Electronic Supplementary Information

Recycling application of waste Li-MnO_2 batteries as efficient catalysts based on electrochemical lithiation improve catalytic activity

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Materials

Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 4.5% to 4.9% active oxygen) was obtained from Shanghai Ansin Chemical Co. Ltd. and used as an oxidant. Rhodamine B ($C_{28}H_{31}ClN_2O_3$) was obtained from Shanghai Aladdin Reagent Co. Ltd. and used as an organic pollutant. Sodium phosphate dibasic dehydrate (Na_2HPO_4, 99%), Sodium phosphate monobasic dehydrate ($NaH_2PO_4 \cdot 2H_2O$), and N-Methyl pyrrolidone (NMP, C_5H_9NO) were provided by Shanghai Aladdin Reagent Co. Ltd. All of these chemicals were used as received without any further purification. These waste and new Li-MnO_2 batteries from the Sony 2032 type Button Battery.

The related treatment of the recycled MnO_2

As a comparison, the appropriate amount of the recycled MnO_2 was treated with NMP for 1 h at 100 °C to remove the binder on surface of the lithiated MnO_2. And then the samples was collected and washed with deionized water and ethanol several times before vacuum drying at 60 °C overnight. Meanwhile, the recycled MnO_2 was placed in a Muffle furnace, and then the temperature was increased to 400 °C at 2 °C/min in an air atmosphere 2 h based on the thermodynamic behavior obtained by TG analysis. The reprocessing may be regenerated the recycled MnO_2[1].

The detailed preparation of phosphate buffer solution

The phosphate buffer solution was prepared by mixing 1.85 g/L Na_2HPO_4 and 1.52 g/L NaH_2PO_4 in 1 L deionized water[2].

The detailed procedures of the experimental cycle

For the recycling experiment about the reusability of catalyst, the several parallel experiments were performed in the each cycle to ensure that the subsequent catalyst is sufficient. For the recycling experiment of catalyst, and the catalyst was collected by filtering and washed with absolute ethanol and deionized water for several times before vacuum drying at 60 °C overnight.

Table S1 The metal contents of the cathode material

Metals	Mn	Li
Content (wt%)	55.6	4.22

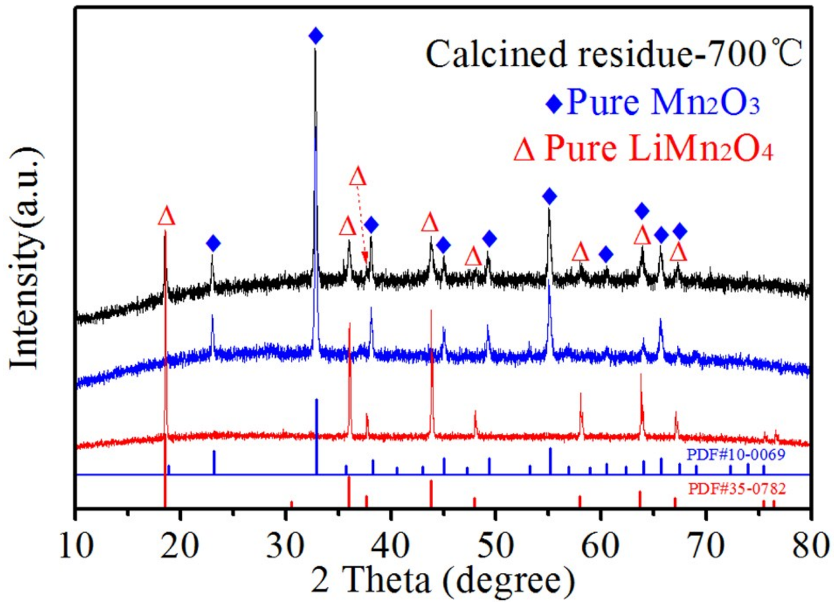

Fig. S1 XRD pattern of the recycled MnO_2 in an air atmosphere at 700 °C.

