Supplementary Information for

Morphology-directed synthesis of Co_3O_4 nanotubes based on modified Kirkendall effect and its application in CH_4 combusion

Zhaoyang Fei [1], Shengchao He [1], Lei Li [1], Weijie Ji [1,*], and Chak-Tong Au [2,*]

[1] *Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China, E-mail: jiwj@nju.edu.cn; Fax: +86-25-83317761*

[2] *Department of Chemistry, Hong Kong Baptist University, Hong Kong, China, E-mail: pctau@hkbu.edu.hk, Fax: +852-3411-7348*

Experimental Details

Sample preparation

In an optimized procedure, $CoCl_2 \cdot 6H_2O$ of 2 mmol was dissolved in 100 ml deionized water, followed by the addition of 100 ml oxalic acid solution (0.1 M) under stirring. A pink precipitate was generated after 3 h. The product was dispersed into 50 ml ethanol, and an ethanol solution of NaOH (0.1 M, 50 ml) was added dropwise into the suspension under stirring. After 3 h, the product was collected using a centrifuge and washed with deionized water and ethanol. The Co_3O_4 NTs were generated through calcination of the as-obtained product in air at 350°C or 550°C for 3 h, and are denoted hereinafter as Co_3O_4 NTs (350°C) and Co_3O_4 NTs (550°C), respectively. In the case that the pink precipitate generated in the reaction of $CoCl_2$ with oxalic acid was calcined in air at 350°C, the product was Co_3O_4 nanorods (NRs). The Co_3O_4 NPs were prepared by a low-temperature urea combustion process. First, a 50 ml $Co(NO_3)_2$ (0.096 mol) solution was stirred at 50°C for 1 h. After the addition of urea (0.192 mol), the solution was heated at 80°C (12 h) for slow evaporation of water. The resulting powder was ground in a grinder and calcined in air at 400°C for 6 h.

Characterization

N_2 adsorption-desorption measurement was performed on an ASAP-2020 instrument at 77 K. XRD analysis was conducted on a Philips X'Pert MPD Pro

X-ray diffractometer, with Cu-Ka radiation (λ = 0.1541 nm) in the 2θ range of 10–80°. Scanning electron microscopy (SEM) images were collected on a S-4800 scanning microscope whereas TEM images were taken on a JEOL JEM-1010/2010 transmission electron microscope operated at 200 kV. Thermogravimetric analysis (TGA) of the β-$Co(OH)_2$ and $CoC_2O_4 \cdot 2H_2O$ precursors was carried out on a TG-DTA/DSC apparatus (STA449C, Germany) with the sample kept in flowing Ar and heated from 50 to 600°C (heating rate: 10°C/min). H_2-TPR measurement was performed in a U-shape quartz reactor with the sample (50 mg) kept under a H_2-Ar mixture (v/v=5/95). Before switching the gas feed to H_2-Ar stream, the sample was pretreated in Ar stream at 120°C for 1 h, and then cooled to room temperature. The TPR profile was recorded with temperature programming from 50 to 500°C at a rate of 10°C/min. H_2 consumption was monitored by a thermo-conductive detector. O_2-TPD was carried out in the U-shape quartz reactor. Catalyst of 400 mg was pretreated in Ar steam at 300°C for 1h, then oxygen adsorption was conducted in pure O_2 at 200°C for 1 h. After cooling to room temperature, the system was purged with Ar (60 ml/min) for 1 h. After that, the temperature was raised to 700°C at a rate of 10°C/min in Ar flow (60 ml/min), and the effluent gases from the reactor were analyzed with a thermo-conductive detector.

Catalytic reaction

Catalytic activity of different materials was evaluated in a continuous-flow

quartz reactor (200 mg catalyst) at atmospheric pressure. The feed is 2% CH_4 and balanced air. The reaction was operated in the 150-400°C range at a GHSV of 6000 ml/g_{cat}·h. Before reaction, the catalyst was pretreated in air (40 ml/min) at 200°C for 1 h. The outlet products were analysed by on-line gas chromatography (GC-122). In each case, complete oxidation of CH_4 could be confirmed since CO_2 was the only carbon-containing product detected, and the calculated carbon balance further confirmed that.

