Facile and efficient two-step formation of renewable monomer 2,5-furandicarboxylic acid from carbohydrates over NiOx catalyst

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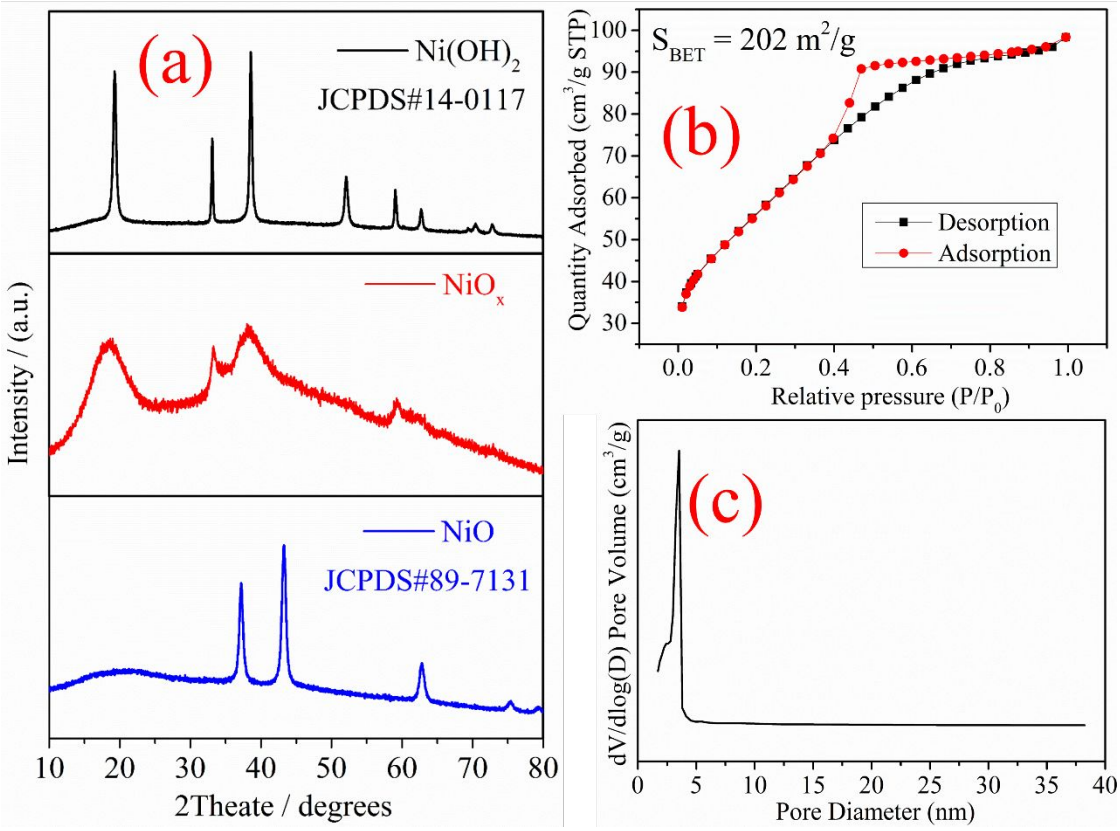

Figure S1. The XRD patterns of the synthesized catalysts (a), N_2 adsorption/desorption isotherm of NiO_x (b), pore size distribution curves of NiO_x (c).