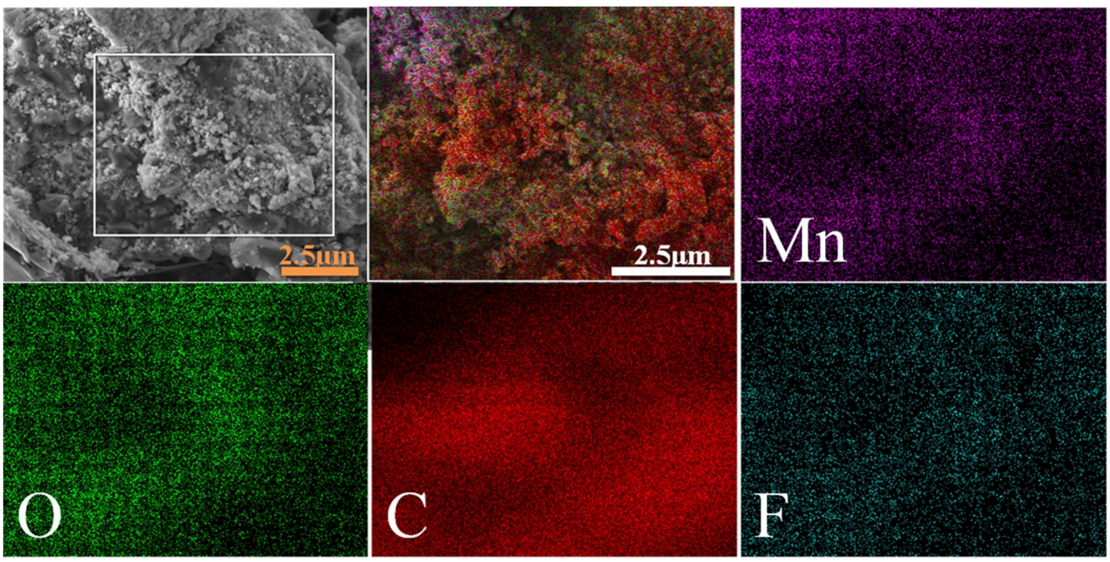

Fig. S2 EDX elemental maps of the recycled MnO_2.

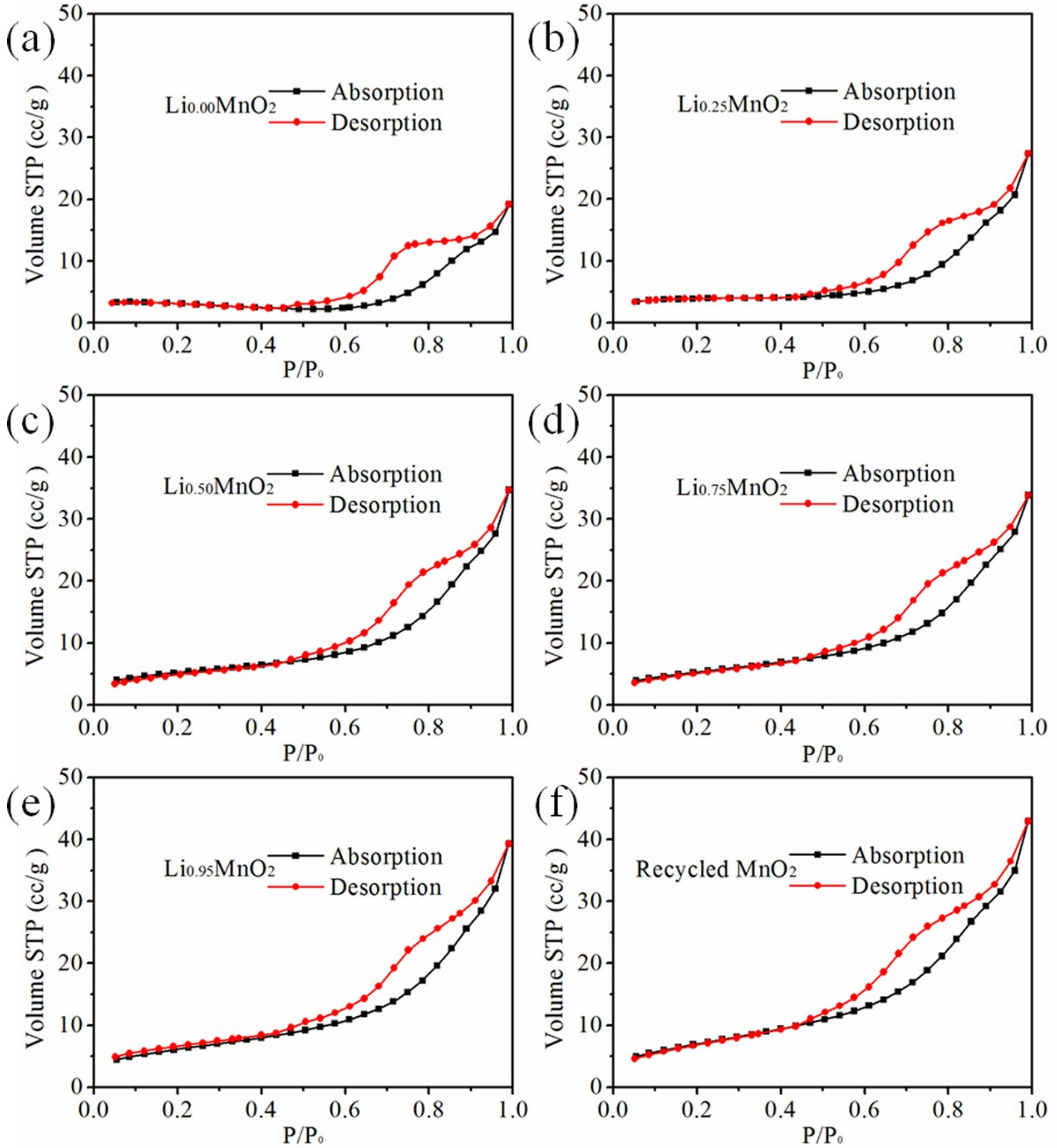

Fig .S3 N_2 adsorption/desorption isotherms of the the Li_xMnO_2 cathode (x=0, 0.25, 0.5, 0.75 and 0.95) and recycled MnO_2.

