

SUPPORTING INFORMATION

Template-free synthesis of 3D hierarchical nanostructured NiCo₂O₄ mesoporous ultrathin nanosheets hollow microspheres for excellent methanol electrooxidation and supercapacitors

Gaowen Chen, Yizhi Gao and Hui Zhang*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, P.O. Box 98, Beijing 100029, China.

Email: huizhang67@gst21.com;

Fax: +8610-6442 5385;

Tel.: +8610-6442 5872

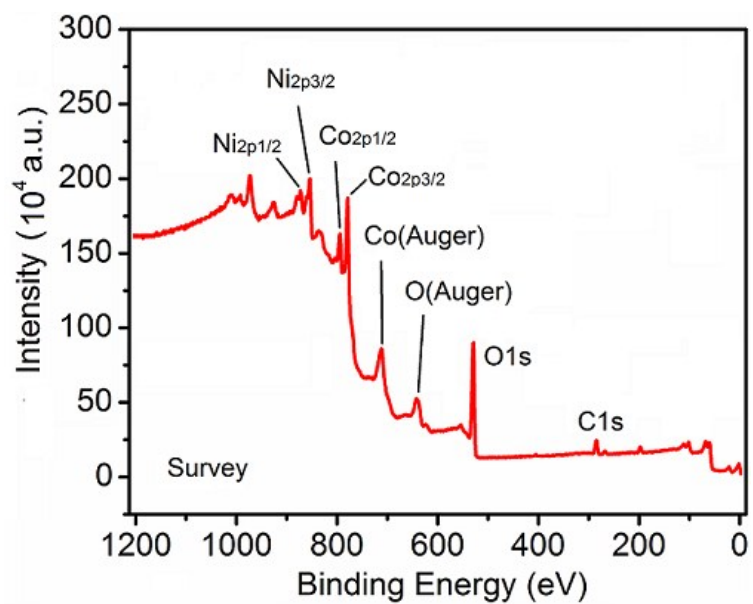


Fig. S1 XPS survey scan of the H-NiCo₂O₄.

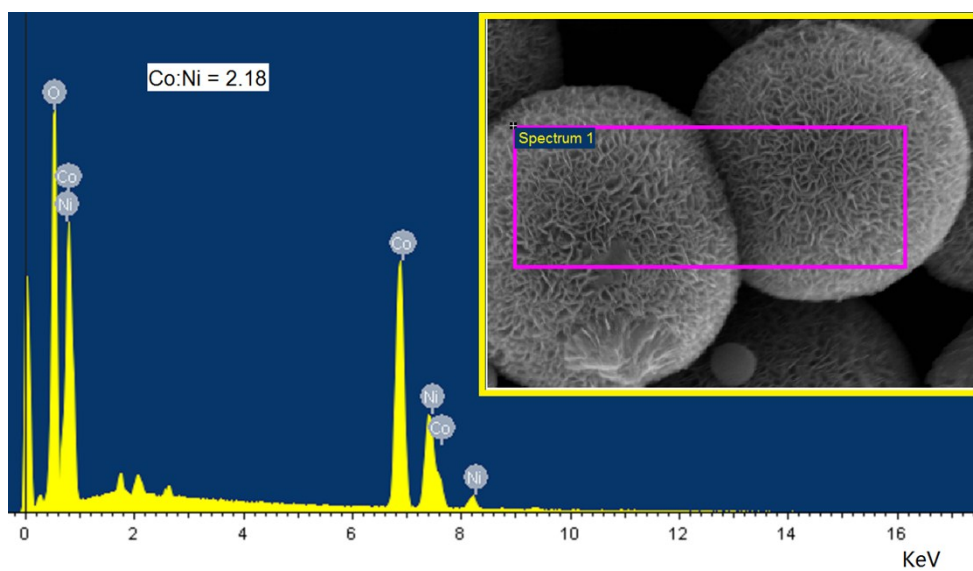


Fig. S2. EDX image of H-NiCo₂O₄.

