Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Inert metal induces the modulation of unsaturated aldehyde absorption mode for enhanced selective hydrogenation †

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Experimental section

Material

Iridium (III) chloride hydrate ($IrCl_3 \cdot xH_2O$), Cadmium chloride ($CdCl_2$), Gallium (III) 2,4-pentanedionate ($Ga(acac)_2$), Tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), Zinc chloride ($ZnCl_2$), Indium chloride ($InCl_3$), carbon black (CB), Citric acid (CA), Ethylene glycol (EG), cinnamaldehyde (CAL) were all purchased from Acmec (Shanghai, China). All the chemicals were used without any further purification.

Synthesis of Ir/CB and IrM/CB

In a typical procedure for preparing Ir/CB, 15 mg $IrCl_3 \cdot xH_2O$ (0.05 mmol), 96 mg CA, 50 mg CB and 12 mL EG were mixed in a 20 mL vial, stirred for 30 min and subsequently sonicated for 30 min, sealed the vial and heated at 180 °C for 5 h. Then, the mixture was allowed to cool down to room temperature naturally. The black powder product was centrifuged and washed with water and EtOH twice respectively, heated at 60 °C under vacuum for 12 h.

For preparing IrM/CB, the synthesis method was similar to Ir/CB, except for extra adding 0.025 mmol, 0.05 mmol, 0.1 mmol, 0.25 mmol, 0.5 mmol of $CdCl_2$, $Ga(acac)_2$, $SnCl_4 \cdot 5H_2O$, $ZnCl_2$, and $InCl_3$, the obtain products were donated as $IrM_{0.5}$, IrM_1, IrM_2, IrM_5, IrM_{10}. Detailed metal loading of different catalysts was listed in Table S1.

Synthesis of Ir and Ir-M nanoparticle

The synthesis method was similar to that of Ir/CB and $IrCd_5$/CB, simply without carbon black in the preparation procedure.

Characterization

HRTEM images, atomic resolution STEM images and EDS element mappings were all recorded by Cs-corrected transmission electron microscopy (ARM200F, JEOL). The XRD patterns were collected by powder X-ray diffraction (XRD, Rigaku, SmartLab), equipped with Cu Kα X-ray source (λ=1.540598 Å). X-ray photoelectron spectroscopy (XPS) spectra were detected by a VG Scientific ESCALAB 250 instrument. The XPS spectrum deconvolution was performed by using the XPS PEAK 41 program with Lorentzian-Gaussian functions after subtraction of a Shirley background. The C 1s (284.8 eV) was used as the reference for the calibration. Metal content of the catalysts was analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo Fisher, iCAP RQ).

Surface valence bands

The surface valence bands of Ir and $IrCd_5$ was obtained by the same instrument of XPS test. Energy level and density of states is integrated from negative infinity to the Fermi level to obtain the total energy of electrons occupying orbital d. Divide the total energy by the number of electrons to get the average energy of the d electrons, which is the d-band center.

FT-IR spectra measurement

The as-prepared Ir or $IrCd_5$ was ground evenly with potassium bromide. Then 2.5 μL styrene was added into the mixture. The mixtures were kept at room temperature for 2 min, and then were flaking as pellets for test on Shimadzu IRAffinity-IS spectrometer in the spectral range from 4000 cm^{-1} to 500 cm^{-1}.

H_2-TPD measurement

In the H_2-TPD test, a 100 mg sample was sealed in a quartz reactor and first treated with a mixture of H_2 and Ar (1/9, v/v) at 500 °C. Subsequently, Ar was introduced at 450 °C for 60 min, and then cooled to 25 °C. During the process of obtaining a stable baseline from the Ar purge, the temperature was ramped up to 400 °C at a heating rate of 10 °C/min.

Styrene-TPD measurement

For styrene-TPD measurement, 100 mg of sample was sealed in the reactor, after preheating in He atmosphere at 200 °C for 60 min, cooled to 50 °C. Then the mixture gas of styrene/He was introduced into reactor for 60 min, and then the reactor was purged by He for 30 min. Finally, the reactor was heated from 50 to 550 °C with a heating rate of 10 °C min^{-1}. The desorption of styrene was monitored by a thermal conductivity detector.

