Hierarchical Polymorph $MnCO_3$ Series: Induced by Cobalt Doping via One-pot Hydrothermal Route for CO Catalytic Oxidation

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Table 1. The surface areas and the compositional data of the as prepared P_1-P_6 samples.

Samples	Content (/ M%) Co/ Co+Mn	S_{BET}[a] (m^2g^{-1})	Atom ratio[b] (%) (Co/(Mn+Co))
P1	0	34.305	0
P2	1.5	25.486	1.1
P3	5	34.016	3.8
P4	10	79.029	8.8
P5	15	97.677	14.2
P6	20	131.747	19.4
Commercial $MnCO_3$		5.1	

[a] The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method.

[b] The atom ratio (Co/Mn) data measured by EDS Analysis followed by the calculation Co/ (Co+Mn)

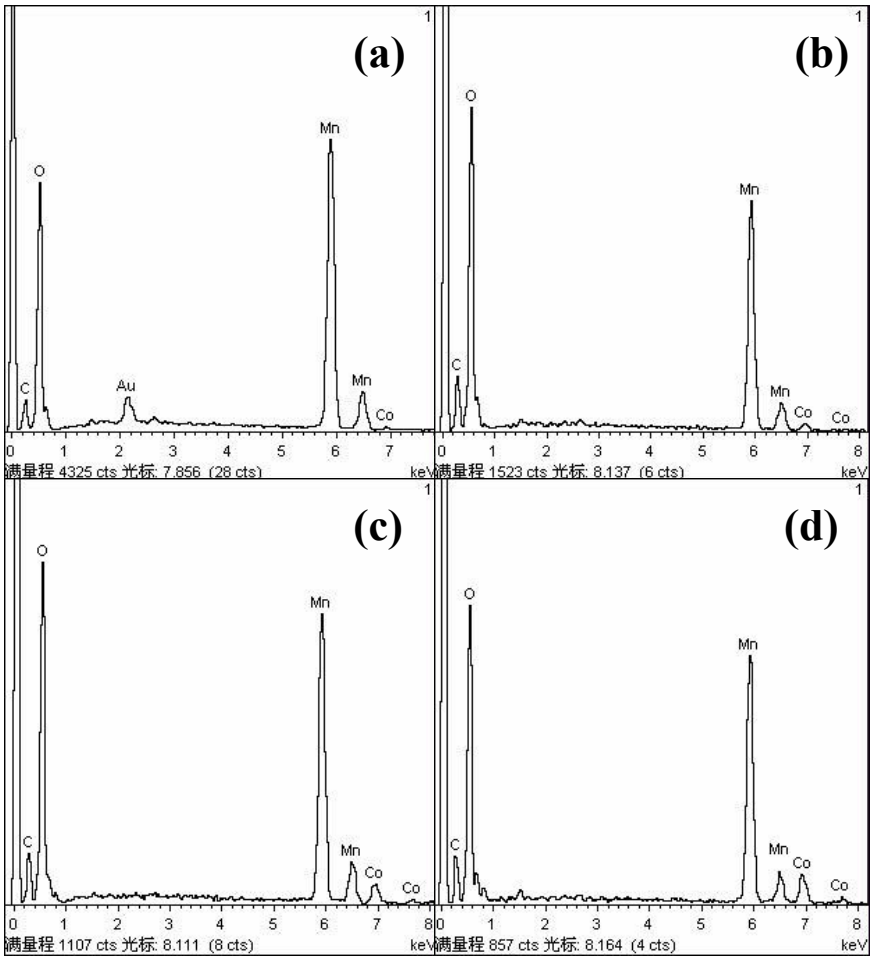

Figure S1. EDS spectra of Co-doped samples a-d: P_2- P_5. (The peaks of Au seen in (a) are come from gold plating on the sample for before SEM examination)