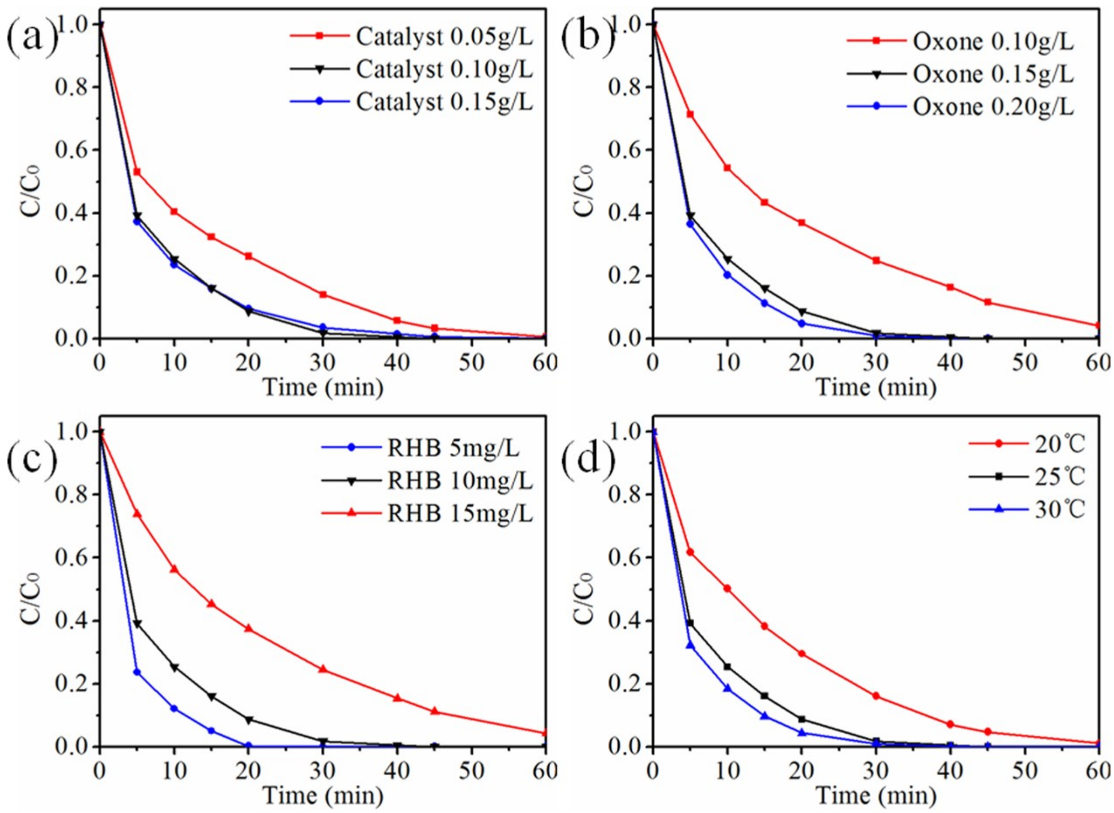

Fig S4 The effect of single factor on degradation reaction. (a) catalyst concentration; (b) oxidant concentration; (c) RhB concentration; (d) reaction temperature. Unless otherwise stated, the reaction conditions are based on: [RhB]=10mg/L, catalyst loading = 0.1g/L, Oxone loading = 0.15g/L, and T = 25 °C.