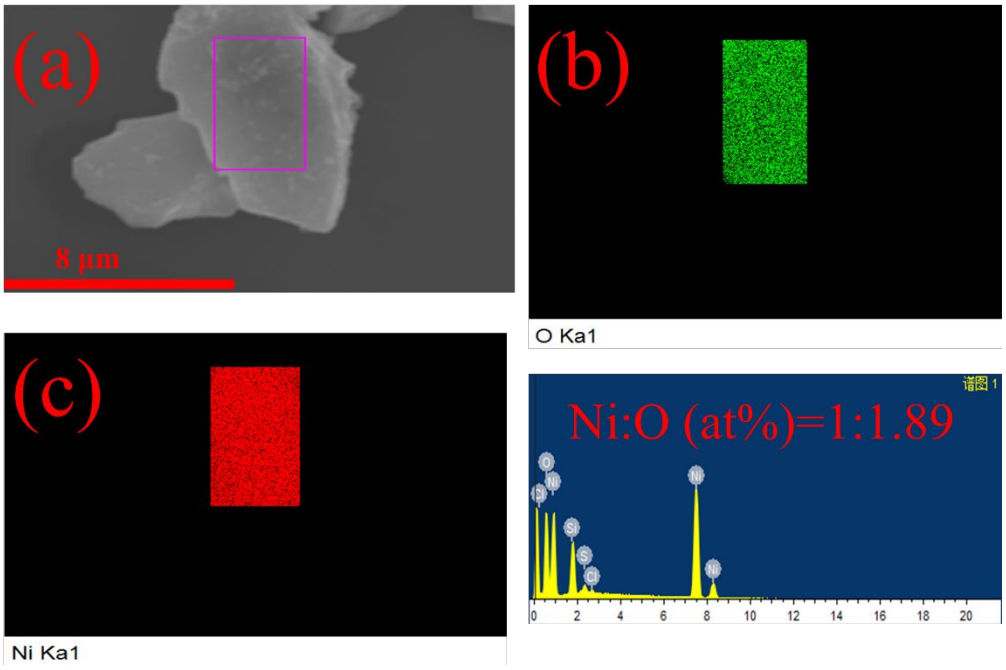

Figure S2. SEM image (a) and EDX elemental maps of the prepared NiO_x (b) O, (c) Ni.

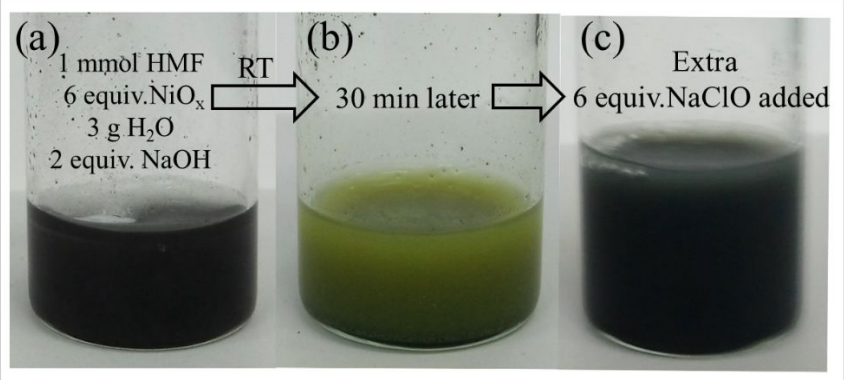

Figure S3. The photos of the sample in Table 1, entry 2 before (a) and after (b) reaction. The photo (c) was taken after 6 equivalents of NaClO were added into (b) mixtures. An FDCA yield of 85% and full HMF conversion were detected after 10 min reaction of the addition of 6 equivalents of NaClO.

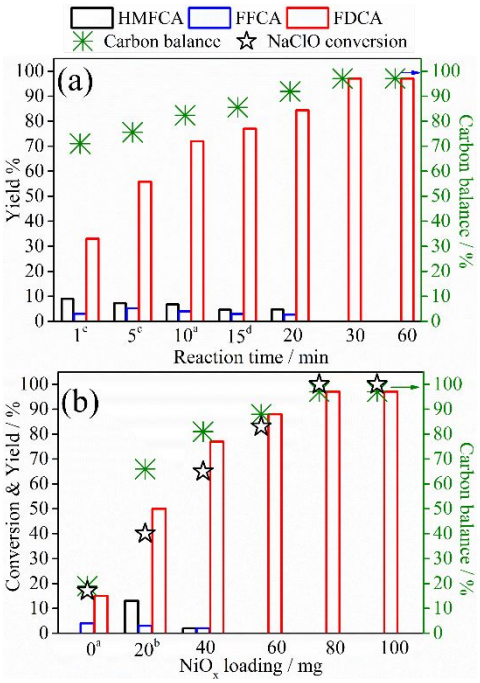

Figure S4. Effect of NiO_x loading (a) and reaction time (b). If not specified, the default reaction conditions are as follows: HMF (1 mmol), NiO_x (80 mg), 7.5wt% NaClO aqueous solution (6 mmol NaClO), 25 ℃, 30 min. The HMF conversion was 100% except in the marked samples. ([a] 96%, [b] 98%, [c] 90%, [d] 99%, [e] 63%).

Table S1. The effect of the type of the oxidant.

Entry	Oxidant	HMF conversion (%)	FFCA yield (%)	FDCA yield (%)
1[a]	1 MPa O_2	65	2	3
2[b]	6 mmol H_2O_2	26	4	2
3[b]	6 mmol TBHP	15	3	0
4	6 mmol NaClO	100	0	97
5[b]	3 mmol $NaClO_2$	13	2	0
6[b]	1.5 mmol $NaClO_4$	23	5	0

Reaction condition: HMF (1 mmol), oxidant, NiO_2 (80 mg), 25 ℃, 30 min. [a] $NaHCO_3$ (2 mmol), H_2O (3 g), 100 ℃, 2 h. [b] $NaHCO_3$ (2 mmol), H_2O (3 g).

