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Supporting information for

"Extremely selective detection of ppb-levels indoor xylene using $CoCr_2O_4$ hollow spheres activated by Pt doping"

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Experimental Section

Preparation of pure, Pt-, Au-, and Pd-$CoCr_2O_4$ hollow spheres:

Pure $CoCr_2O_4$ hollow spheres were prepared by one-pot ultrasonic spray pyrolysis of an aqueous solution (200 mL) containing Cobalt (II) nitrate hexahydrate (0.375 g, $Co(NO_3)_2 \cdot 6H_2O$, >98%, Sigma-Aldrich, UK), Chromium (III) nitrate nonahydrate (1.020 g, $Cr(NO_3)_3 \cdot 9H_2O$, >99.99%, Sigma-Aldrich, USA), and citric acid (1.005 g, $C_6H_8O_7$, 99.5%, Sigma-Aldrich, Japan). The spray-pyrolysis equipment consisted of the droplet generator, tubular reactor, and powder-collecting chamber. The droplets of the solution were generated by five ultrasonic transducers (frequency = 1.67 MHz), which were carried into a tubular quartz reactor (temperature = 600 °C, length = 1200 mm, diameter = 50 mm) by air at a flow rate of 10 L/min. A Teflon bag filter was used to collect the precursor powders. The $CoCr_2O_4$ hollow spheres were prepared by annealing the precursor powders at 700 °C for 2 h in air.

The Pt-, Au-, and Pd-$CoCr_2O_4$ hollow spheres were synthesized by the same procedure after the addition of chloroplatinic acid solution, 8 wt% in H_2O (0.015 mL, H_2PtCl_6, Sigma-Aldrich, USA), palladium nitrate hydrate (0.0014 g, $Pd(NO_3)_2 \cdot xH_2O$, Sigma-Aldrich, USA), and gold chloride trihydrate (0.0012 g, $HAuCl_4 \cdot 3H_2O$, Sigma-Aldrich, USA) in the solution, respectively. The ratio between Pt, Au, and Au and Co and Cr ([Pt, Au, or Au]/[Co + 2Cr]) were fixed to 0.3 wt%. The Pt-, Au-, and Pd-$CoCr_2O_4$ spheres were prepared by the heat-treatment of the precursor powders at 700 °C for 2 h in air.

Characterization:

The morphologies of the sensing materials were investigated by using field emission scanning electron microscopy (SEM, SU-70, Hitachi Co., Ltd., Japan) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL, Japan). The phases and crystal structures were analyzed via X-ray diffractometry (XRD, D/MAX-2500, Rigaku, Japan) with CuK_{α} radiation (λ = 1.5418 Å). The chemical states of each sample were observed using X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo Scientific, USA). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 4300 DV, Perkin Elmer Instruments, USA) was used to determine the concentration of Pt, Au, and Pd in the $CoCr_2O_4$ hollow spheres. The specific surface areas of the spheres were determined from a Brunauer–Emmett–Teller (BET) analysis of nitrogen-adsorption measurements (BET, TriStar 3000, Micromeritrics, Norcross, MN, USA).

Gas sensing characteristics:

The pure, Pt-, Au-, and Pd-$CoCr_2O_4$ hollow spheres were made in a slurry form and drop-coated on an alumina substrate (size: 1.5 × 1.5 mm^2, thickness: 0.25 mm) with two Au electrodes on the top (spacing: 200 μm) and a micro-heater on the bottom. The sensors were heat-treated at 450°C for 2 h to remove residual water-related species (e.g., hydroxyl groups) and to stabilize the sensors. For the measurement, the sensors were contained in a specially designed, low volume (1.5 cm^3) quartz tube to minimize delay in changing the atmosphere controlled by a four-way valve. The flow rates for both dry air and analytic gases were 200 cm^3 min^{-1}. The concentration of analytic gases was controlled by changing the mixing ratio between 5 ppm of *p*-xylene, toluene, ethanol, trimethylamine, ammonia, formaldehyde, benzene, and carbon monoxide (in air balance) and synthetic dry air. The direct-current 2-probe resistance of the sensor was measured using an electrometer (6487 Picoammeter, Keithley, Tecktronic Inc., USA) interfaced with a computer. The gas responses ($S = R_g R_a^{-1}$; R_g: resistance in analytic gas, R_a: resistance in air) of the sensors were evaluated in the range of 250 – 350°C.

