Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Nonprecious Catalytic Honeycombs Structured with Three Dimensional Hierarchical Co_3O_4 Nano-arrays for High Performance Nitric Oxide Oxidation

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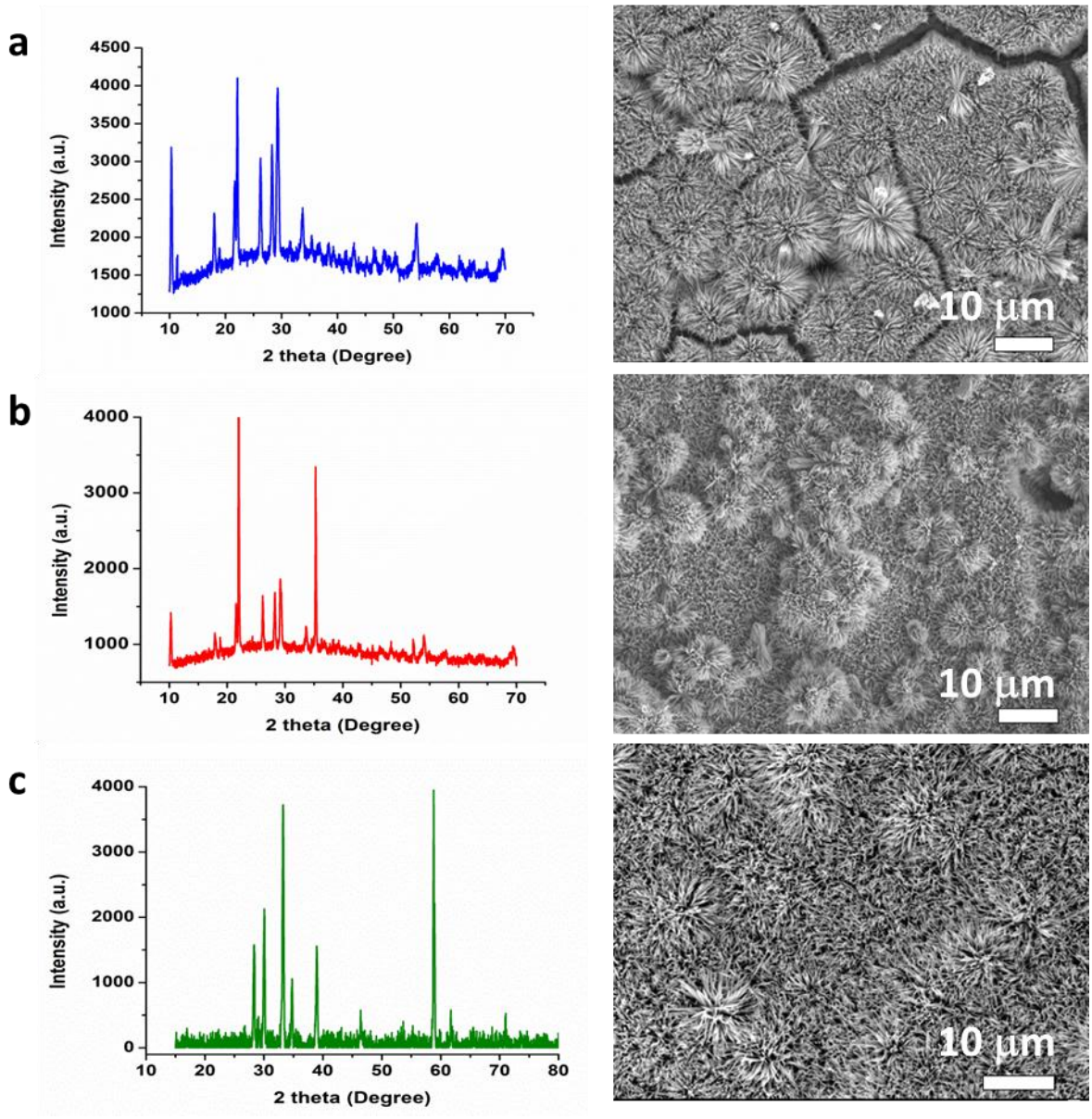

Figure S1. SEM images and corresponding XRD patterns of precursor cobalt hydroxyl carbonate nano-arrays on honeycomb substrate synthesized from a) cobalt nitrate; b) cobalt acetate and c) cobalt chloride.