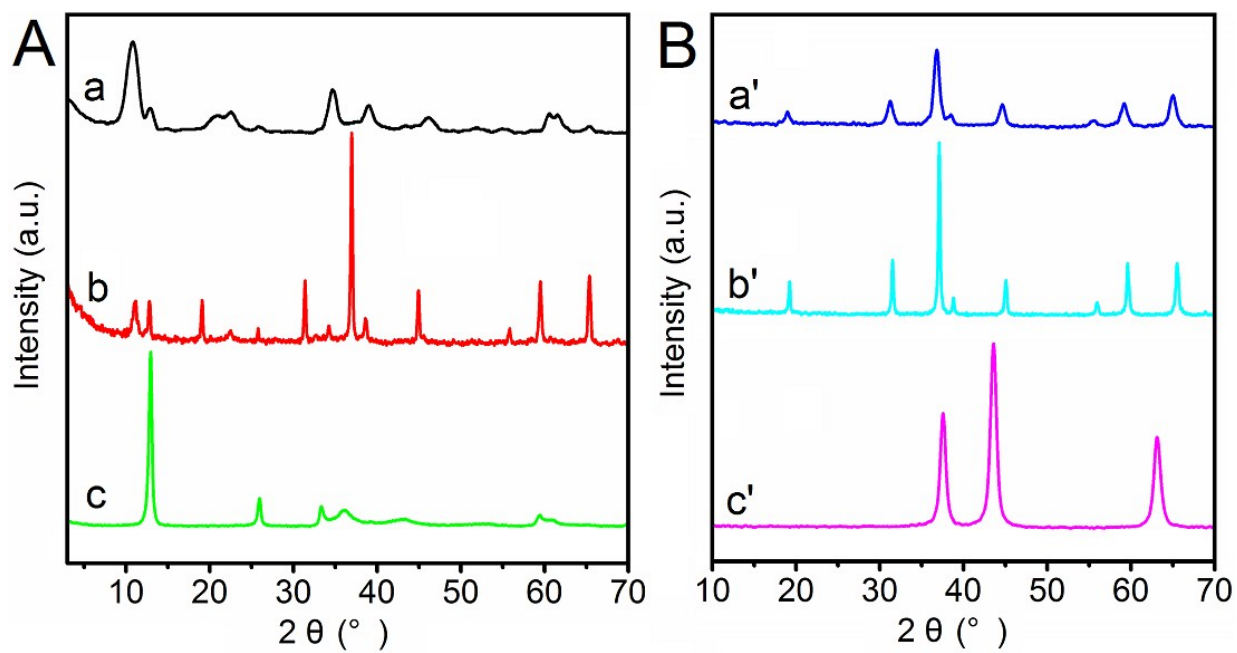


Fig. S3. XRD patterns of the precursors (A: S-NiCo-pre (a), Co-pre (b), Ni-pre (c) and calcined products (B: S-NiCo₂O₄ (a'), Co₃O₄ (b'), and NiO (c')).