Table S1 Physicochemical properties of various Co_3O_4 nanostructures

Catalyst	S_{BET} (m^2/g)		H_2-TPR peak temp. (℃)		O_2-TPD peak temp. (℃)	R_A [b]
	Fresh	*After Reaction* [a]	*First peak*	*Second peak*	*Low-/high-temp.*	($mmol_{CH4}$ m^{-2} h^{-1})
Co_3O_4 NTs (350 ℃)	44.7	43.5	251	383	189/393	0.22
Co_3O_4 NTs (550 ℃)	40.5	39.8	282	388	195/393	0.23
Co_3O_4 NRs (350 ℃)	36.9	35.7	324	476	203/415	0.16
Co_3O_4 NPs	47.6	45.5	371	545	264/450	0.04

[a] After 30 h time on stream

[b] Specific activity per surface area at 300 °C.

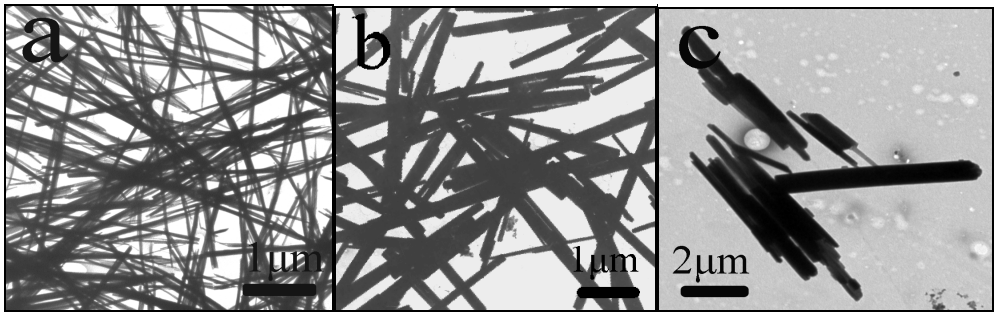

Fig. S1 TEM images of CoC_2O_4 NRs generated at different concentration of oxalic acid solution: (a) 0.01M, (b) 0.1 M, and (c) 0.5 M.

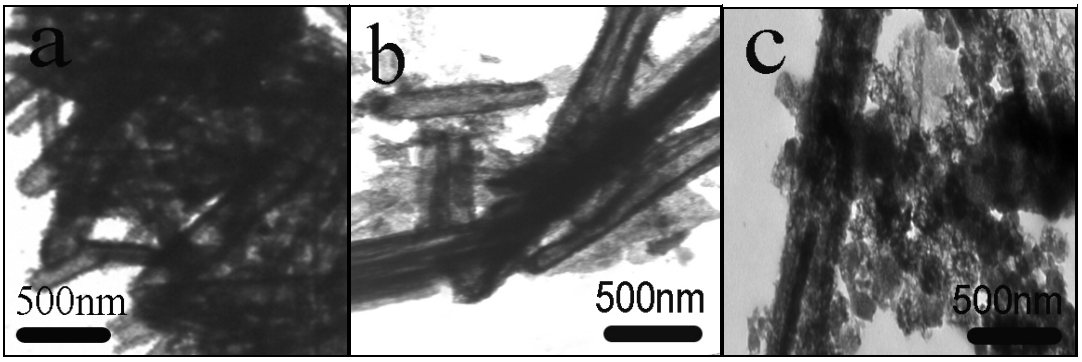

Fig. S2 TEM images of $Co(OH)_2$ NTs obtained at different concentration of NaOH solution: (a) 0.1 M, (b) 0.25 M, and (c) 0.5 M.