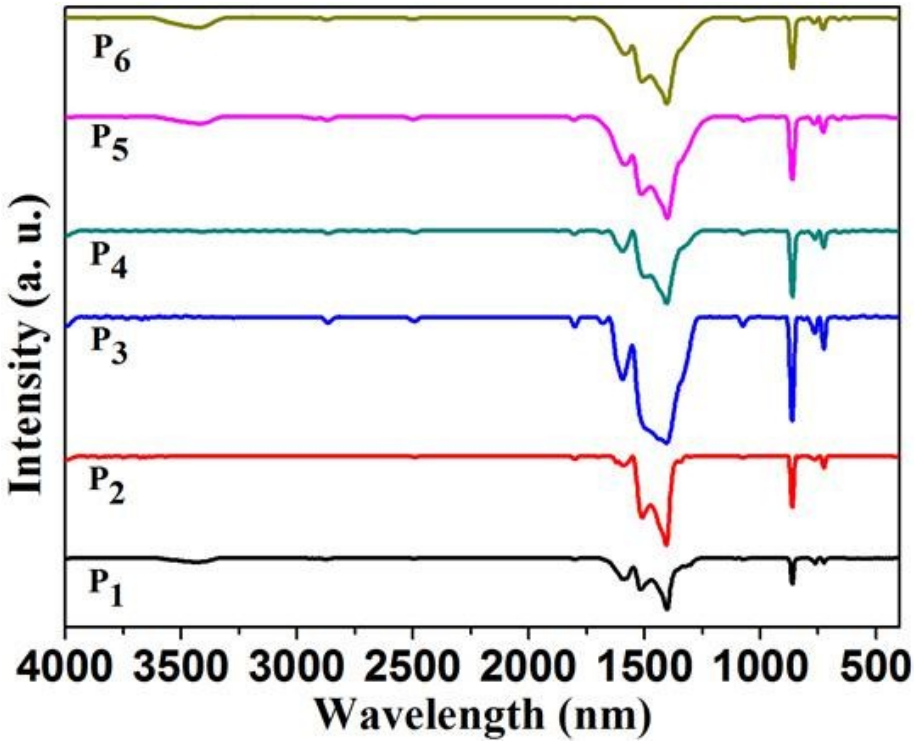

Figure S2. FTIR spectra of as-prepared undoped and doped $MnCO_3$ samples

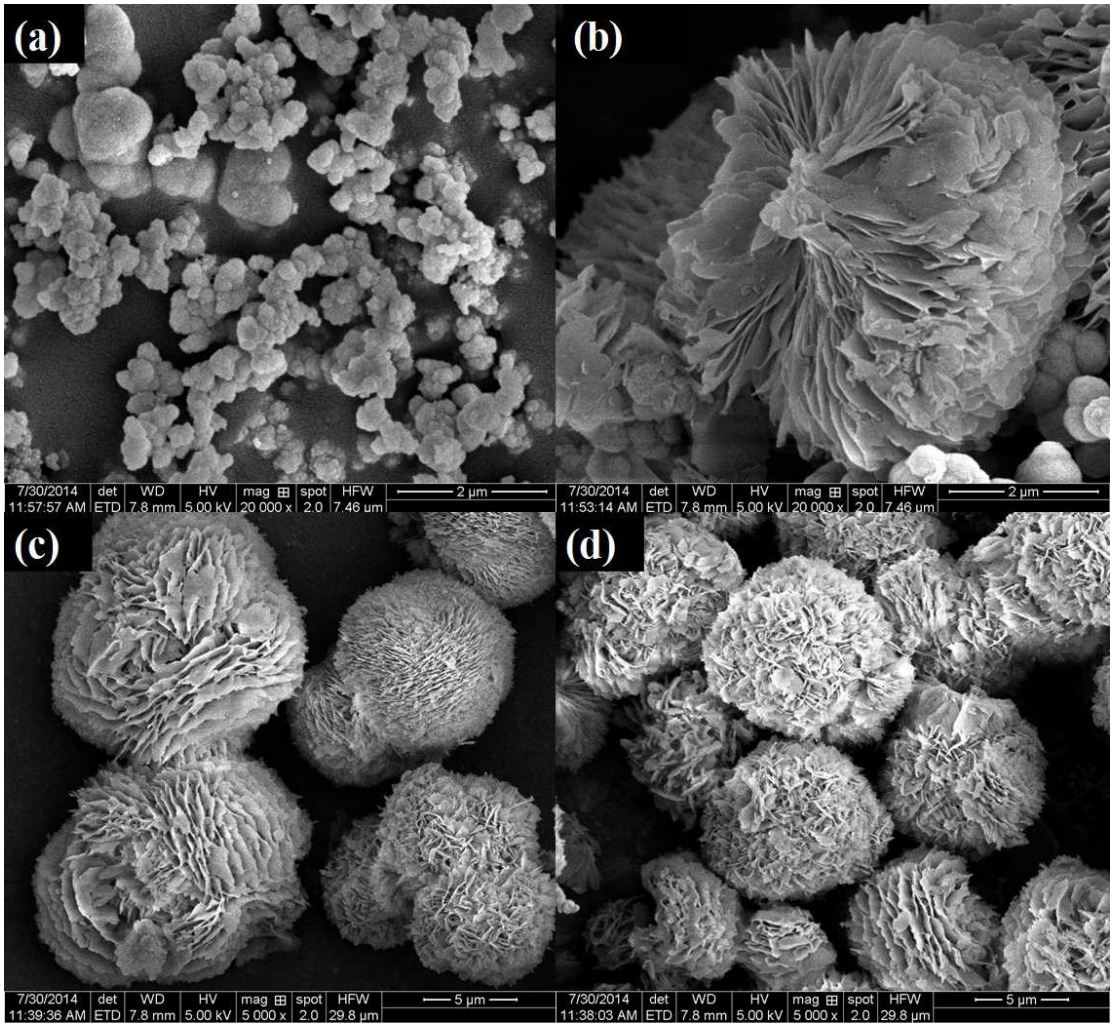

Figure S3. SEM of Co-doped P_5 sample obtained at 210 ^{o}C for different solvothermal time: (a) 70 min, (b) 4 h, (c) 8 h and (d) 12 h.