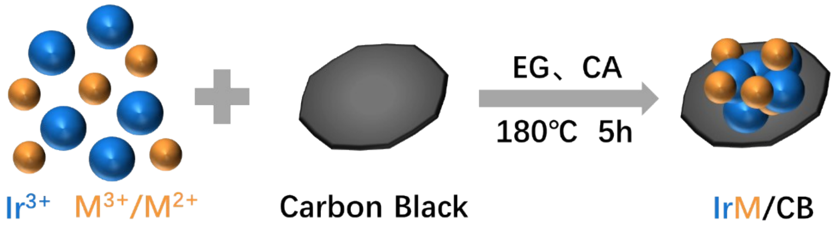
Catalyst evaluation

In a 20 ml vial, 5 mg catalyst was dispersed in 1 ml water and 1 ml isopropanol, 0.5 mmol cinnamaldehyde was added into the above mixture, sonicated for 5 min. The glass vial was sealed into stainless-steel autoclave, purged with pure H_2 for at least 3 times to remove air, and eventually kept the H_2 pressure at 1 MPa. The reaction was carried out at 30 ℃ with stirring at 600 rpm for 12 h. After the reaction finished, the supernatant was collected by centrifugation and then analyzed by gas chromatography-mass spectrometry (GC-MS, SHIMAZU QP 2010SE).

Computational details

Density functional theory (DFT) calculations were conducted to optimize structures by Vienna ab initio simulation package (VASP).[1] The projector augmented wave (PAW) potentials with a planewave cutoff energy of 400 eV were implemented to compute the interaction between the ionic cores and valence electrons.[2,3] Ir(111) slab model was constructed with three atomic layers and a vacuum space larger than 15 Å. For IrCd(111) model, eight Ir atoms were replaced with Cd atoms at the first layer of Ir(111) slab, with the Ir/Cd ratio equals to 5:1, consistent with the experimental results. The Gamma(Γ) centered 3×3×1 Monkhorst-Pack sampling was used for Brillouin zone. The convergence criteria of electronic energies and atomic forces for all calculations were 10^{-5} eV and 0.03 eV/Å. Because the supercell is large enough (a=b=10.86 Å, c=24.43 Å, cinnamaldehyde (CAL) molecules length: 7.62 Å), both the parallel and vertical adsorption configurations of CAL were considered. In all the calculations, the top one atomic layer of the surfaces was allowed to relax together with the CAL adsorbate, while the bottom two layers were keep fixed to present the bulk properties. The binding energy, E_b, is given by the following equation:

$$E_b = E_{slab/ads} - E_{molecule} - E_{slab}.$$



Scheme S1 Synthesis method of IrM/CB catalyst.

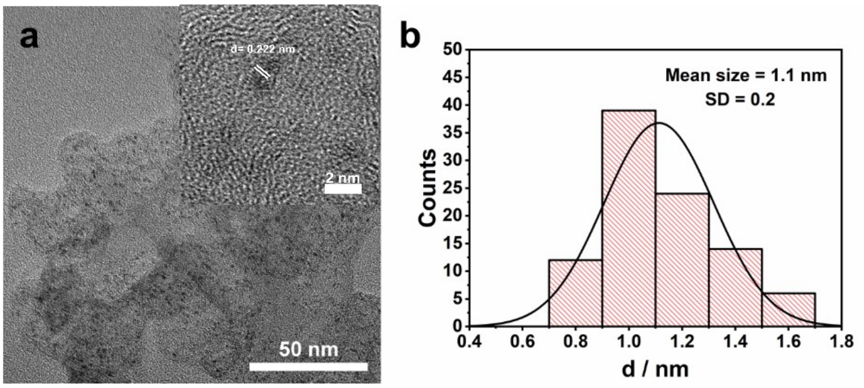


Fig. S1 (a) TEM and HRTEM image of Ir supported on CB and (b) corresponding nanoparticle size distribution of Ir.