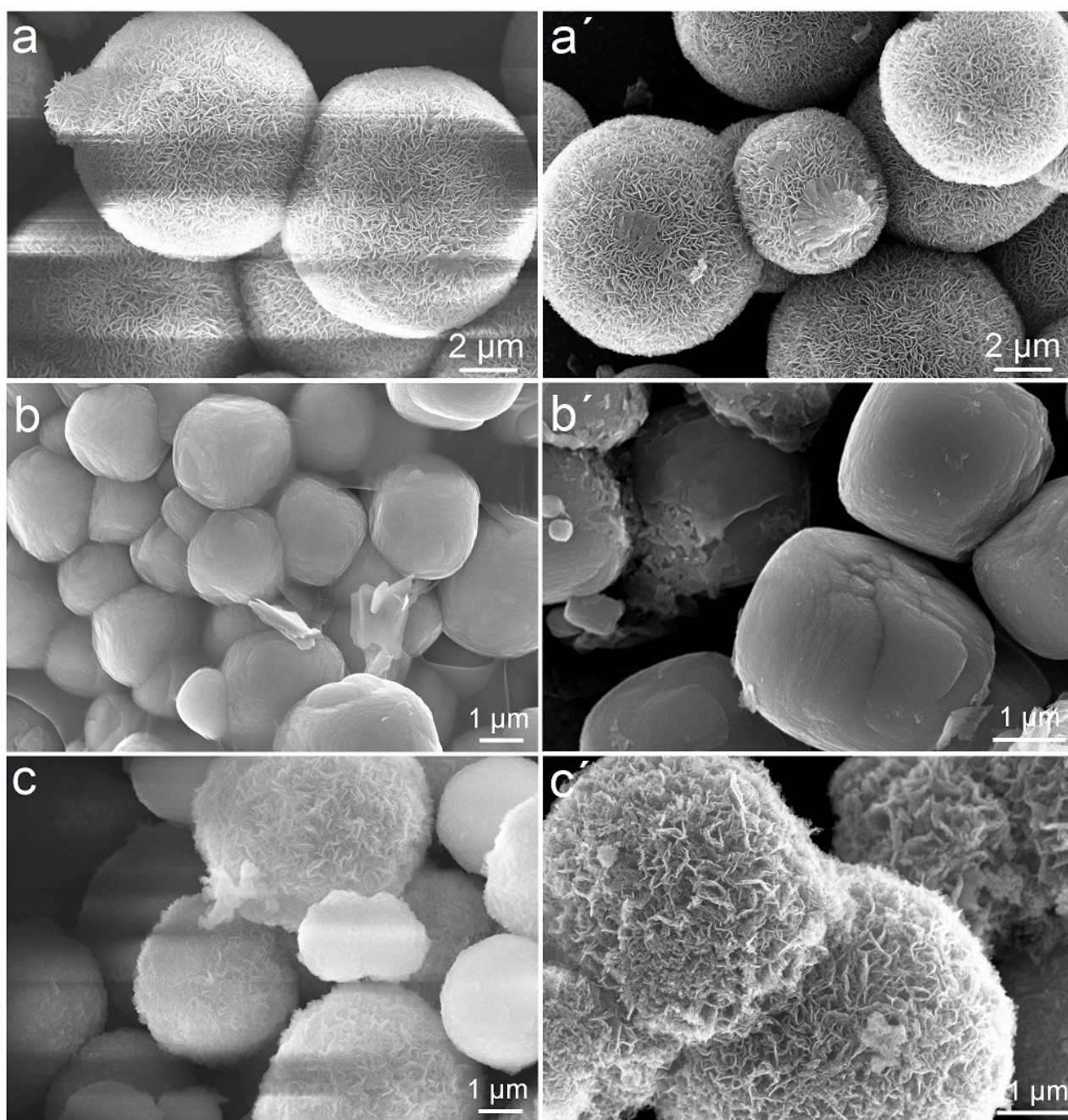


Fig. S4. SEM images of S-NiCo-pre (a), S-NiCo₂O₄ (a'), Co-pre (b), Co₃O₄(b'), Ni-pre (c) and NiO (c').