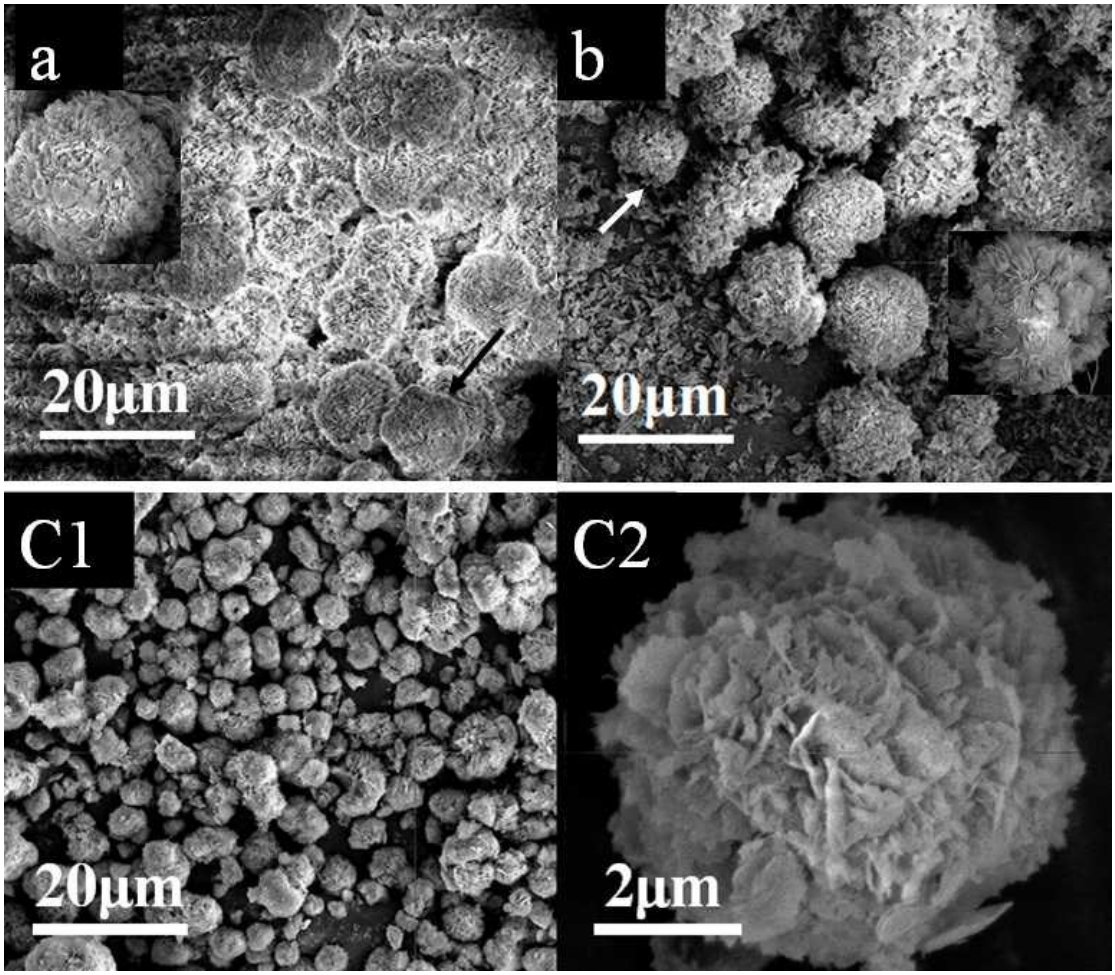

Figure S4. SEM of Co-doped samples with different cobalt content by prolonged reaction time to 36 h: 5% Co^{2+} (a), 10% Co^{2+} (b) the magnified samples (arrow indicated) are inserted in a and b; and of P_5 samples after catalysis for 6 times (C1, C2).

It is observed (Fig. S4a and b) that large-sized flake-spheres appear after the reaction for 36 h, in the presence of