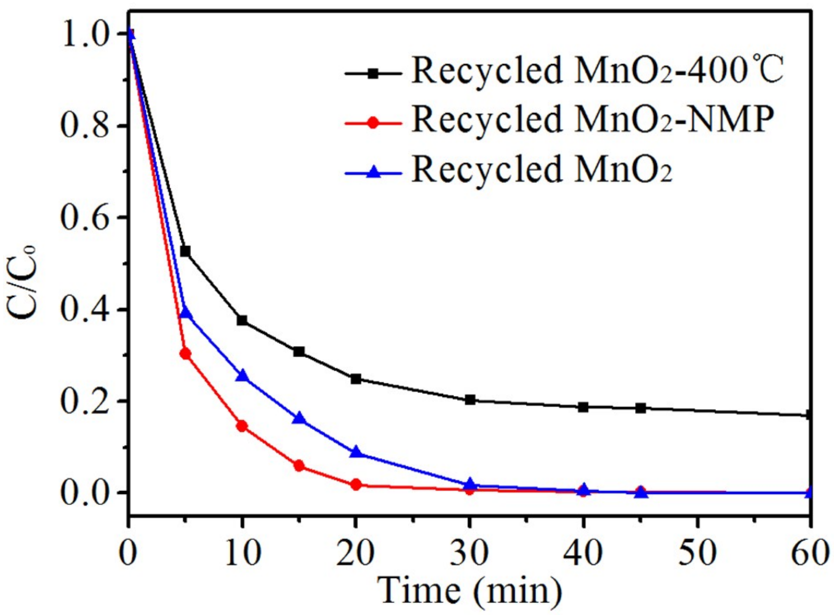

Fig S5 Tests of catalytic activation for the recycled MnO_2 before and after being treated with NMP and treated under 400 °C. Unless otherwise stated, the reaction conditions are based on:

[RhB]=10mg/L, catalyst loading = 0.1g/L, Oxone loading = 0.15g/L, and T = 25 °C.

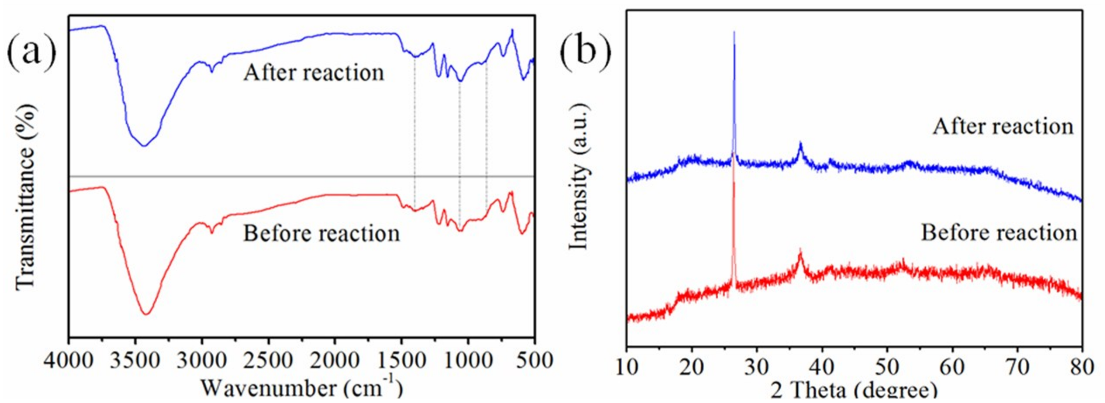

Fig S6 (a) FT-IR spectra and (b) XRD patterns of the recycled MnO_2 catalysts before and after reaction.