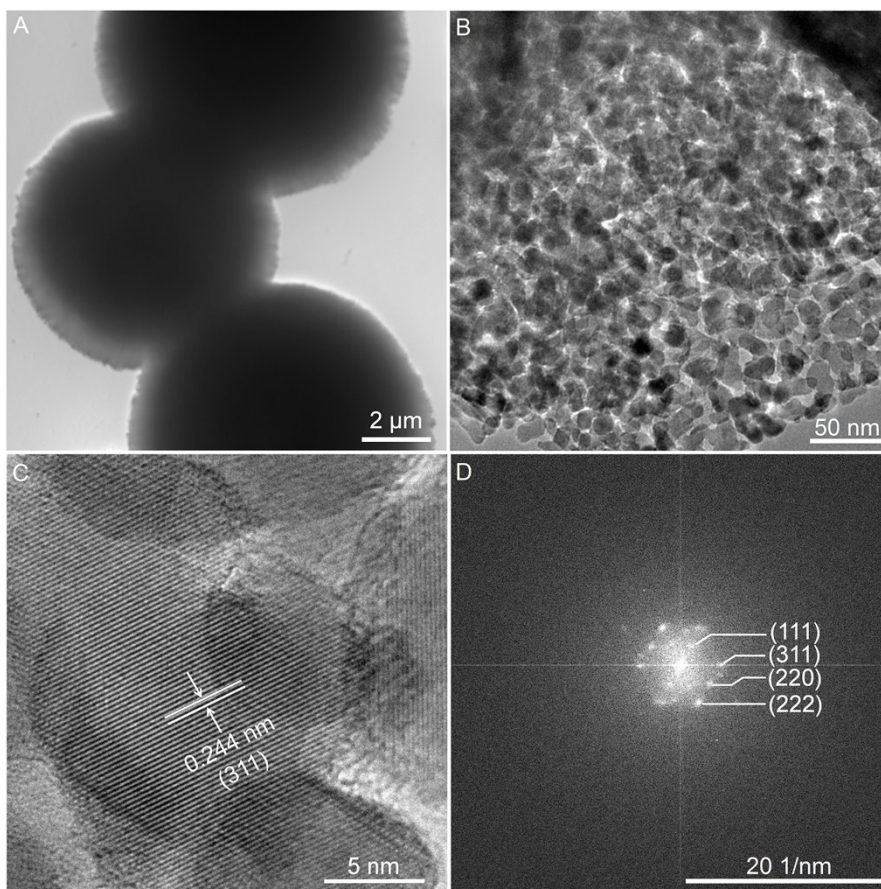


Fig. S5. TEM (A), HRTEM (B, C) and SAED (D) images of S-NiCo₂O₄.

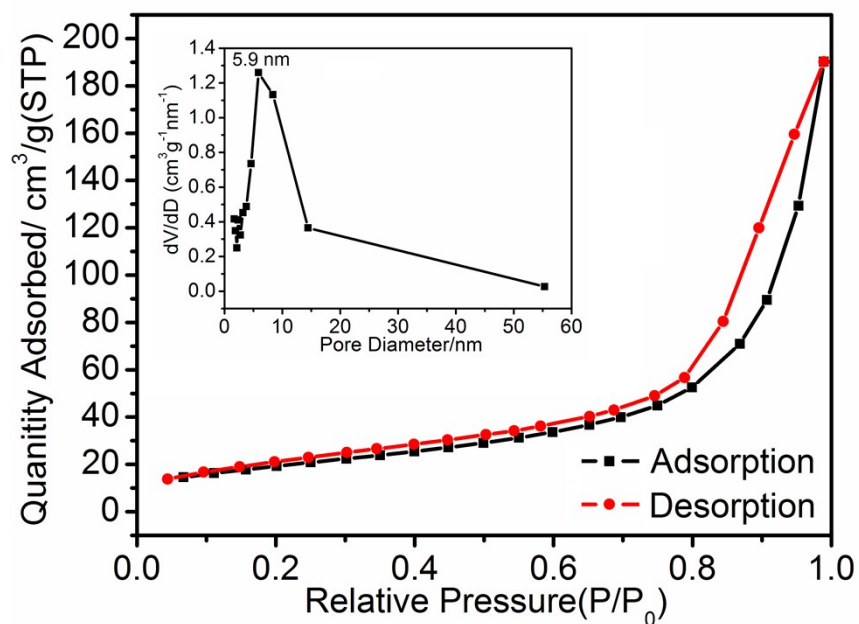


Fig. S6. N₂ adsorption-desorption isotherm of S-NiCo₂O₄ (inset: BJH pore size distribution).