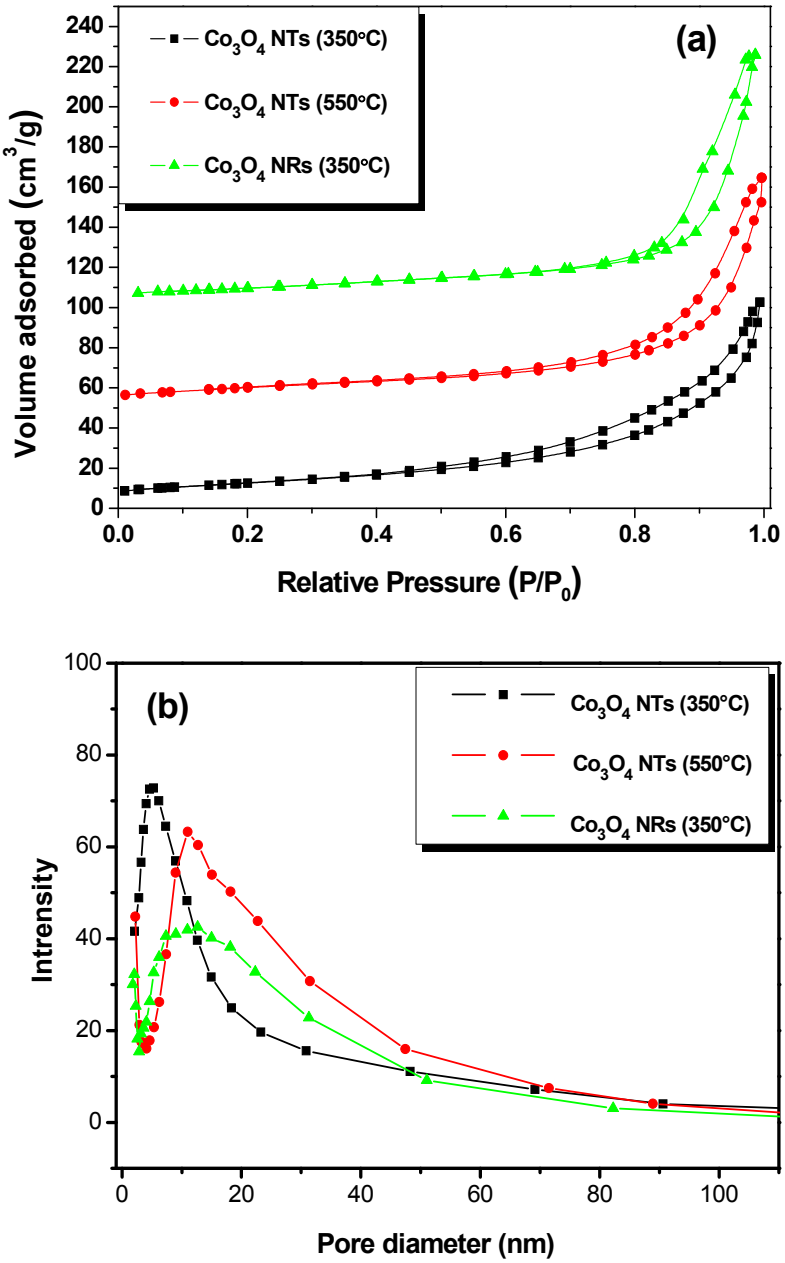

Fig. S3 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of Co_3O_4 nanostructures.