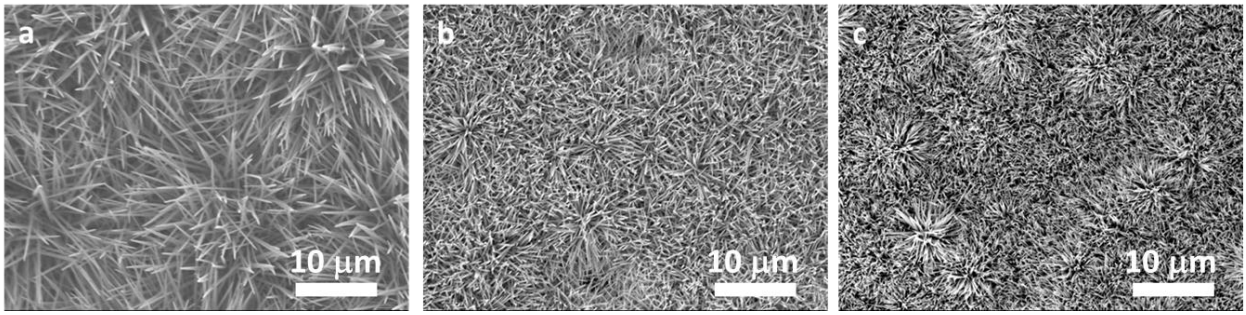

Figure S2. Morphology of Co_3O_4 nano-arrays prepared from cobalt chloride after a) 4 hours; b) 8 hours and c) 12 hours.

The morphology evolution of Co_3O_4 prepared from cobalt chloride show that elongated reaction time only increases the density of nano-arrays and improves the uniformity.