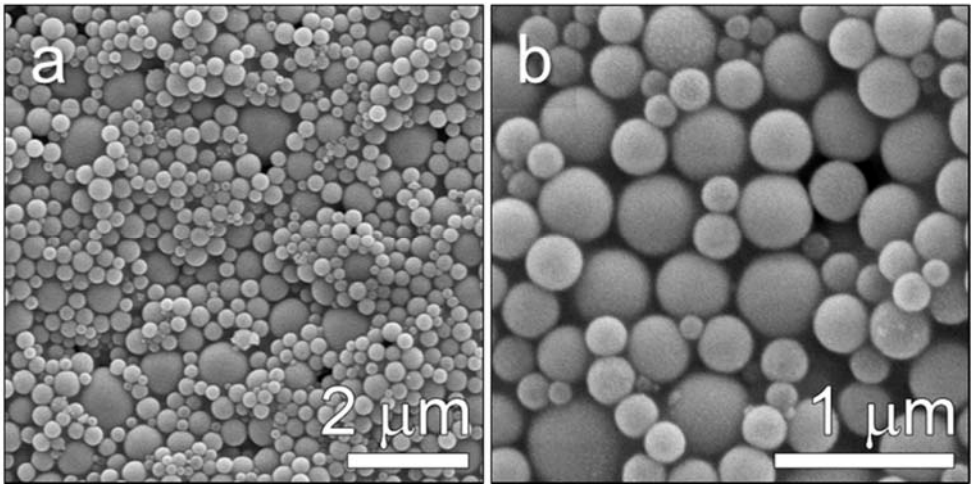

Figure S1. (a) Low and (b) high magnification SEM images for Pt-CoCr precursor spheres after spray pyrolysis.

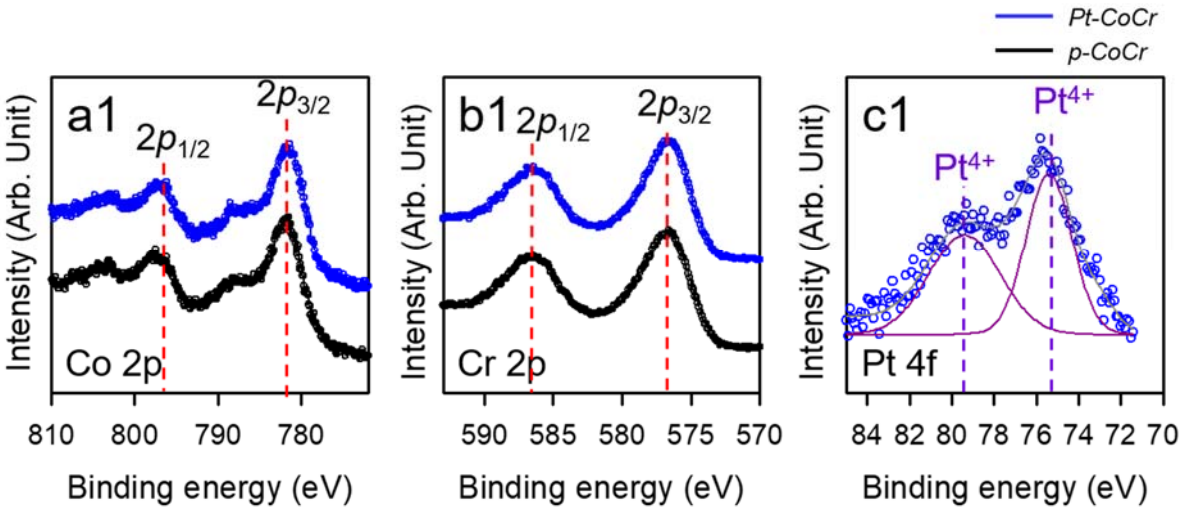

Figure S2. XPS spectra for (a) Co 2p, (b) Cr 2p, and (c) Pt 4f of Pt-CoCr (blue) and p-CoCr (black).

