Furthermore, extensively studied COF-based photocatalysts rely on reversible covalent linkages that are susceptible to hydrolytic cleavage, leading to deactivation over time. To address these concerns, we adopted a specific design strategy in this work. By converting reversible imine bonds into irreversible

benzothiodiazole linkages through a dehydrogenation cyclization reaction, we significantly enhanced the robustness of the organic framework. Moreover, the incorporation of polycyclic aromatic structures in our photocatalyst could further improves its resistance to oxidation. The effectiveness of this strategy has been validated by the excellent stability of our material under acidic conditions and elevated temperatures over 30 day outdoor tests. While we are encouraged by these results, we fully agree that improving the long-term stability of organic photocatalysts is an ongoing challenge for the field. We think that future advancements in this area may benefit from the integration of more robust structural units, such as imide linkages or those nitrogen-containing fused aromatic rings. These continued optimizations will be crucial for meeting the stringent requirements of large-scale practical applications.

On the other hand, traditional inorganic semiconductors, such as TiO_2 and $BiVO_4$ possess excellent inherent structural stability. However, their application in photocatalytic H_2O_2 production is often limited by a relatively narrow light-harvesting range and a tendency to facilitate the decomposition of H_2O_2 (*Small* **2022**, *18*, 2104561). In our system, such characteristics may hinder the accumulation of H_2O_2, which is essential for achieving high metal leaching efficiency.

To clarify our rationale for selecting the photocatalyst, the relevant discussion is presented in the manuscript on paragraph 4 as follows: "*Traditional inorganic semiconductors, such as TiO_2, offer inherent structural stability; however, their photocatalytic performance is often constrained by a narrow light absorption range and a tendency to catalyze the decomposition of H_2O_2. In contrast, metal-free organic semiconductor photocatalysts, most notably covalent organic frameworks (COFs), have recently emerged as promising alternatives for H_2O_2 photosynthesis by virtue of their tunable structures and high photocatalytic activities. Nevertheless, their long-term stability remains a critical challenge primarily due to the presence of reversible chemical linkages (commonly imine bonds) in constructing their crystalline polymer frameworks. These dynamic bonds are susceptible to hydrolytic cleavage under acidic or basic conditions and are vulnerable to oxidative degradation by reactive oxygen species (ROS) generated during photocatalysis, ultimately leading to progressive structural collapse and performance decay over time. To address these limitations, rational linkage engineering, particularly the replacement of labile linkages with more robust, irreversible covalent bonds, is essential for improving the structural robustness and operation lifespan of polymeric photocatalysts under harsh reaction environments.*"

3. Also, the current economic model is evaluated based on a 3-month operational lifespan for the photocatalyst dispersion. If the replacement interval of the photocatalyst can be extended from 3 months to 12 months, the total profit is projected to increase by approximately 50%.

Reply to the reviewer and revision made: We thank the reviewer for this comment. The operational lifespan of the photocatalyst significantly impacts the system's economic viability. This perspective aligns with our sensitivity analysis in the manuscript, where we explicitly stated that extending the photocatalyst replacement interval from 3 months to 12 months could potentially increase the total projected profit by approximately 50%. At current stage, the 3-month operational lifespan is established for TEA based on our practical outdoor experiment. Extending the lifespan to 12 months or even longer will require the development of more stable photocatalysts. At present, while our dehydrogenation cyclization strategy has successfully

improved stability to some extent, further enhancement, as stated in the above question, could be achieved by introducing even more chemically inert linkages or building units. Furthermore, the optimization of the oil-phase sacrificial agent is equally vital for long-term performance.

For the revision, related discussion was updated on paragraph 22 in the manuscript as follows: “Additionally, improving photocatalyst stability via structural engineering offers a viable pathway to higher profitability, for instance, extending the photocatalyst replacement interval to 12 months could increase overall profit by ~50%.”

4. The continuous consumption of 0.6 M acetic acid solution (3,000 L per month) is a major component of the operating costs. Establishing an acid recovery system after leachate treatment could minimize hazardous waste emissions and reduce the cost of purchasing chemical reagents.