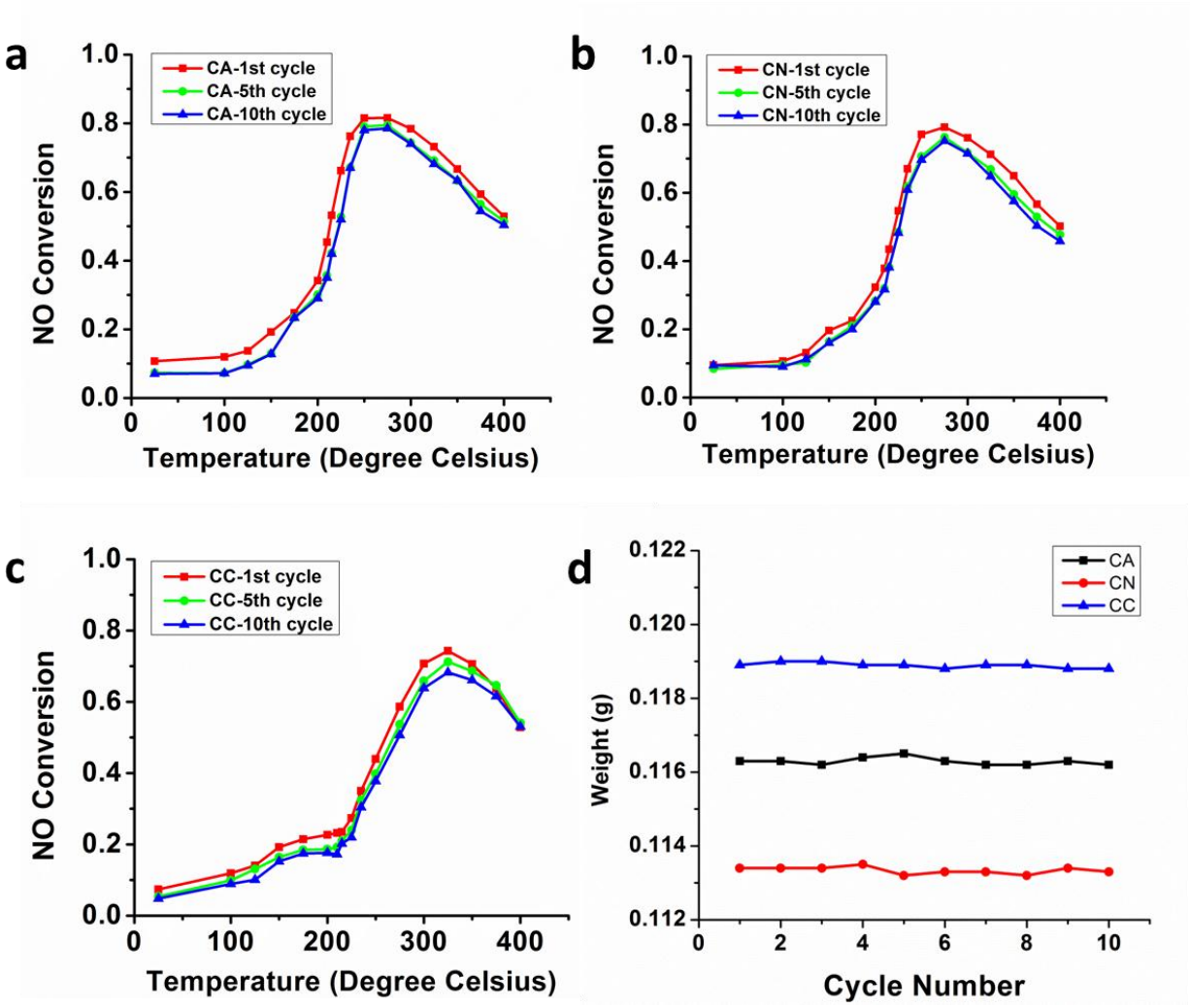

Figure S3. Cyclic catalytic NO oxidation performance by (a) CA; (b) CN and (c) CC. (d) Weight measurement of catalytic honeycombs during cyclic test.

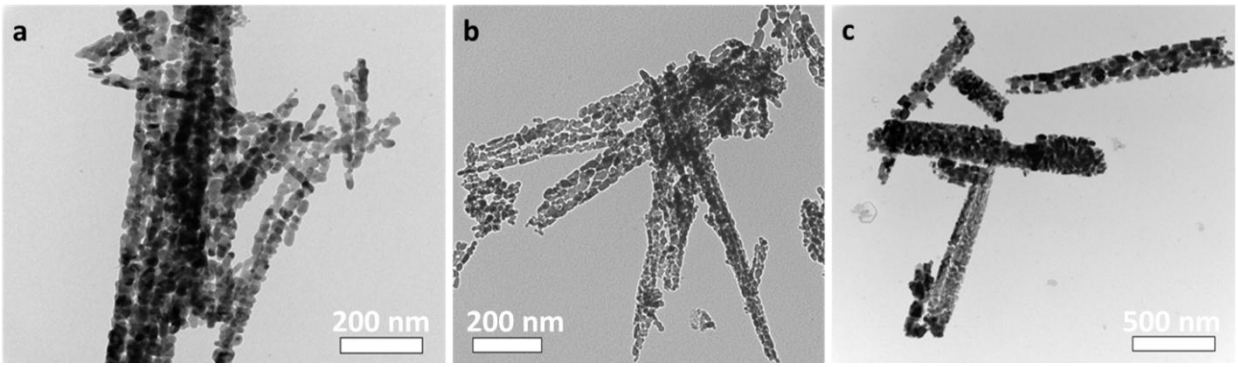

Figure S4. TEM characterization of Co_3O_4 nano-arrays prepared from a) cobalt nitrate; b) cobalt acetate and c) cobalt chloride.