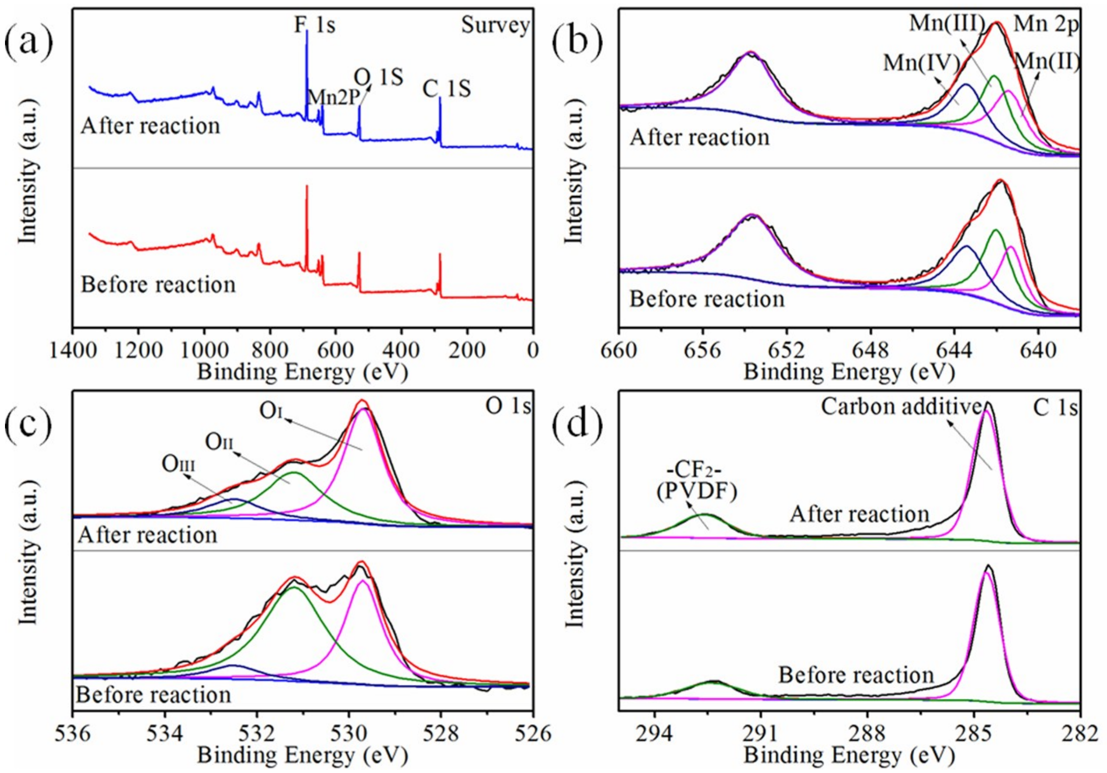

Fig .S7 XPS spectra of the fresh and used the recycled MnO_2: (a) survey spectra of the sample, (b) Mn 2p, (c) O 1s, and (d) C 1s.

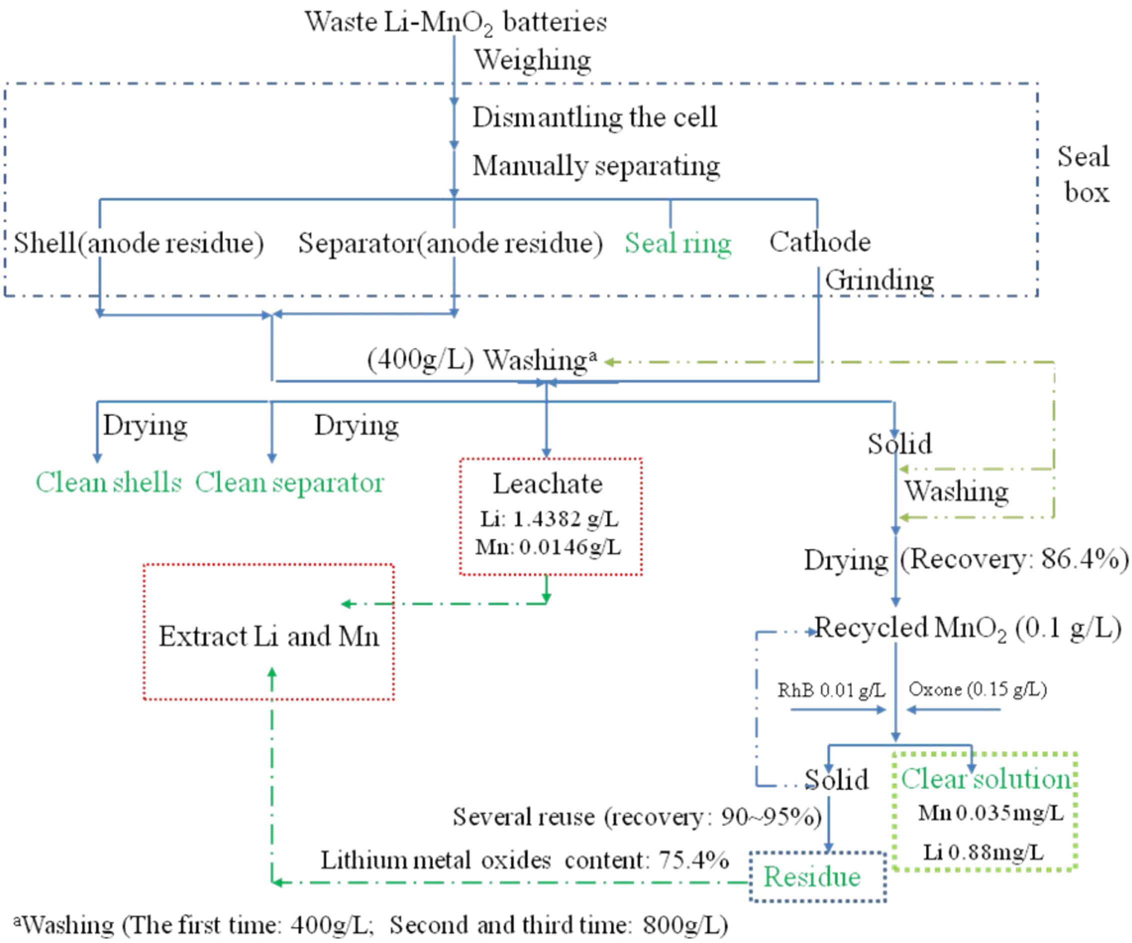

Fig. S8 A proposed green process for the recycling of cathode materials from the waste Li-MnO_2.