Reply to the reviewer and revision made: We thank the reviewer for this important suggestion. The TEA in our manuscript shows that acetic acid consumption accounts for about 5% of the total LCP, representing a relatively small portion of the overall cost. Recycling acetic acid is theoretically feasible through fractional distillation, while this process requires additional capital investment for the distillation setup and incurs substantial energy costs for heating. To provide a clearer comparison, we estimated the total costs of the acetic acid recovery system, including the cost of acetic acid, the distillation setup (https://detail.1688.com/offer/619755148514.html) and the operating power for heating. At our current scale, daily consumption of 200 L of 0.6 M acetic acid (120 mol) leaves approximately 51 mol of residual acid, after accounting for 69 mol consumed by complexation with Co^{2+} and Li^{+}. Assuming a 90% recovery efficiency, the monthly cost of acetic acid recovery is calculated as follows:

Cost of aqueous phase per month = cost of water ($) + cost of acetic acid ($) = 11 days × 193.4 L × 0.00056 $/L + 11 days × 6.6 L × 0.36 $/L = 27.3 $/month

Cost of 200 L distillation setup per month = cost of facility ($) / lifetime (month) = (9798 $) / 120 month = 81.7 $/month

Cost of electricity per month = 0.8 kW × 4 h × 11 days × 0.05 $/kWh = 1.76 $

Cost of acetic acid recycling system per month = 27.3 $/month + 81.7 $/month + 1.76 $/month = 110.76 $/month

On the basis of above calculation, the cumulative expenses of acetic acid recycling system (110.76 $/month) significantly outweigh the cost of replenishing fresh acid reagents (37.2 $/month, as detailed in Supplementary Information) at this stage. Consequently, while we recognize the merits of acid recovery, it currently diminishes the overall economic viability of the system. Nevertheless, we agree that optimizing the recovery process is a valuable direction and we intend to explore more energy-efficient separation technologies, such as possible membrane separation to further enhance the system's sustainability.

For the revision, the following discussion was included in the manuscript on paragraph 22: “Further opportunities for cost optimization include the efficient recovery of acetic acid through membrane separation technology or the extraction of value-added byproducts, *i.e.* 1-octanal — which has a 5-fold value premium over 1-octanol — through fractional condensation systems.”

5. When discussing TpIm performance degradation, should it be clarified more specifically

whether imine bond breakage is caused by ROS oxidative attack, acidic hydrolysis, or a synergistic effect of both?

Reply to the reviewer and revision made: We thank the reviewer for this insightful question. To clarify the mechanism behind the imine bond cleavage observed in our control sample (TpIm), we conducted several control experiments during the revision. First, to isolate the effects of the acidic environment, we performed photocatalytic H_2O_2 production using pure water. As shown in **Fig. R12a**, TpIm exhibits significant performance degradation, retaining only 14% of its initial activity after 3 cycles (totaling 12 hours). Meanwhile, the characteristic imine stretching peak at 1622 and 1056 cm^{-1} in the infrared spectrum nearly disappears, indicating cleavage of the linkage units. These observations confirm that ROS play a crucial role in material deactivation. We then assessed the chemical stability of TpIm in 2 M HCl under dark conditions to exclude light-induced ROS generation. As shown in **Fig. R12b**, after 16 hours of acid treatment, the imine vibration bands were significantly attenuated, confirming that acid exposure promotes bond breakage. These results align with previous reports, demonstrating that the instability of imine-linked polymers stems from the combined effects of ROS-mediated oxidative attack and acidic hydrolysis. Specifically, ROS generated during the photocatalytic process could directly attack imine linkages, causing its oxidative cleavage (*J. Am. Chem. Soc.*, **2022**, 144, 9902-9909; *Nat. Commun.* **2026**, *17*, 3046). This instability could be further exacerbated in acidic environments, because the protonation of imine nitrogen atoms lowers the activation energy for nucleophilic attack by water and ROS, thereby accelerating structural degradation (*J. Am. Chem. Soc.*, **2012**, 134, 19524-19527; *Nat. Commun.* **2018**, *9*, 2600).

For the revision, Fig. R12a,b were placed in the Supplementary Information as Supplementary Fig. 11c,e. The related statement was also added in the manuscript as follows: "In stark contrast, TpIm exhibits poor chemical stability in acidic solution, even under dark conditions, due to hydrolytic cleavage of the imine bonds (Supplementary Fig. 11a). Moreover, significant performance decay is observed in both acidic and neutral aqueous media (Supplementary Fig. 11b,c). This degradation is accompanied by noticeable catalyst mass loss and increased transparency of the catalyst dispersion (Supplementary Fig. 11d). Spectroscopic analyses of the recovered TpIm further confirm severe molecular and morphological degradation (Supplementary Fig. 11e,f).."