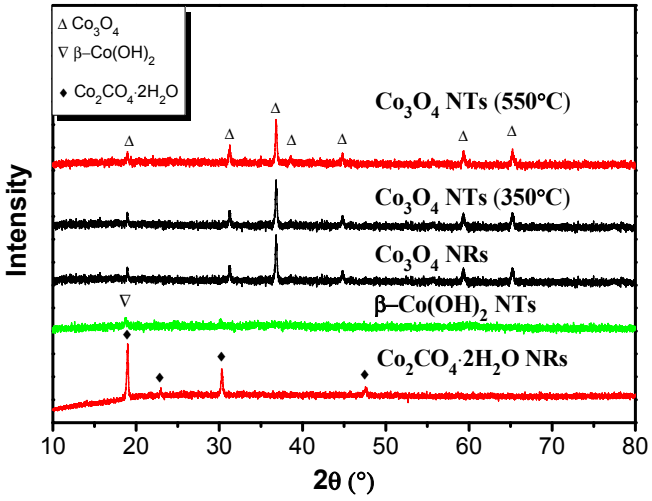

Fig. S4 XRD patterns of as-prepared Co_3O_4 NTs, NRs and related precursors.

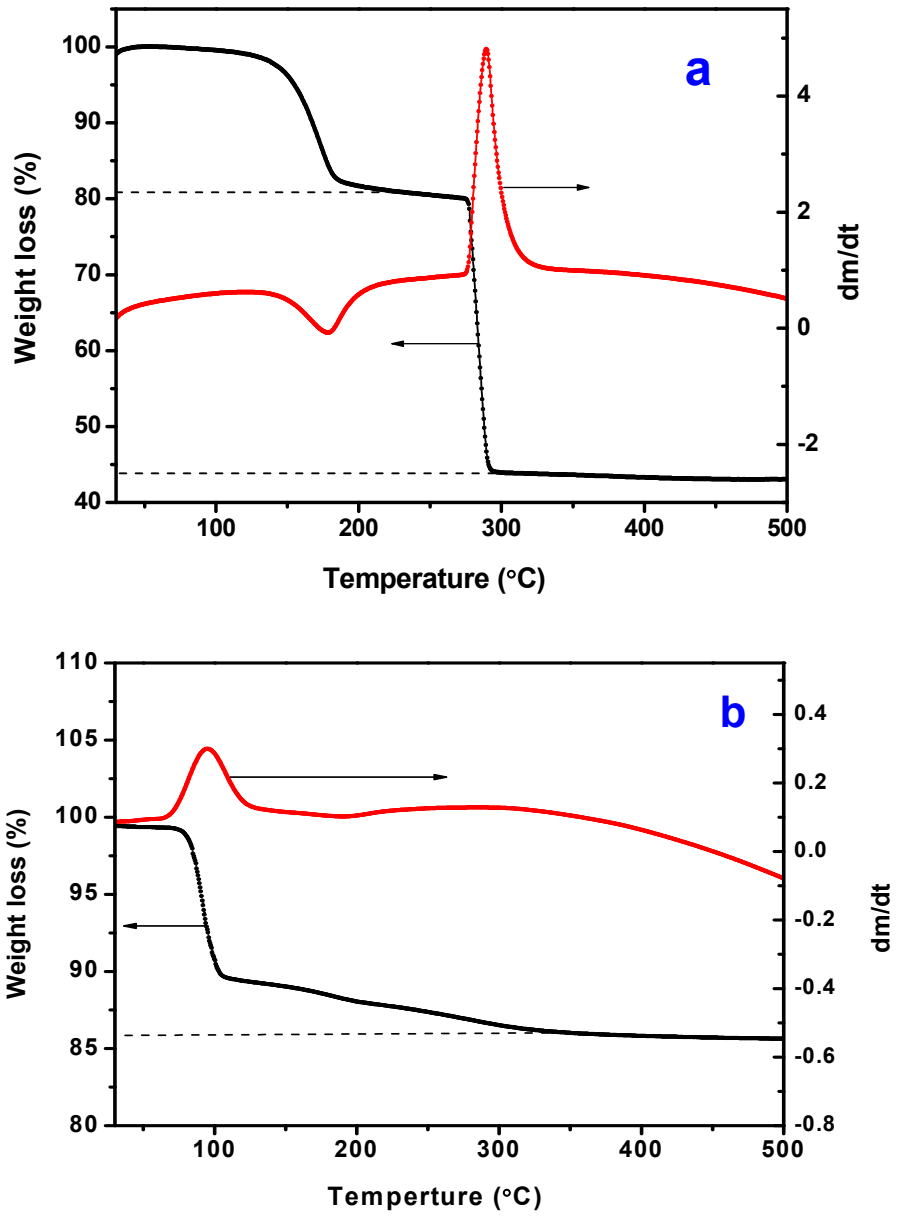

Fig. S5 TGA profiles of (a) $CoC_2O_4 \cdot 2H_2O$ NRs and (b) β-$Co(OH)_2$.