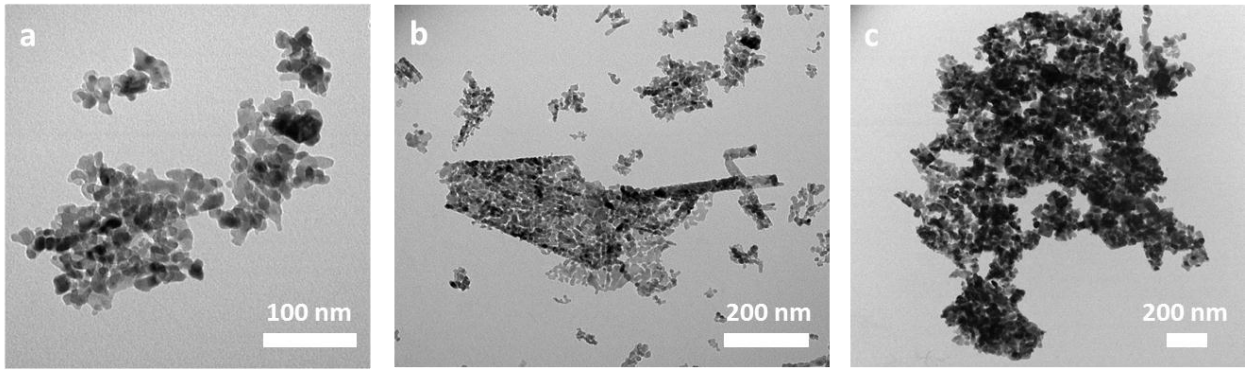

Figure S5. TEM characterization of Co_3O_4 nanopowders prepared from a) cobalt acetate; b) cobalt nitrate and c) cobalt chloride.

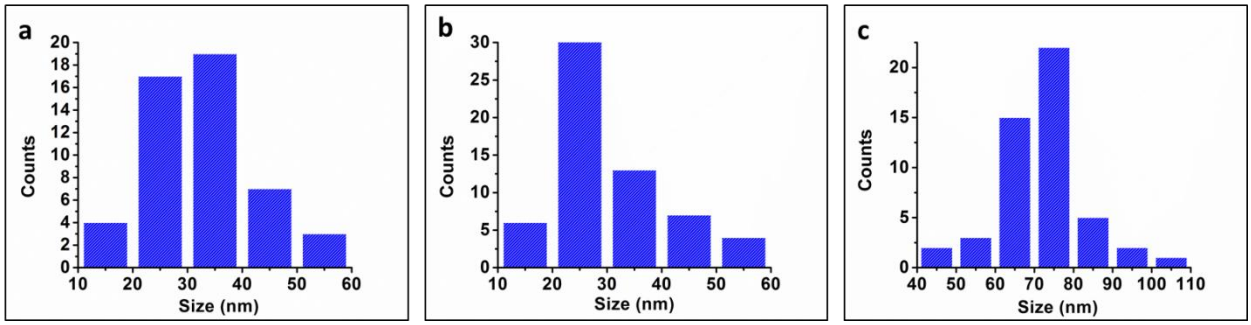

Figure S6. Statistical grain size distribution of Co_3O_4 prepared from different cobalt sources as observed in the TEM images in Figure S4. a) cobalt nitrate; b) cobalt acetate; c) cobalt chloride.