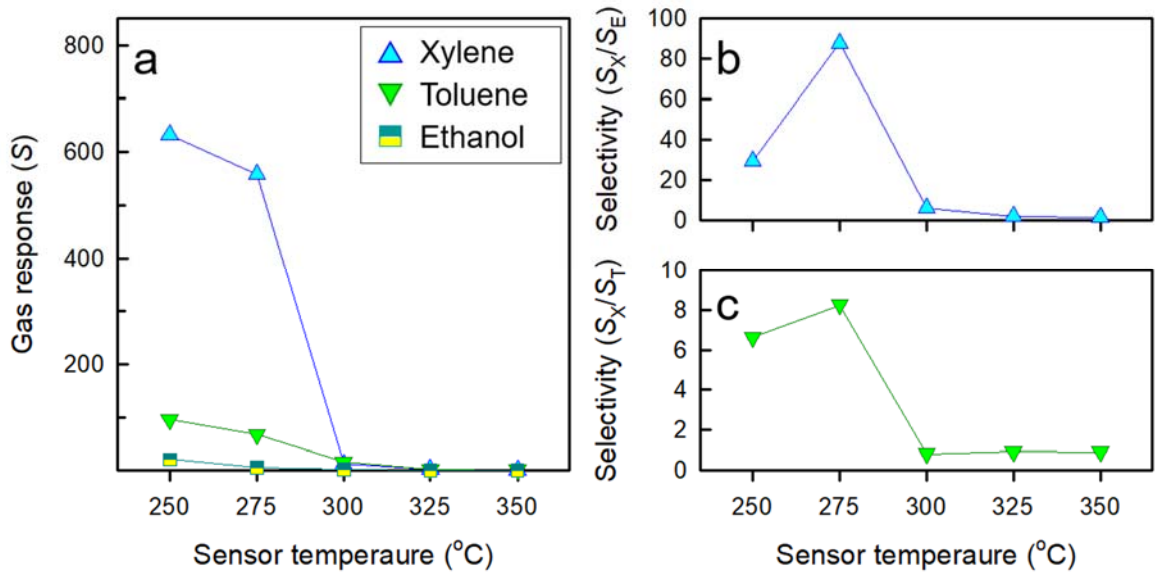

Figure S3. (a) Gas responses of Pt-CoCr to 5 ppm of xylene, toluene, and ethanol at 250 – 350°C. (b, c) Xylene selectivity (S_X/S_E or S_X/S_T) at the same temperatures.

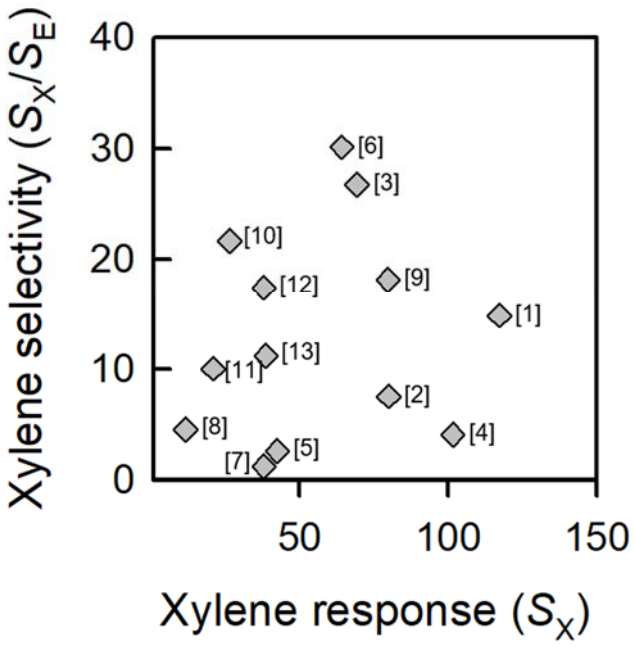

Figure S4. The xylene selectivity (S_X/S_E) and response (S_X) reported in the literature.[1-13]