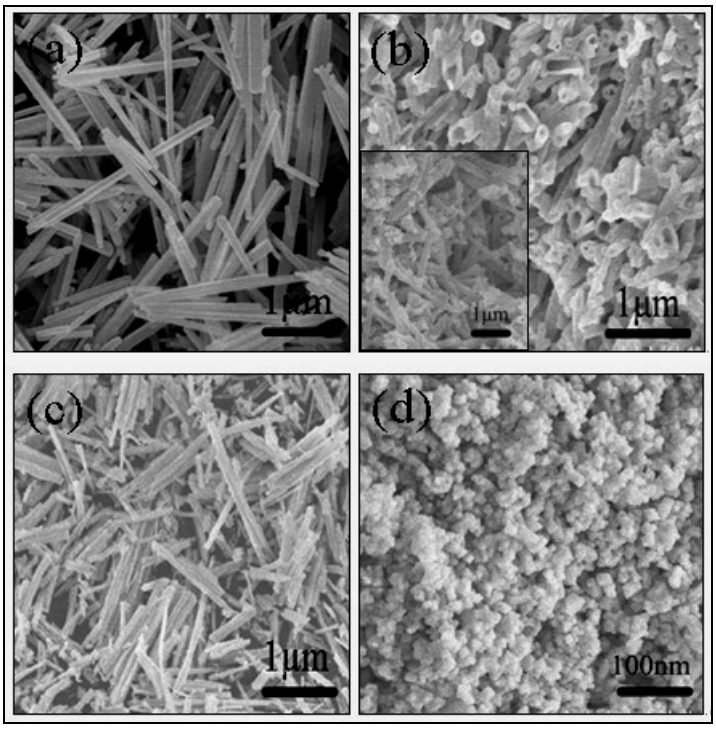

Fig. S6 SEM images of (a) $CoC_2O_4 \cdot 2H_2O$ NRs, (b) Co_3O_4 NTs(350°C) [the inset is Co_3O_4 NTs(550°C)], (c) Co_3O_4 NRs, and (d) Co_3O_4 NPs.

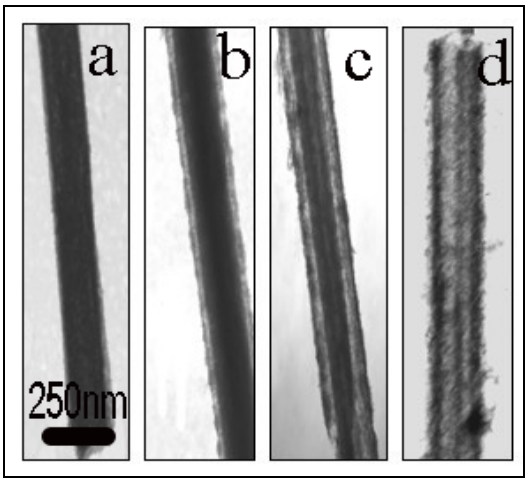

Fig. S7 TEM images of the evolution of $Co(OH)_2$ NTs at different reaction time: (a) 10 min, (b) 30 min, (c) 90 min, and (d) 150 min.