cobalt ions (5% and 10% content), indicating the prolonged time is an equal promoter as increased Co^{2+} doping for the occurrence of perfect spheres. Fig. S4C1 and C2 show that the morphology remained well even after sixth catalytic usages, indicating our products own wonderful stability.

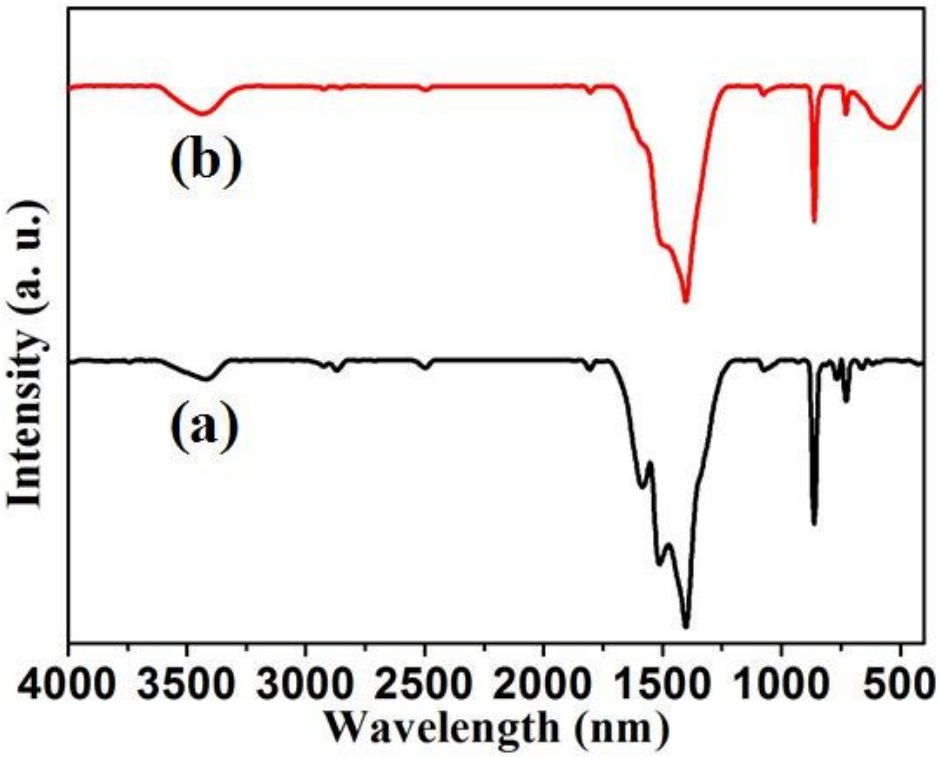

Figure S5. FTIR spectra of P_5 sample (a) before and (b) after catalysis for 6 times.