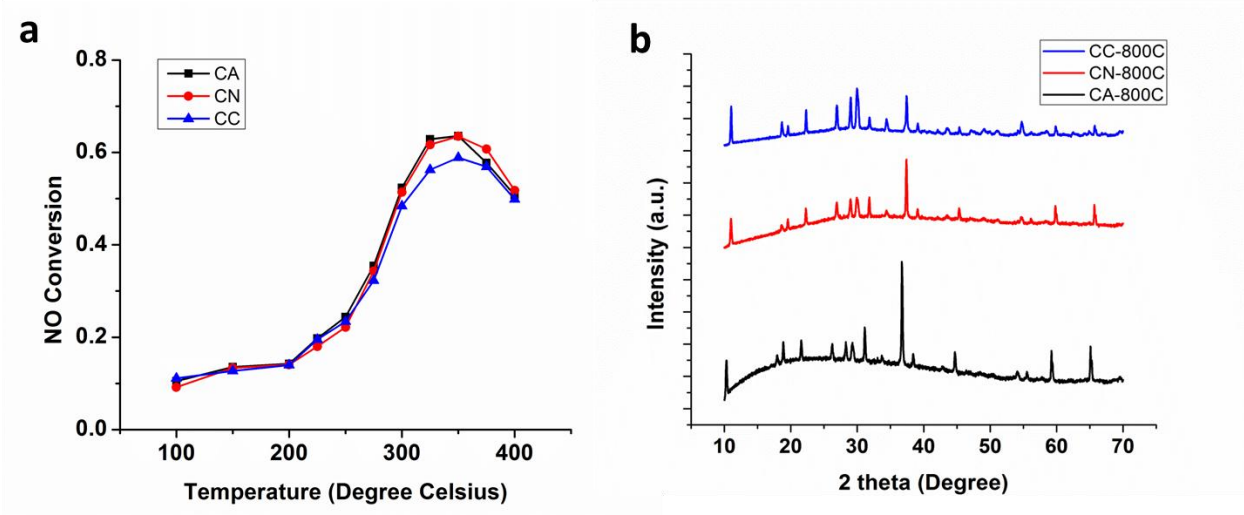

Figure S7. a) Catalytic NO oxidation performance of Co_3O_4 nano-arrays based catalytic honeycombs prepared by annealing at 800 °C. b) XRD spectra of 800 °C annealed Co_3O_4 nano-arrays honeycombs.

Table S1. Apparent activation energy, pre-exponential factor and turn-over frequency.

Temperature (°C)	Conversion	Rate (mol g^{-1} s^{-1})	TOF (s^{-1})
110	10%	6.54×10^{-7}	8.1×10^{-5}
120	12%	7.70×10^{-7}	9.5×10^{-5}
130	14.2%	9.11×10^{-7}	1.12×10^{-4}
140	16.3%	1.05×10^{-6}	1.29×10^{-4}
150	18.8%	1.21×10^{-6}	1.49×10^{-4}

Co_3O_4 prepared from cobalt acetate: Apparent activation energy $E_a = 20.6\ kJ/mol$.

Pre-exponential factor $k_0 = 5433\ mol \cdot g^{-1} \cdot s^{-1}$

Temperature (°C)	Conversion	Rate (mol g^{-1} s^{-1})	TOF (s^{-1})
110	10.9%	7.16×10^{-7}	8.6×10^{-5}
120	12.9%	8.47×10^{-7}	1.02×10^{-4}
130	15.2%	9.98×10^{-7}	1.2×10^{-4}
140	17.3%	1.14×10^{-6}	1.37×10^{-4}
150	19.8%	1.30×10^{-6}	1.57×10^{-4}

Co_3O_4 prepared from cobalt nitrate: Apparent activation energy $E_a = 20.1\ kJ/mol$.

Pre-exponential factor $k_0 = 5102\ mol \cdot g^{-1} \cdot s^{-1}$

Temperature (°C)	Conversion	Rate (mol g^{-1} s^{-1})	TOF (s^{-1})
110	9.80%	6.13×10^{-7}	8.56×10^{-5}
120	11.60%	7.25×10^{-7}	1.01×10^{-4}
130	13.60%	8.50×10^{-7}	1.18×10^{-4}
140	15.70%	9.82×10^{-7}	1.37×10^{-4}
150	17.80%	1.11×10^{-6}	1.55×10^{-4}

Co_3O_4 prepared from cobalt chloride: Apparent activation energy $E_a = 20.1\ kJ/mol$.