Table S2. The effect of the amount of NaClO.

Entry	NaClO (mmol)	NaClO Conversion (%)	HMF conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Carbon balance (%)
1	3	99	84	20	6	43	82
2	4	99	94	15	6	65	92
3	6	98	100	0	0	97	97

Reaction condition: HMF (1 mmol), NiO_x (80 mg), 7.5 wt% NaClO aqueous solution, 25 ℃, 30 min.

Table S3. Comparison of NiO_x catalytic system with the recently published works for the production of FDCA.

Entry	Reaction Temperature (°C)	Reaction Time	Substrate Concentration (wt%)	FDCA yield	E factor [a]	Ref.
1	120	16 h	0.6	97	132	*ChemSusChem* 11.13 (2018): 2083-2090.
2	130	4 h	0.19	99	432	*Green chem.* 20.17 (2018): 3921-3926.
3	85	10 h	0.6	93	138	*Appl. Catal., B, 244 (2019): 965-973.*
4	90	6 h	0.25	70	458	*Green Chem. (2019). DOI: 10.1039/c9gc01283d*
5	**25**	**30 min**	**4.2**	**97**	**20**	***This work***

[a] E factor $= \frac{Total\ waste\ (Kg)}{Product\ (Kg)}$

Figure S5. The photo of NiO_x and NaClO mixtures. The photo was taken when adding NiO_x (80 mg) to 7.5 wt% NaClO aqueous solution (3 g) 1 minute later. The conversion of NaClO was 58% after 30 minutes agitation.

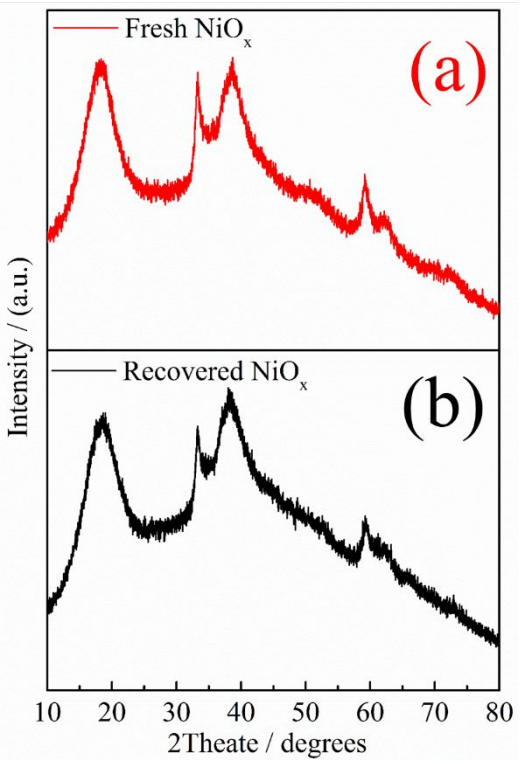

Figure S6. XRD patterns of (a) fresh NiO_x and (b) NiO_x reused after eleven runs for the oxidation of pure HMF.