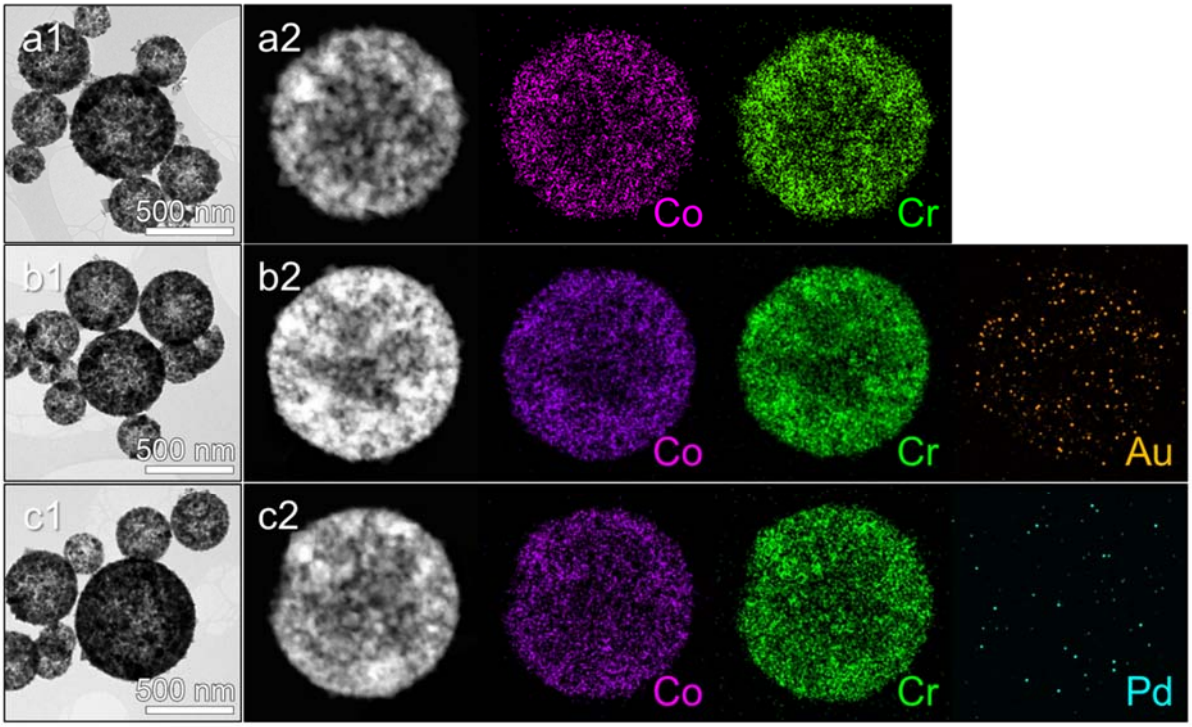

Figure S5. (a1-c1) TEM and (a2-c2) elemental-mapping images of (a) p-CoCr, (b) Au-CoCr, and (c) Pd-CoCr.

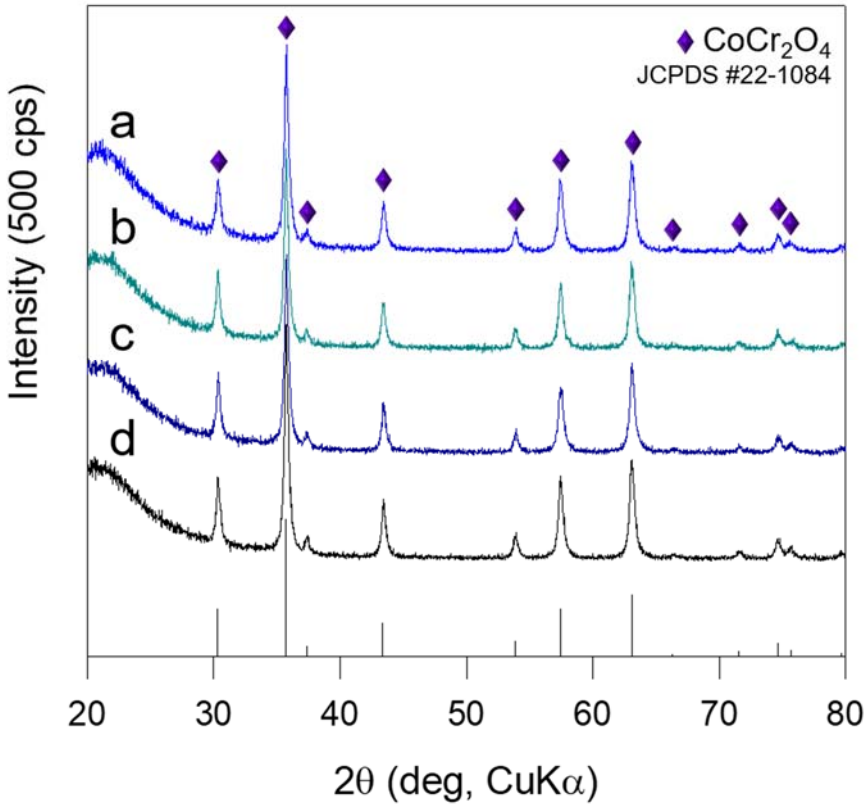

Figure S6. XRD patterns of (a) Pt-CoCr, (b) Au-CoCr, (c) Pd-CoCr, and (d) p-CoCr.