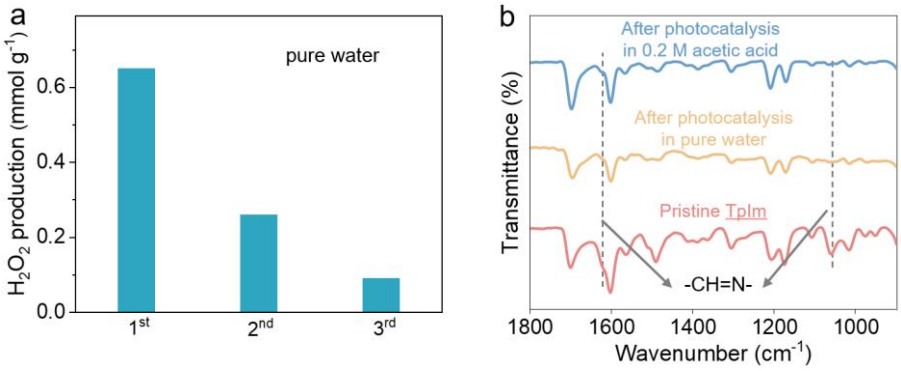

Fig. R12 | a, Photocatalytic cycling tests for H_2O_2 production on TpIm in water showing a gradual decline in activity over successive cycles. **b,** FT-IR spectra of pristine TpIm, acid-treated TpIm, and TpIm after the photocatalytic cycling test.

6. How does this design systematically address the core challenges of H_2O_2 decomposition and catalyst deactivation in traditional homogeneous recycling processes?

Reply to the reviewer and revision made: We thank the reviewer for this important question. Our design addresses the critical limitations of homogeneous recycling by integrating molecular engineering with a unique biphasic reaction configuration. Regarding the challenge of H_2O_2 decomposition, we have demonstrated that the accumulation of Co^{2+} inevitably triggers the rapid decomposition of the photogenerated H_2O_2 (**Fig. R11**), which inevitably leads to the termination of leaching reaction. Our strategy circumvents this by employing a continuous flow reaction system, which allows for the periodic extraction of the lower metal-rich aqueous phase and the replenishment of fresh acetic acid solution. This dynamic management of the reaction environment, therefore, prevents the accumulation of high concentrations transition metals in the system, a stark contrast to homogeneous methods where complex catalyst separation is required to mitigate such side reactions.

The issue of photocatalyst deactivation is addressed through a synergistic approach involving both material innovation and spatial separation. It has been identified that the instability of traditional organic frameworks primarily stems from oxidative attack by ROS and acidic hydrolysis (**Fig. R13**). By implementing a dehydrogenation cyclization strategy, we converted reversible linkages into irreversible, polycyclic benzothiodiazole structures, significantly enhancing the robustness of the organic backbones against chemical degradation. Notably, this structural resilience is further complemented by the inherent advantages of our biphasic system. The photogenerated H_2O_2 could spontaneous and effective migration into the aqueous phase, effectively minimizing its local accumulation around the catalyst and reducing the risk of ROS-induced oxidation (*Angew. Chem. Int. Ed.* **2019**, *58*, 5402-5406; *J. Am. Chem. Soc.*, **2022**, *144*, 9902-9909). Moreover, the oil phase serves as a sacrificial electron donor that rapidly scavenges photogenerated holes, preventing self-oxidative deactivation of the organic framework (*Nat. Energy*, **2019**, 4, 746-760). Consequently, the optimization of both molecular structure and reaction system not only suppresses H_2O_2 decomposition but also enhances the long-term stability of the photocatalyst, offering a viable solution to these limitations of homogeneous systems.

To highlight the critical advantages of our continuous photocatalytic recycling system, related discussion is stated on paragraph 16 in our manuscript as follows: "*Moreover, the spatial decoupling of H_2O_2 photosynthesis from chemical leaching within the reactor allows for periodic leachate extraction and reactant replenishment without the need for catalyst separation, thus enabling continuous operation for extended periods, from days to months.*"

7. TEA is pivotal to this technology's practical viability, but several core assumptions lack robust supporting evidence. Please provide more reliable substantiation!