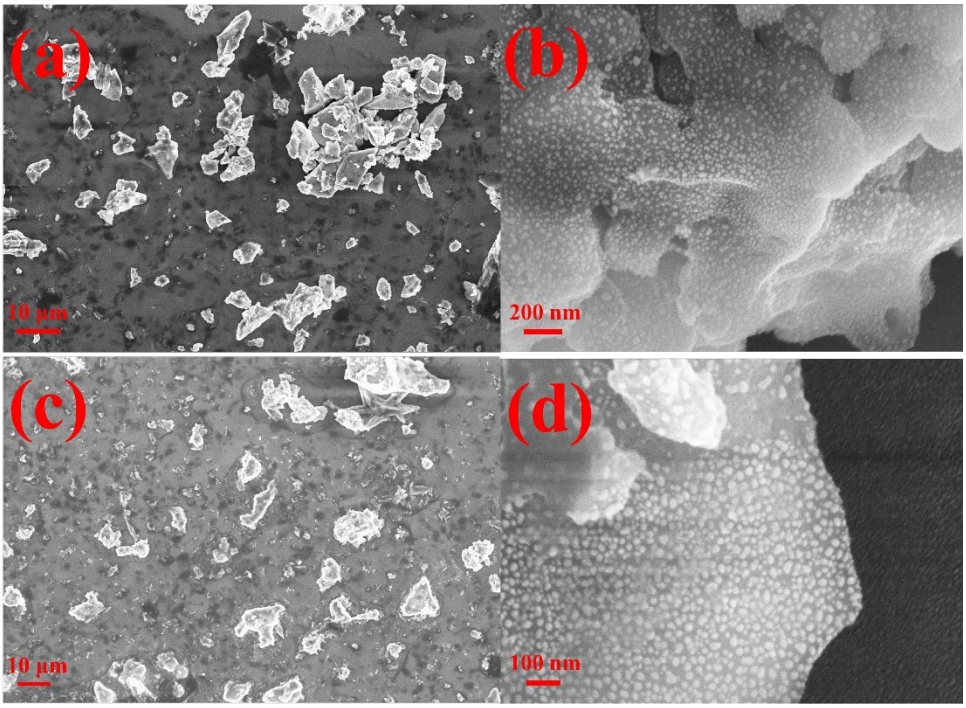

Figure S7. SEM images of (a), (b) fresh NiO_x and (c), (d) NiO_x reused after eleven runs for the oxidation of pure HMF.

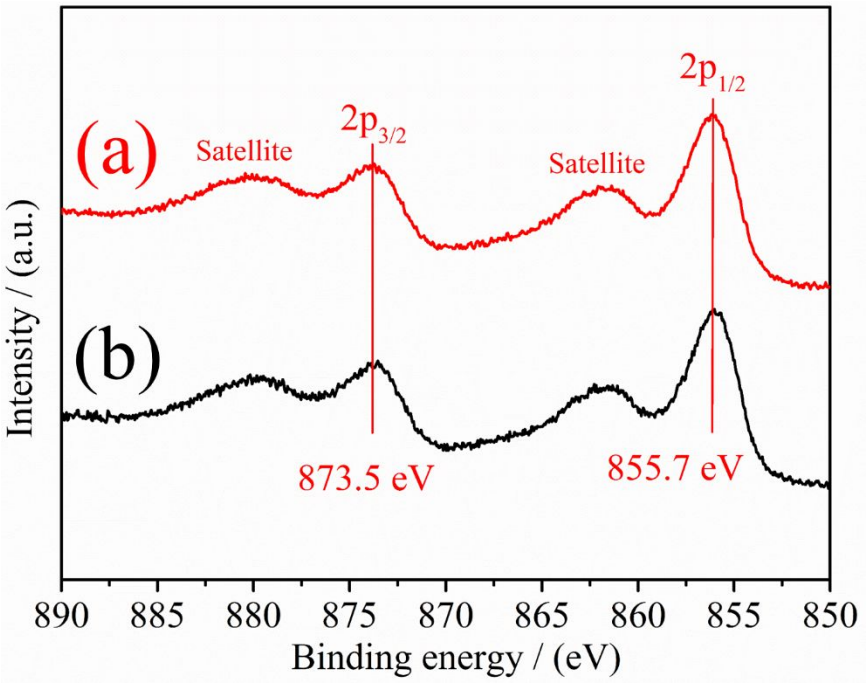

Figure S8. High-resolution XPS spectra Ni 2p of fresh NiO_x (a) and NiO_x reused after eleven runs (b) for the oxidation of pure HMF.

Table S4. Surface area and carbon deposit of fresh NiO_x and reused NiO_x.

Enry	Material	Surface area (m^2/g)	Carbon deposit (wt%) [c]
1	NiO_x-fresh	202	0.00
2	NiO_x- reused after eleven runs [a]	198	0.34
3	NiO_x- reused after three runs [b]	168	3.30
4	Refreshed NiO_x by NaClO	197	0.68

[a] The substrate is pure HMF. [b] The substrate is glucose derived crude HMF. [c] Determined by an Elementar Vario EL III (Germany).

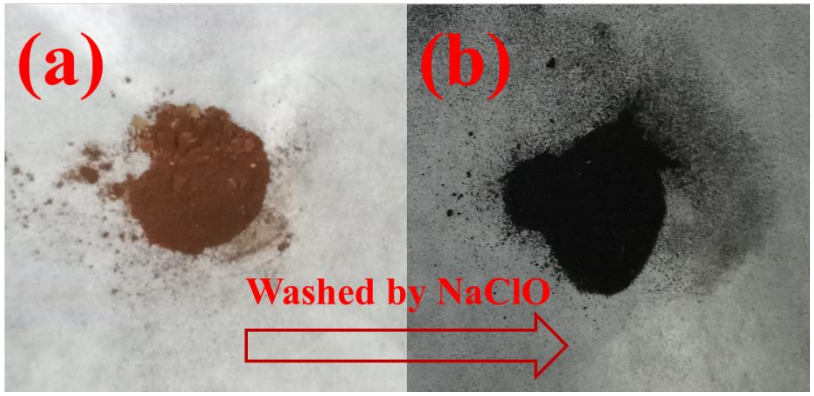

Figure S9. The NiO_x recovered from the reusability test of the oxidation of glucose-derived crude HMF in third runs (a), the regenerated NiO_x by washing with 10 mL 7.5 wt% NaClO aqueous solution for 30 minutes (b).