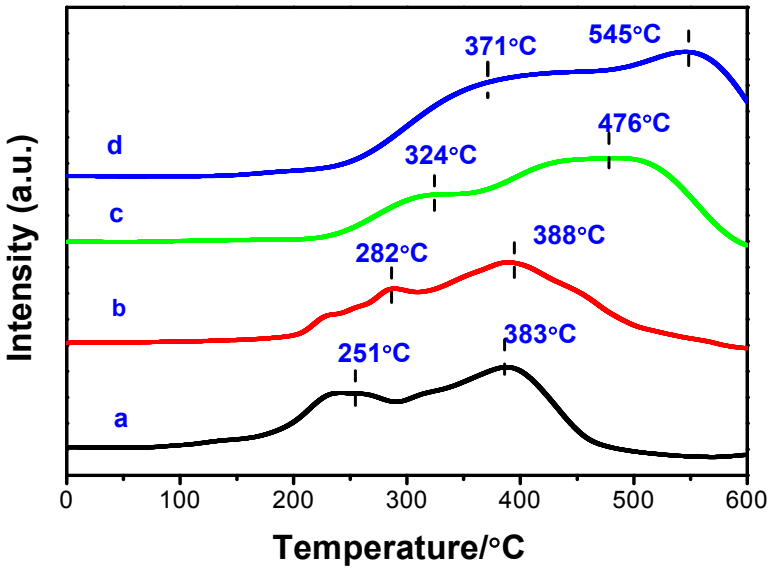

Fig. S8 H_2-TPR profiles of (a) Co_3O_4 NTs(350°C), (b) Co_3O_4 NTs(550°C), (c) Co_3O_4 NRs, and (d) Co_3O_4 NPs.

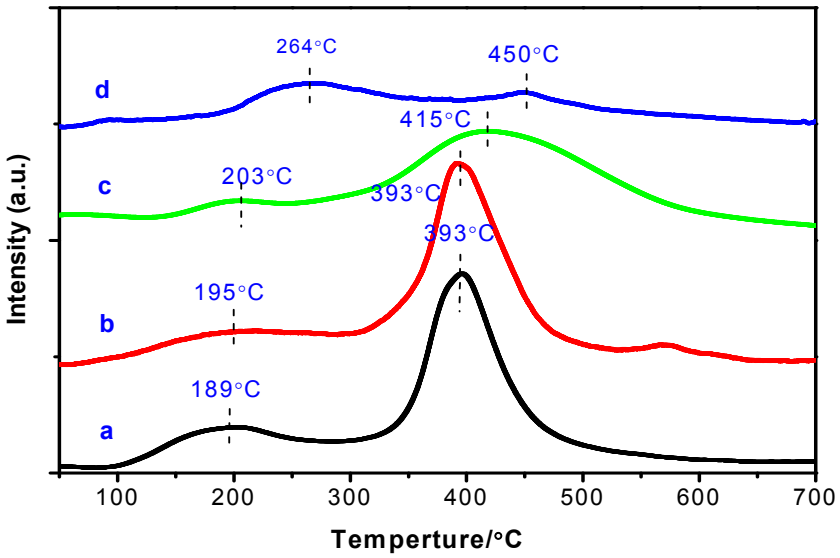

Fig. S9 O_2-TPD profiles over (a) Co_3O_4 NTs(350°C), (b) Co_3O_4 NTs(550°C), (c) Co_3O_4 NRs, and (d) Co_3O_4 NPs.