Table S2 The metal contents of the leachate from previous washing[a]

Metals	Mn	Li
Concentration (g/L)	0.0146g/L	1.4382g/L

[a]washing (the first time: 400g/L; Second and third time: 800g/L)

Table S3 The metal contents of the cleaning solution from subsequent washing

Metals	Mn	Li
Concentration (mg/L)	0.07mg/L	20.87mg/L

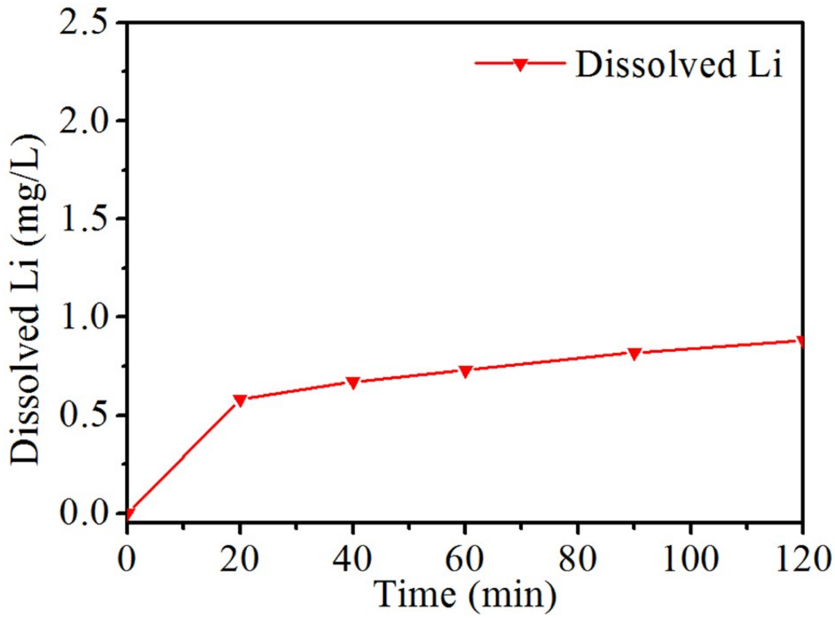

Fig. S9 Dissolution of Mn from the recycled MnO_2 under degradation.. The reaction conditions: [RhB]=10 mg/L, catalyst loading = 0.1 g/L, oxone loading = 0.15 g/L, and T = 25^{o}C.

Table S4 Summary of the recycling for waste batteries.

Batteries types	Major reagents	Recycling method	Material obtained	Application and performance	Ref
LIBs[a]-NCM	NMP NaOH Oxalic acid Na_2CO_3	Metals ion of leaching in oxalic acid and precursor calcined at 900 °C	Regenerated NCM	·Battery ·Initial discharge capacity of 168 mA h g^{-1} at 0.2C, and 91.5% retained after 150 cycles.	[3]
Ni-Cd	H_2SO_4 Na_2CO_3	Dissolution with H_2SO_4. Formation of precipitate $CdCO_3$ and calcination at 500 °C.	CdO nanoparticle	·Photocatalytic ·The removal efficiency of 28 mg/L RB5 dye was 65.42 %, 61.80 % and 67.01 % for pH=4.00, pH=5.97 and pH=8.00 in 480 min, respectively.	[4]
LIBs-NCM	NaOH	Al foil dissolution with NaOH and recycled cathode materials calcined at 600 °C	Ni-Co-Mn oxides	·Air battery ·The energy efficiency was 75% at a current density of 10 mA/cm^2 in an air battery	[5]
LIBs-LFP	DMAC[b]	DMAC dissolve binder and solid phase sintering.	Regenerated $LiFePO_4$	·Battery ·Discharge capacities of 120 mA h g^{-1} at 0.1C, and capacities of 144 mA h g^{-1} with doping ratio of 3 : 7 at 700 °C.	[6]
LIBs-LCO	Citric acid H_2O_2	Sol and a gel reaction and thermal annealing at 450 °C.	$Co_3O_4/LiCoO_2$	·Photocatalytic ·90% of 3 mg/L methylene blue dye removed in 10 h and 100% after 24 h with 60 mg/L catalyst and 60 ml/L H_2O_2.	[7]
Zn–MnO_2	Carbon nanotube	Calcination at 350 °C and ball mill with Mn_3O_4 and CNT	Mn_3O_4/carbon nanotube	·Battery and electrocatalyst ·Reversible specific capacitance of 580 mA h g^{-1} after 100 cycles. Positive onset potential of -0.15 V.	[8]
LIBs-LFP	H_3PO_4 Li_2CO_3 Glucose	Acid-leaching solution refluxed at 85 °C, and carbonization with glucose	$LiFePO_4$/C	·Battery ·Capacity of 159.3 mAh g^{-1} at 0.1C and 86.3 mAh g^{-1} at 20C rate, capacity of 105 mAh g^{-1} after 500 cycles at 5C.	[9]
Zn-MnO_2	H_2SO_4 H_2O_2 Citric acid	Metals dissolved with H_2SO_4 and H_2O_2, and the sticky gel calcined at 400°	$Mn_{0.6}Zn_{0.4}Fe_2O_4$	·Electric Fenton ·89.2% of 0.1 mM BPA removed in 60 min at current density of 3.36 mA/cm^2 with 1 mM PDS , and 77.5% of BPA removed in 60min after third cycle.	[10]
Li-MnO_2	-	Washing	Recycled MnO_2	·Catalyst ·~100% of 10 mg/L RhB removed in 45 min with 0.1 g/L catalyst and 0.15 g/L Oxone. ·97.9 % of RhB removed in 60 min after fifth cycle	This work