Reply to the reviewer and revision made: We thank the reviewer for this important suggestion. The core assumptions integrated into our TEA include material costs, reactor scale, operational time and replacement interval. To ensure the robustness and transparency of our economic model, we have strictly aligned all parameters with current market data and validated engineering benchmarks. Specifically, the costs for all chemical reagents and solvents are

sourced directly from commercial procurement platforms, with the corresponding URLs provided in both Manuscript and Supplementary Information. Regarding the reactor configuration, the assumption of a 1 m^2 irradiation area coupled with a 0.2 m^3 solution volume is based on scalable engineering models whose feasibility has been validated in prior photocatalytic studies (*Nature* **2021**, *598*, 304-307; *Adv. Mater.*, **2025**, *37*, 2420199; *Chem. Catal*., **2025**, *5*, 101238). To further account for real-world environmental constraints, the operational time of 15 days per month is directly informed by historical meteorological data for Suzhou, China, providing a realistic assessment of solar availability (https://www.tianqi24.com/suzhou/history2025.html). According to the data, around 180 days in 2025 are sunny or partly cloudy. Notably, the operational window could be further extended in regions with higher annual irradiance, such as Northwest China. Furthermore, the replacement interval of photocatalyst and solvents is established based on the actual results in our experiments.

For the revision, a comprehensive discussion of these assumptions, including detailed calculations and analyses, has been provided in *Supplementary Note* of the Supplementary Information.

8. In addition to qualitative comparison, it is recommended to conduct a quantitative comparison, roughly comparing the expected energy consumption, chemical usage, and carbon emissions of this method with those of traditional pyrometallurgy and hydrometallurgy, emphasizing the environmental benefits of "solar-driven" processes and "mild conditions".

Reply to the reviewer and revision made: We thank the reviewer for this constructive suggestion. To illustrate the environmental benefits of solar-driven recycling processes, a quantitative comparison was performed with traditional approaches. A treatment amount of 5 kg $LiCoO_2$ was chosen for comparison, representing the current monthly processing capacity of the solar-driven system described in the manuscript. Typically, pyrometallurgy mainly relies on coal combustion to maintain high temperatures exceeding 1000 °C, which results in a substantial carbon footprint of approximately 24-27 kg of CO_2 for recycling 5 kg of $LiCoO_2$, as estimated from the coal demand for high-temperature operation using the GREET model (https://greet.anl.gov/). While hydrometallurgy operates at lower temperatures (60-90 °C), it necessitates the use of concentrated strong acids (e.g. H_2SO_4, HCl) and commercial H_2O_2 stock, with the electricity required for reactor heating estimated at 6-9 kWh (*Nat. Sustain.*, **2019**, *2*, 148-156). Based on the U.S. Energy Information Administration (0.388 kg of CO_2 emissions per kWh), this equates to a carbon emission of 2.3-3.5 kg (https://www.eia.gov/tools/faqs/faq.php?id=74&t=11). In contrast, our strategy utilizes solar energy to simultaneously drive reducing agent generation and system heating, resulting in near-zero carbon emission. To facilitate a more direct comparison of these methodologies, we have summarized the key metrics in **Table R1**. This comparison highlights the significant environmental benefits of our proposed solar-driven strategy.

For the revision, Table R1 was added in the supplementary Information as Supplementary Table 1. Related description was also updated on paragraph 22 in the manuscript as follows: "The above analysis clearly highlights the strong economic potential of our solar-driven recycling system, along with significant environmental benefits including low waste emissions

and carbon footprints (Supplementary Table 1). This contrasts with traditional pyrometallurgy and hydrometallurgy, which are typically plagued by high energy consumption and toxic waste management issues."

Table R1. A quantitative comparison of energy consumption, chemical usage, and carbon emissions among pyrometallurgical, hydrometallurgical and solar-driven recycling of $LiCoO_2$.

Parameters	Pyrometallurgy	Hydrometallurgy	**Solar-driven recycling (this work)**
Temperature	800-1700 °C	60-90 °C	**80 °C**
Heating source	Fossil fuel	Electricity	**Solar energy**
Chemicals	\	Conc. H_2SO_4/HCl Conc. H_2O_2	**Diluted acetic acid** **1-Octanol**
CO_2 emission (for 5 kg $LiCoO_2$)	24-27 kg	2.3-3.5 kg	**Near-zero**
Waste generation	Toxic gas (NO_x, SO_x)	Acidic wastewater	**Acidic wastewater**
Hazards	Harmful gas emission	Strong acid corrosion	\

9. The manuscript title is suggested to include the photocatalyst name and the key conclusion of the work to increase the attractiveness of the readers.

Reply to the reviewer and revision made: We thank the reviewer for this kind suggestion. During the revision, the title was updated as "Continuous Solar-driven Recycling of Lithium-ion Battery Cathode Materials Enabled by A Stable Benzobisthiazole-linked Polymeric Photocatalyst".