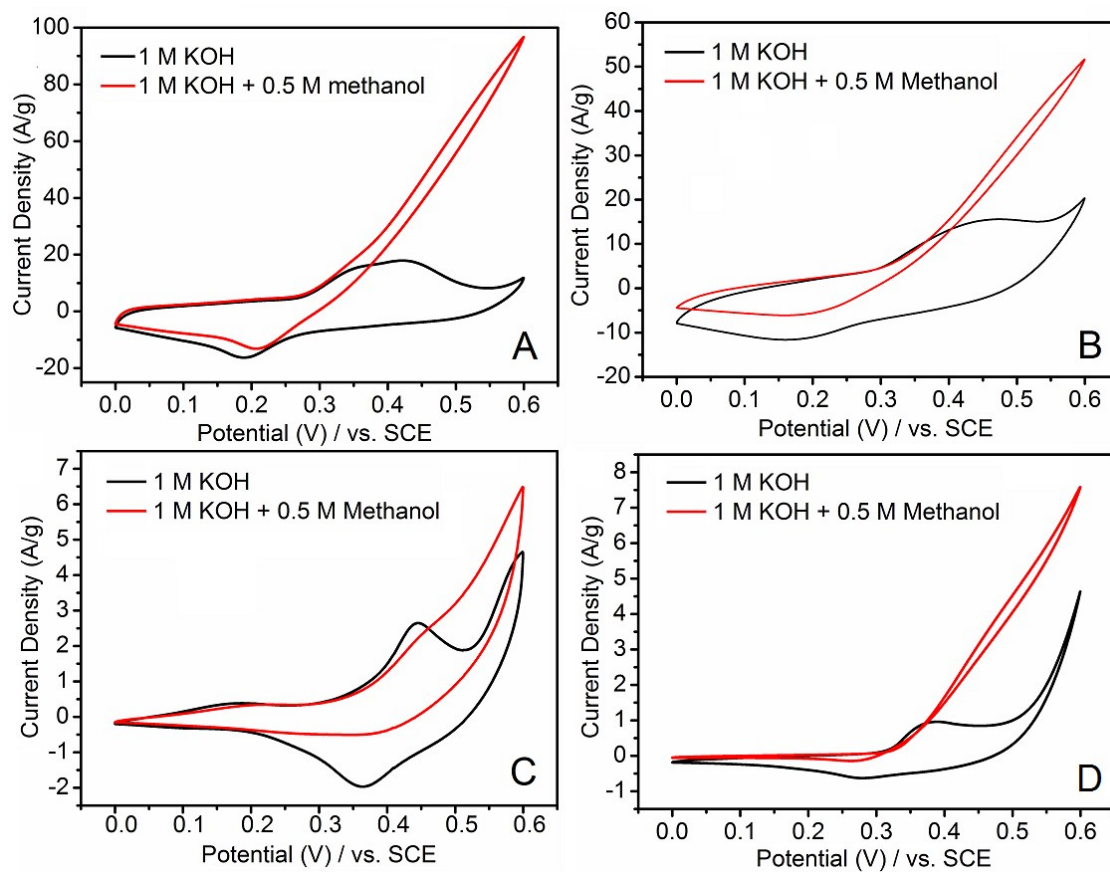


Fig. S7. CV curves of variously modified electrodes in 1 M KOH with and without 0.5 M methanol at a scan rate of 50 mV s^{-1} : (A) H-NiCo₂O₄ (B) S-NiCo₂O₄, (C) Co₃O₄, and (D) NiO.

Table S1. The methanol electro-oxidation performance of different NiCo₂O₄ electrodes using SCE as reference electrode at a scanning rate of 50 mV/s.

Samples	Morphology	Loading/ mg/ cm ²	Working electrode	Current density at 0.6 V / A/g	Onset potential/ V	Cycle time/ Retention/ s/%	Cycles/ Retention / cycle/% ^a	Refs.
H-NiCo ₂ O ₄	3D hollow spheres consisting of porous ultrathin nanosheets	1.41	GCE	96	0.27	1000/80	500/79(90)	This Work
S-NiCo ₂ O ₄	3D solid spheres consisting of porous ultrathin nanosheets	1.41	GCE	52	0.32	1000/70	-	This Work
Hollow NiCo ₂ O ₄	Urchin-like hollow spheres consisting of nanorods	1.41	GCE	24.5	~ 0.30	1000/84	500/85	1
Solid NiCo ₂ O ₄	Urchin-like solid spheres consisting of nanorods	1.41	GCE	12.5	~ 0.33	1000/56	-	1
NiCo ₂ O ₄ ^b	Nanosphere-like NiCo ₂ O ₄ consisting of porous nanosheets	-	Ni Foam	65	0.37	1000/84	500/89(97)	2
NiCo ₂ O ₄ ^{b,c}	Porous nanostructured nanoparticles	~5.0	Stainless Steel mesh (5mg/cm ²)	98 mA/cm ²	0.39	1800/77	-	3
NiCo ₂ O ₄ /SS ^{b,c}	Nanosheets grown on stainless steel (SS)	~1.0	NiCo ₂ O ₄ /SS	54	0.42	1000/94	1000/82(91)	4