[a]LIBs:(NCM: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$; LCO: $LiCoO_2$; LFP: $LiFePO_4$); [b]DMAC: dimethyl acetamide.

Table S5 Various catalysts in heterogeneous PMS activation for organic pollutants degradation

Catalysts	Catalyst synthesis	Pollutant	Amount of leaching metals	Performance	Ref
Monolithic CoCA-A	·Hydrothermal ·Freeze-dried ·Calcination	Phenol	Co:0.014 mg/L in 60 min	·87% of 20 mg/L phenol removed in 60 min with 1.0 g/L catalyst and 2.6 mM Oxone ·67% of phenol removed in 60 min after third run	[11]
Corolla-like δ-MnO_2	·Hydrothermal	Phenol	Mn: 3.0 mg/L in 3 h	·100% of 20 mg/L phenol removed in 30 min with 0.2 g/L catalyst and 2.0 g/L Oxone ·100% of phenol removed in 60 min after third run	[12]
$Co_xMn_{3-x}O_4$	·Hydrothermal ·Calcination	Rhodamine B	Co and Mn: <0.1 mg/L in 80 min	·~ 100% of RhB removed in 80 min with 0.02 g/L catalyst and 0.2 g/L Oxone ·87.0% of RhB removed in 80 min after fifth cycle	[13]
Mn_3O_4/rGO	·Hydrothermal	Orange II	Mn: 0.02 mg/L in 90 min	·100% of Orange II removed in 90 min with 0.05 g/L catalyst and 1.5 g/L Oxone ·~ 100% of Orange II removed in 90 min after fifth cycle	[14]
$CoFe_2O_4$/TNTs	·Hydrothermal ·Impregnation ·Calcination	Rhodamine B	Co: 0.39 mg/L in 60 min	·97% of 100 mg/L RhB removed in 60 min with 0.20 g/L catalyst and 4.0 g/L Oxone. ·~ 94.4% of RhB removed in 60 min after third cycle	[15]
Mn-MGO	·Hydrothermal	Bisphenol A	Mn: ~ 2.1 mg/L in 30 min	·95% of 0.4 mmol/L BPA removed in 30 min with 0.5 g/L catalyst and 5.0 mmol/L PMS. ·86% of BPA removed in 30 min after fifth run	[16]
MnFeO Nanospheres	·Aging ·Calcination	Bisphenol A	Mn: 0.02 mg/L in 30 min	·95% of 10 mg/L BPA removed in 30 min with 0.1 g/L catalyst and 0.2 g/L Oxone ·~ 54% of BPA removed in 30 min after third cycle	[17]
CuO-Co_3O_4@MnO_2	·Aging ·Impregnation ·Calcination	Phenol	Co: 0.06 mg/L Cu: 0.08 mg/L in 100 min	·100% of 300ppm phenol removed in 100 min with 0.1 g/L catalyst and 0.5 g/L Oxone ·84% of phenol removed in 100 min after third cycle	[18]
Recycled MnO_2	·Direct acquisition from waste Li-MnO_2 batteries	Rhodamine B	Mn: 0.035 mg/L Li: 0.88 mg/L in 120 min	·~100% of 10 mg/L RhB removed in 45 min with 0.1 g/L catalyst and 0.15 g/L Oxone. ·97.9% of RhB removed in 60 min after fifth cycle	This work

Simplified assessment of economic and energy consumption

The recycling of waste Li-MnO_2 batteries proposed in this study mainly involves dismantling and simple washing process. We assume that one ton of waste Li-MnO_2 batteries were processed per day in china. The average wage of per labor is $39 per day that base on the working day is 300 days per year (average 25 days per month) in china. Meanwhile, the working time is about 8 hours every day. The industrial electricity charge and water price are $0.20/kWh (maximum) and $0.40/t (maximum) respectively.