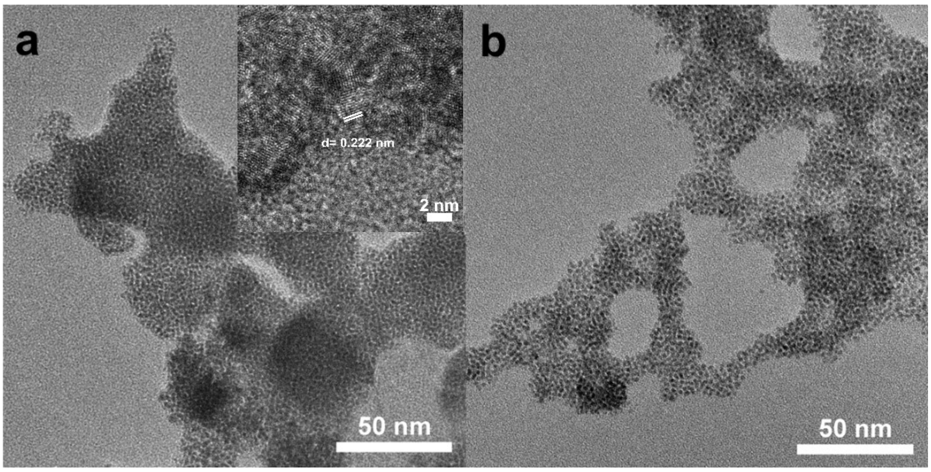


Fig. S2 (a) TEM and HRTEM images of metallic Ir and (b) TEM image of $IrCd_5$ synthesized without carbon black.

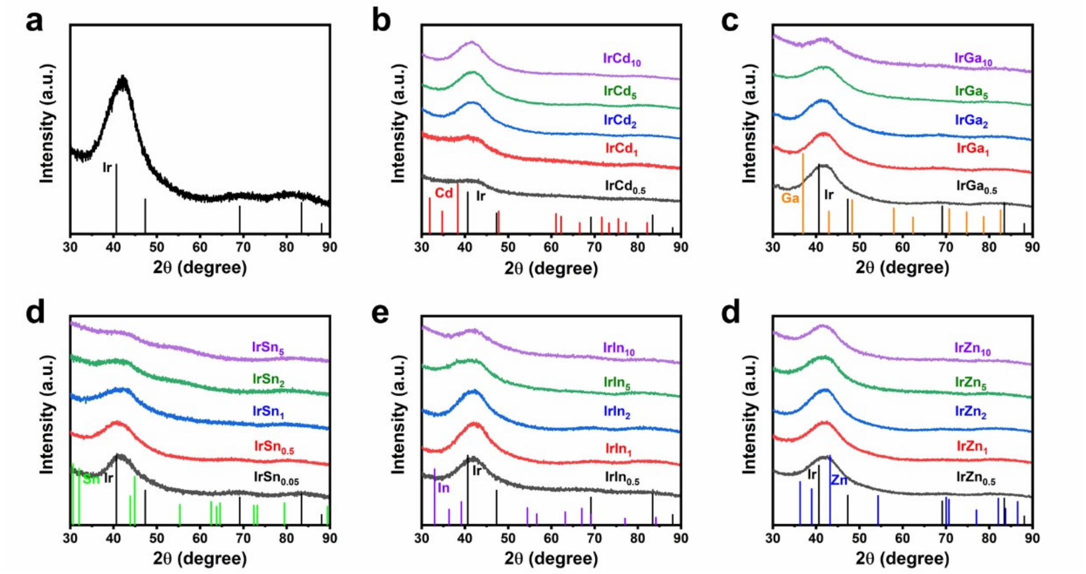


Fig. S3 XRD patterns of carbon black supported (a) Ir, (b) IrCd$_x$, (c) IrGa$_x$, (d) IrSn$_x$, (e) IrIn$_x$, (f) IrZn$_x$.