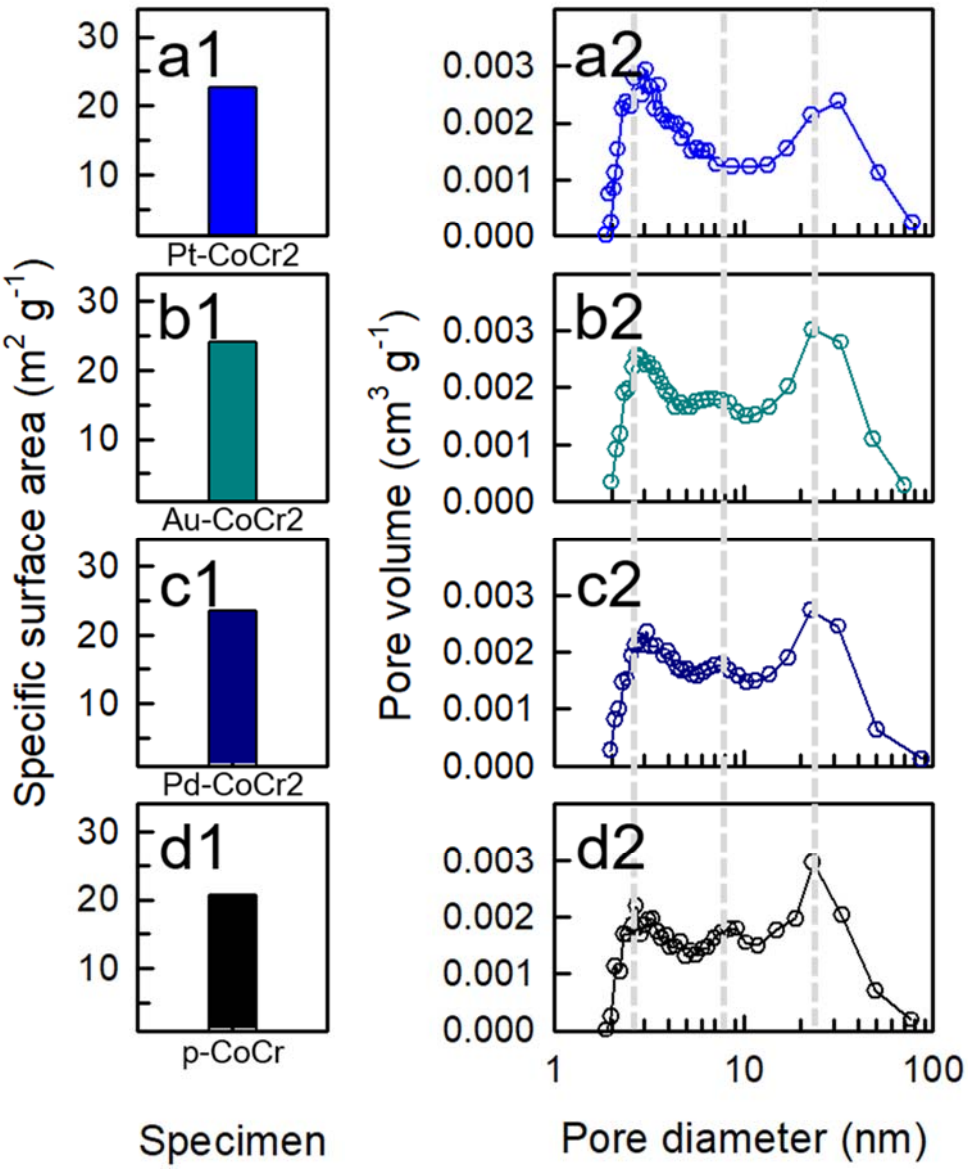

Figure S7. (a1-d1) BET specific surface areas and (a2-d2) pore size distributions of (a) Pt-CoCr, (b) Au-CoCr, (c) Pd-CoCr, and (d) p-CoCr hollow spheres.