Considering the residuals rate and interest rate, depreciation cost of equipment is calculated as Eq. (S1) while the cost of equipment maintenance cost is calculated as Eq. (S2)

$$C_D = C_O \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} \qquad \text{(S1)}$$

C_D—— Depreciation cost of equipment

C_O—— Acquisition cost of equipment

r—— Residuals rate of equipment,4%

i—— Interest rate,10%

n—— Service life, year

$$M_C = C_O \times 0.05 \qquad \text{(S2)}$$

M_C—— Maintenance cost of equipment

C_O —— Acquisition cost of equipment

And the cost of electricity, water and labor are calculated as Eq. (S3), (S4) and (S5):

$$C_P = P \times t \times p_e \qquad \text{(S3)}$$

C_P—— Cost of electricity

P—— Equipment power, kW

t—— Working time of equipment, h

P_e—— Electricity price for industrial uses,$0.20/kWh

$$C_{W} = V \times P_W \qquad \text{(S4)}$$

C_W—— Cost of water

V—— Water consumption, ton/day

P_w—— Water price for industrial uses,$0.4/t

$$C_L = m \times p_s \qquad \text{(S5)}$$

C_L—— Cost of labor

m—— Number of workers

P_S—— Wage of per labor, $39/day

Process I: Crushing and Screening

There is no commercial automatic dismantling equipment of integral separation for button batteries on the market. Therefore, we refer to the commercial crusher to estimate the cost of dismantling process. The crusher (P=11kW, price \$14400, maximum capacity=8 t/h, service life 5 years) work for 1 h every day.

$$C_D = C_O \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} = \left(\$14400 \times \frac{1}{300}\right) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$12.16$$

$$M_C = C_O \times 0.05 = \left(\$14400 \times \frac{1}{300}\right) \times 0.05 = \$2.4$$

$$C_P = P \times t \times p_e = 11kW \times 1h \times \$0.20kW/h = \$2.2$$

$$C_L = m \times p_s = 1 \times \$39 = \$39$$

Compared with mechanical dismantling, the cost of manual dismantling is also calculated. (manual dismantling maximum capacity=1.102kg/h, work time=908h, number of workers=114)

$$C_L = m \times p_s = 114 \times \$39 = \$4446$$

Total cost: \$55.76

After this process, about 382kg cathode materials can be obtained in this study, and about 585kg scrap iron can be also obtained in this study.

Process II: Washing, Filtering and Drying

Stirring cleaning requirement: A mixer (P=5.5 kW, per price=\$3565, maximum capacity =2 t/per, service life = 3 years) is needed to work for 2 h.

$$C_D = (\$14400 \times C_O \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}}$$

$$= \left(\$3565 \times \frac{1}{300}\right) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$3.01$$

$$M_C = C_O \times 0.05 = \left(\$3565 \times \frac{1}{300}\right) \times 0.05 = \$0.6$$

$$C_P = P \times t \times p_e = 5.5kW \times 2h \times \$0.20kW/h = \$2.2$$

$$C_L = m \times p_s = 1 \times \$39 = \$39$$

During the pre-washing process, the consumed water is 5t (the first time: 400g/L; Second and third time: 800g/L).

$$C_W = V \times P_W = 5t \times \$0.4 = \$2$$

The cleaning water of post-treatment of the cathode material can be recycled repeatedly, where their costs are not included in the total cost.

Total cost: \$46.81

Filtering requirement: A self-discharging filtering machine(P=20 kW, per price=\$5800, maximum capacity =4 t/h, service life = 3 years) is needed to work for 1 h.

$$C_D = (\$14400 \times C_O \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}}$$

$$= \left(\$5800 \times \frac{1}{300}\right) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$4.90$$

$$M_C = C_O \times 0.05 = \left(\$5800 \times \frac{1}{300}\right) \times 0.05 = \$1.0$$

$$C_P = P \times t \times p_e = 20kW \times 1h \times \$0.20kW/h = \$4.0$$

$$C_L = m \times p_s = 1 \times \$39 = \$39$$

Total cost: \$48.9

Drying requirement: A conveyor drier (P=40 kW, per price=\$15180, maximum capacity =200kg/per, service life = 5 years) is needed to work for 2h.

$$C_D = (\$14400 \times C_O \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}}$$

$$= \left(\$15180 \times \frac{1}{300}\right) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$12.82$$

$$M_C = C_O \times 0.05 = \left(\$15180 \times \frac{1}{300}\right) \times 0.05 = \$2.53$$

$$C_P = P \times t \times p_e = 40kW \times 2h \times \$0.20kW/h = \$16.0$$

$$C_L = m \times p_s = 1 \times \$39 = \$39$$

Total cost: \$70.35

After this process, about 330.05kg recycled MnO_2 can be obtained in this study.

In summary, the total cost of this recycling process in this study is **\$221.82**.

But, note that the obtained cathode materials as catalysts can be used repeatedly, where the total cost of recycling process of waste batteries should be shared from the number of uses of catalyst. In addition, the recovery of scrap iron can be obtained certain economic benefits.

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