Pre-exponential factor $k_0 = 3840\ mol \cdot g^{-1} \cdot s^{-1}$

The apparent activation energy and pre-exponential factor is obtained by the Arrhenius plot of lnk vs (-1/T). Reaction constant value k was calculated from reaction rate $r = kP_{NO}^{a}P_{O_2}^{b}$ where a and b are the reaction orders determined from Figure 4. The turn-over frequency is calculated by using Co^{3+} as the active sites. The population ratio of Co^{3+} and Co^{2+} is determined from deconvoluted XPS spectra in Figure 5. In CA and CN the Co^{3+} possesses 65% while in CC this proportion is 59%.

TOF calculation:

$$TOF = \frac{Converted\ NO\ (mol \cdot s^{-1})}{Active\ sites\ number\ (mol)}$$

$$Converted\ NO\ (mol \cdot s^{-1}) = \frac{500\ ppm \times conversion\ (\%) \times flow\ rate\ (L \cdot s^{-1})}{22.4\ L/mol}$$

where flow rate=200 mL/min=1/300 (L/s).

$$Active\ sites\ number\ (mol) = 3 \times \frac{m_{Co_3O_4}}{M_{Co_3O_4}} \times \eta$$

where $m_{Co_3O_4}$ stands for the mass of the grown Co_3O_4 nano-arrays on the honeycomb, $M_{Co_3O_4}$ represents the molecular weight of Co_3O_4 (240 g/mol) and η is the portion of Co^{3+}, which is determined by XPS analysis. Specifically, for CA and CN nano-arrays, $\eta = 65\%$ while for CC nano-array, $\eta = 59\%$.

Table S2. Surface area calculation.

With honeycombs	Grain size (nm)	BET surface area (m^2/g)	Pore diameter(nm)
CA-300 C	20-30	12.5	15
CN-300 C	25-40	16.1	15
CC-300 C	60-80	8.4	25

In addition to the grain size, the BET surface area of the honeycombs decorated with Co_3O_4 nano-arrays are listed in Table S2. It can be seen from Figure S4b that CN has a relatively larger pore volume compared with CA, which might contribute to its larger surface area.

The BET surface area of blank honeycombs was measured to be 0.35 $m^2\ g^{-1}$. We assume the measured BET surface area of honeycombs structured with nano-arrays is approximately the linear summation of contributions from blank honeycomb and the nano-arrays. The weight of nano-arrays constitutes ~10% of the total weight of honeycombs. Therefore, the BET surface area of nano-arrays S_A in Figure 6 is calculated by

$$S_A = \frac{S(m_h + m_A) - S_h m_h}{m_A}$$

m_h: mass of the honeycomb;

m_A: mass of the nano-arrays (weight difference of honeycomb substrate before and after nano-arrays growth);

S_h: BET surface area of blank honeycomb;

S: BET surface area of honeycomb structured with Co_3O_4 nano-arrays.

The same computation is used for results in Table S3 and Table S4.

With honeycombs	BET surface area (m^2/g)	Pore size (nm)
CA-powders	4.8	12
CN-powders	3.8	15-20
CC-powders	3.7	30

Table S3. BET surface area characterization and pore size distribution results for Co_3O_4 nanopowders prepared by the same hydrothermal process as nano-arrays synthesized from different cobalt precursors.

With honeycombs	Grain size (nm)	BET surface area (m^2/g)
CA-800 C	150-200	4.3
CN-800 C	150-200	4.2
CC-800 C	150-200	4

Table S4. Grain size and BET surface area results for 800 °C annealed nano-arrays synthesized from different cobalt precursors.