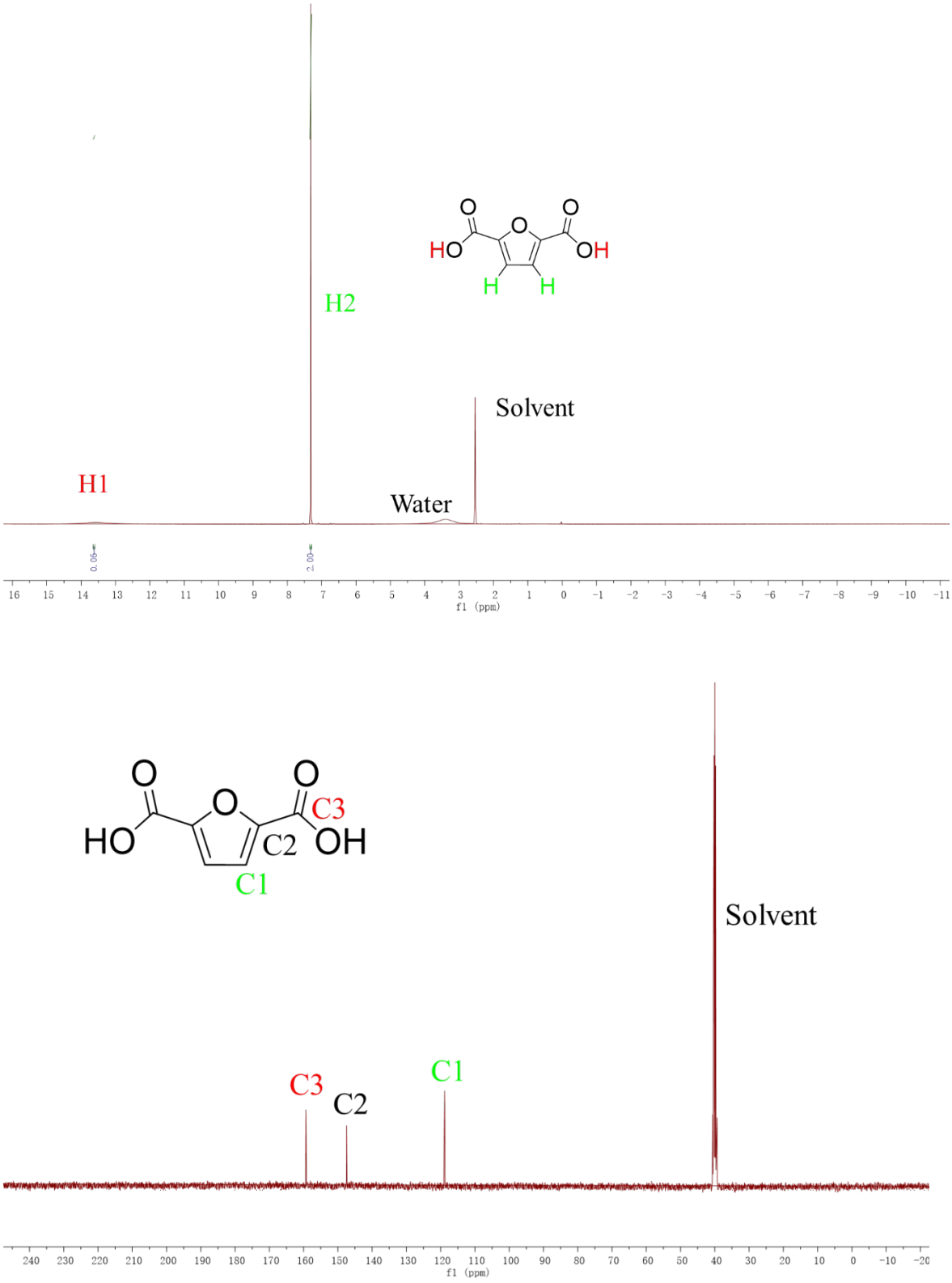

Figure S10. The ^{1}HNMR and ^{13}CNMR spectrum of the obtained FDCA.