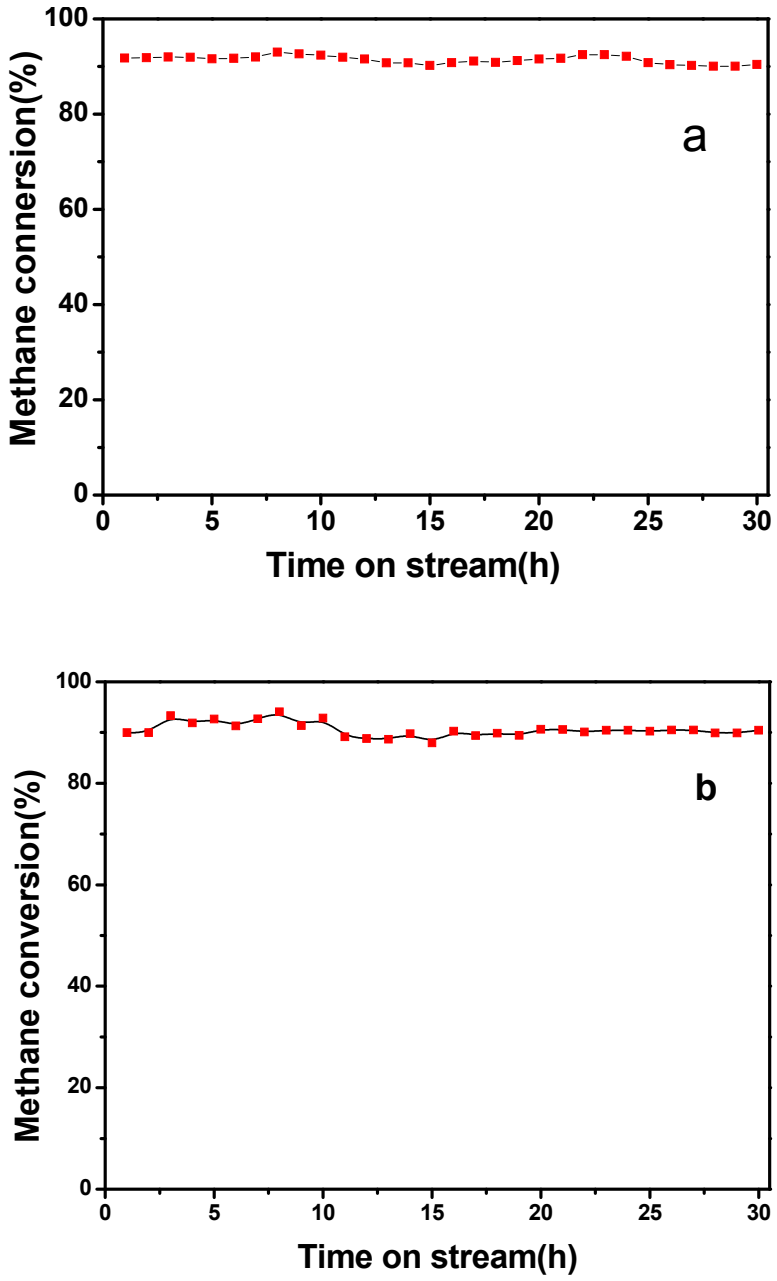

Fig. S10 Durability test of (a) Co_3O_4 NTs(350°C) and (b) Co_3O_4 NTs(550°C) in catalytic methane combustion at 295 and 305°C (T_{90}), respectively.

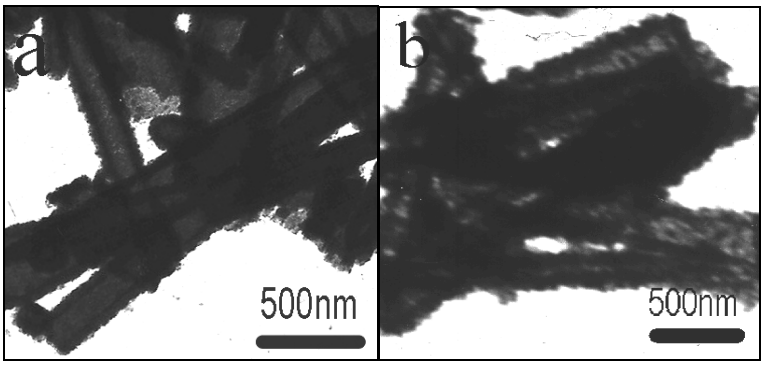

Fig. S11 TEM images of (a) Co_3O_4 NTs (350ºC) and (b) Co_3O_4 NTs (550ºC) after 30-h reaction.