^a Data in blanket is obtained by replacing the electrolyte after recycling.

^b Hg/HgO reference electrode is employed.

^c With a scanning rate of 10 mV/s.

Table S2. Equivalent circuit parameters of electro-oxidation of methanol on the oxide electrodes in KOH solution obtained from Fig. 8.

Electrode	Impedimetric parameters (1M KOH)			
	R_s (Ω cm ²)	C (F/cm ²)	R_{ct} (Ω cm ²)	W, Y_0 (Ω s ^{0.5} cm ⁻²)
H-NiCo ₂ O ₄	1.24	1.38E-5	1.26	0.0409
S-NiCo ₂ O ₄	1.35	1.89E-4	1.70	0.0359
Co ₃ O ₄	1.81	2.51E-5	3.72	0.0042
NiO	1.94	3.82E-5	100.1	0.0016

Electrode	Impedimetric parameters (1M KOH with 0.5M methanol)			
	R_s (Ω cm ²)	C (F/cm ²)	R_{ct} (Ω cm ²)	W, Y_0 (Ω s ^{0.5} cm ⁻²)
H-NiCo ₂ O ₄	1.30	1.53E-5	1.47	0.0355
S-NiCo ₂ O ₄	1.51	7.98E-5	2.42	0.0152
Co ₃ O ₄	1.88	2.64E-5	8.79	0.0023
NiO	1.97	3.80E-5	116.2	0.0014

Table S3. Morphology, synthetic method and specific capacitance of different NiCo₂O₄ electrodes.

Sample Morphology	Synthesis method	Loading /mg	Specific capacitance	Rate performance	Capacity retention	Refs.
3D NiCo ₂ O ₄ hollow microspheres consisting of mesoporous ultrathin nanosheets	Template-free solvothermal method	~6	1701F/g,1A/g	1180 F/g, 10 A/g 1046 F/g, 15 A/g 893 F/g, 20 A/g	78.2% (10A/g, 1000cycles)	This work
NiCo ₂ O ₄ core-in- double-shell hollow spheres	Self-templated	–	1141F/g,1A/g	784 F/g, 15 A/g	94.7% (5A/g, 4000cycles)	5
hollow NiCo ₂ O ₄ flower-like microstructures	fast microwave-assisted hydrothermal route	–	387F/g,1A/g	248 F/g, 10 A/g	96.1% (1A/g, 5000cycles)	6
Uniform mesoporous hollow NiCo ₂ O ₄ sub-microspheres	Template(SiO ₂)-engaged synthesis	8 (mg/cm ²)	678F/g,1A/g	540 F/g, 10 A/g	87% (10A/g, 3500cycles)	7
Hierarchical mesoporous spinel NiCo ₂ O ₄	PVP-assisted hydrothermal method	–	1619F/g,2A/g	571 F/g, 10 A/g	94.7% (6A/g, 1000cycles)	8
Novel 3D flower-like NiCo ₂ O ₄ hierarchitectures	Solvothermal synthesis with PVP	–	1191F/g,1A/g	755 F/g, 10 A/g	78.4% (1A/g, 1200cycles)	9
3D hierarchical flower-shaped NiCo ₂ O ₄ microsphere	Rapid template-free microwave-assisted heating reflux method	3	1006F/g,1A/g	726 F/g, 20 A/g	93.2% (8A/g, 1000cycles)	10

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