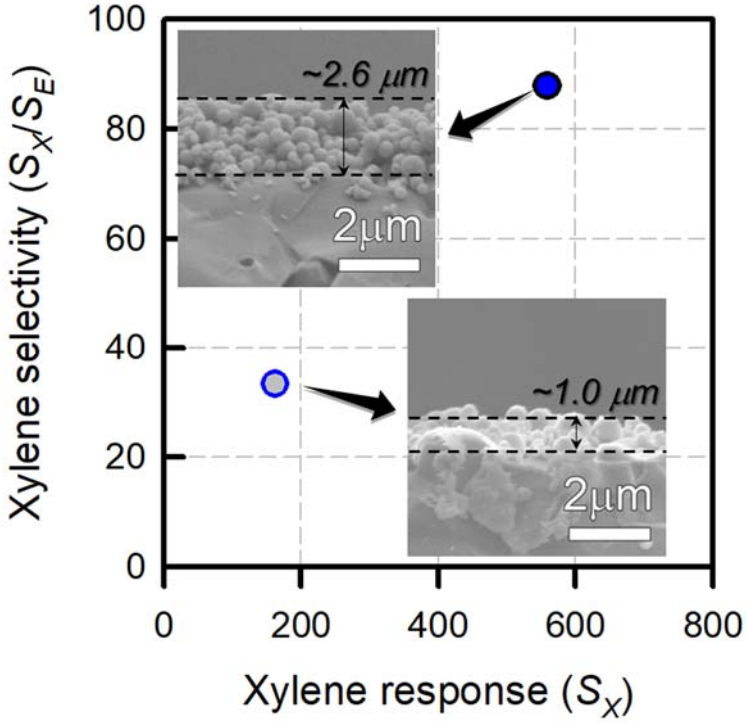

Figure S8. (a) Xylene selectivity (S_X/S_E) and (b) response (S_X) of Pt-CoCr depending on the sensing film thickness.

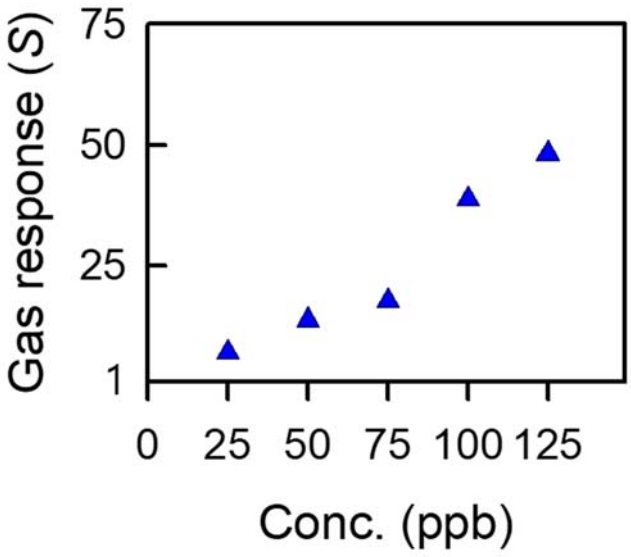

Figure S9. Gas responses of Pt-CoCr sensor to 25 – 125 ppb of xylene at 275^{o}C under the relative humidity of 80 %.

Table S1. The values of 5 ppm xylene selectivity (S_X/S_E) and response (S_X) in the present study compared to the reported values in the literature.[1-13]

No.	Sensing materials	Structure	Temp. (°C)	Response (S_X)	Selectivity (S_X/S_E)	LOD (ppm)	Ref
1	Pt-$CoCr_2O_4$	Hollow	275	558.8	87.8	0.019	This study
2	Pd-$CoCr_2O_4$	Hollow	275	225.8	30.7		This study
3	Au-$CoCr_2O_4$	Hollow	275	365.5	30.9		This study
4	$CoCr_2O_4$	Hollow	275	319.5	25.4		This study
5	$CoCr_2O_4$-Cr_2O_3	Hollow	275	117.2	14.8	≤ 0.25	[1]
6	Co_3O_4	Hollow hierarchical	225	80	7.5	≤ 0.25	[2]
7	$ZnCr_2O_4$	Hetero nanostructure	325	69.2	26.7	≤ 0.25	[3]
8	$NiMoO_4$	Hierarchical	375	101.5	4.06	0.02	[4]
9	Ni-doped ZnO	Nanowire	400	42.44	2.54	0.04	[5]
10	Pd-loaded Co_3O_4	Yolk-shell	250	64.2	30.1	≤ 0.25	[6]
11	Co_3O_4	Hierarchical	150	37.9	1.18	≤ 1	[7]
12	Cr-doped NiO	Hierarchical	400	11.61	4.48	≤ 0,25	[8]
13	Pd-loaded Co_3O_4	Hierarchical	300	79.7	18.1	0.2	[9]
14	Au-loaded $WO_3{\cdot}H_2O$	Nanocube	255	26.4	21.64	0.2	[10]
15	Cr-loaded NiO	Core-shell	220	20.9	~ 10	1	[11]
16	Co_3O_4	Hierarchical nanosheet	150	37.9	17.4	≤ 1	[12]
17	Co_3O_4	Flower	150	38.7	11.18	≤ 1	[13]

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