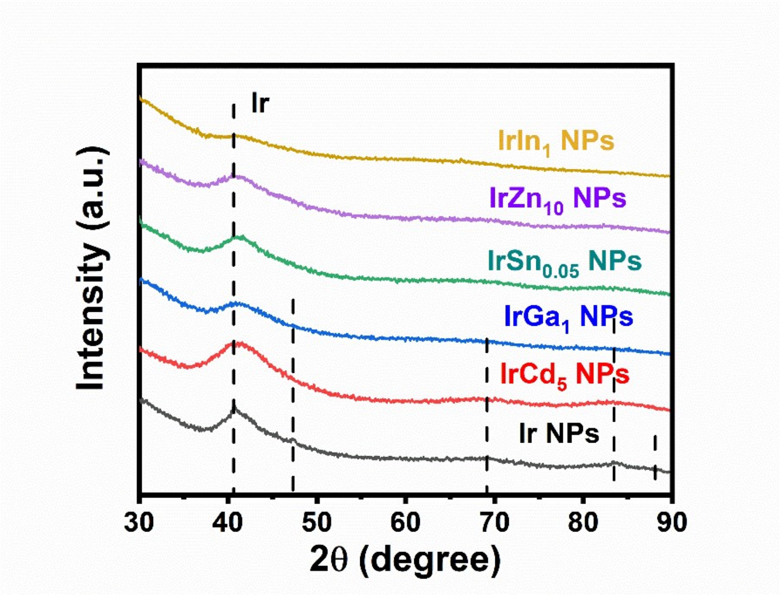


Fig. S4 XRD patterns of Ir-M nanoparticles

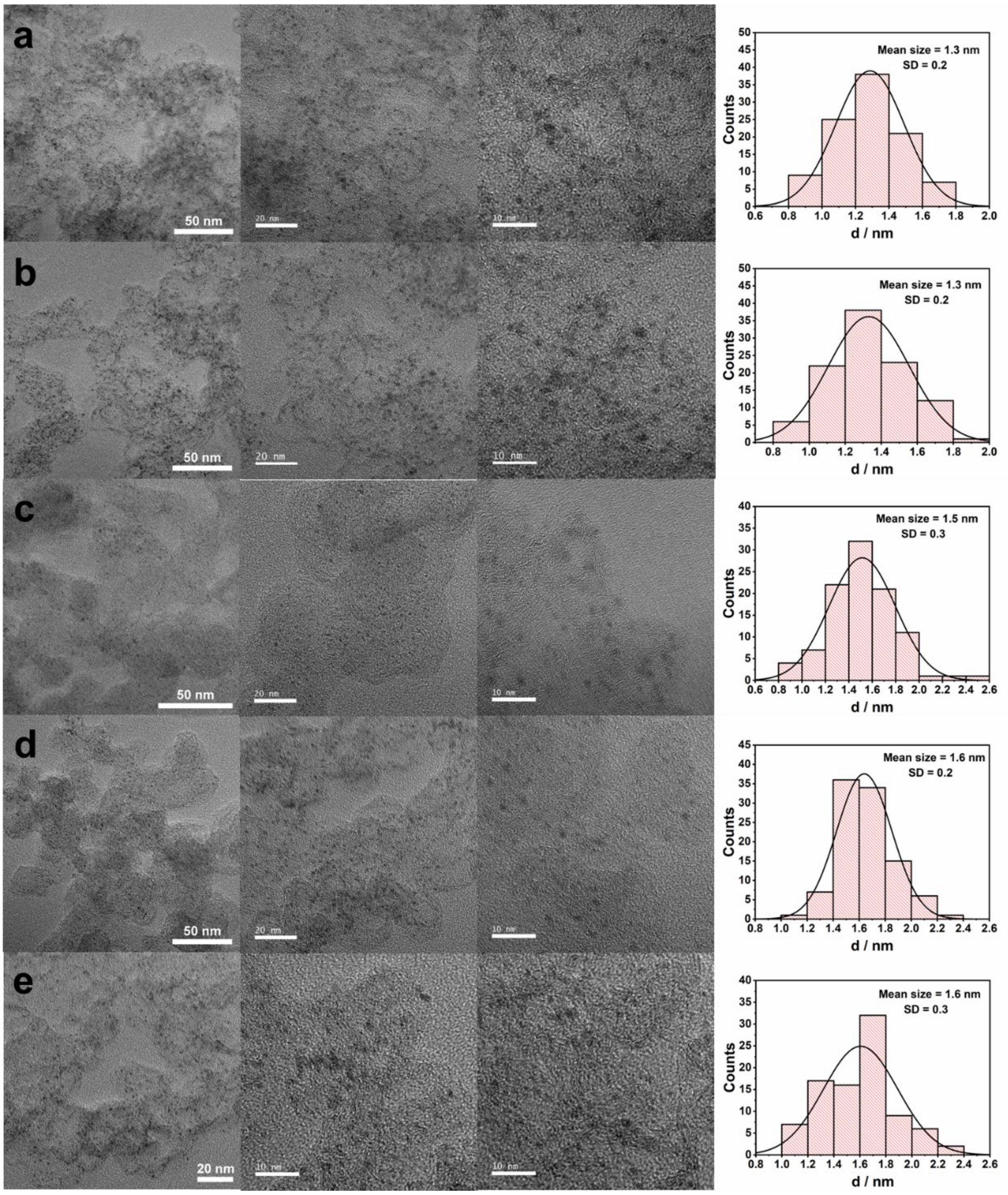


Fig. S5 TEM images and corresponding nanoparticle size distribution of (a) $IrCd_{0.5}$ (b) $IrCd_1$ (c)$IrCd_2$ (d) $IrCd_5$ and (e) $IrCd_{10}$.

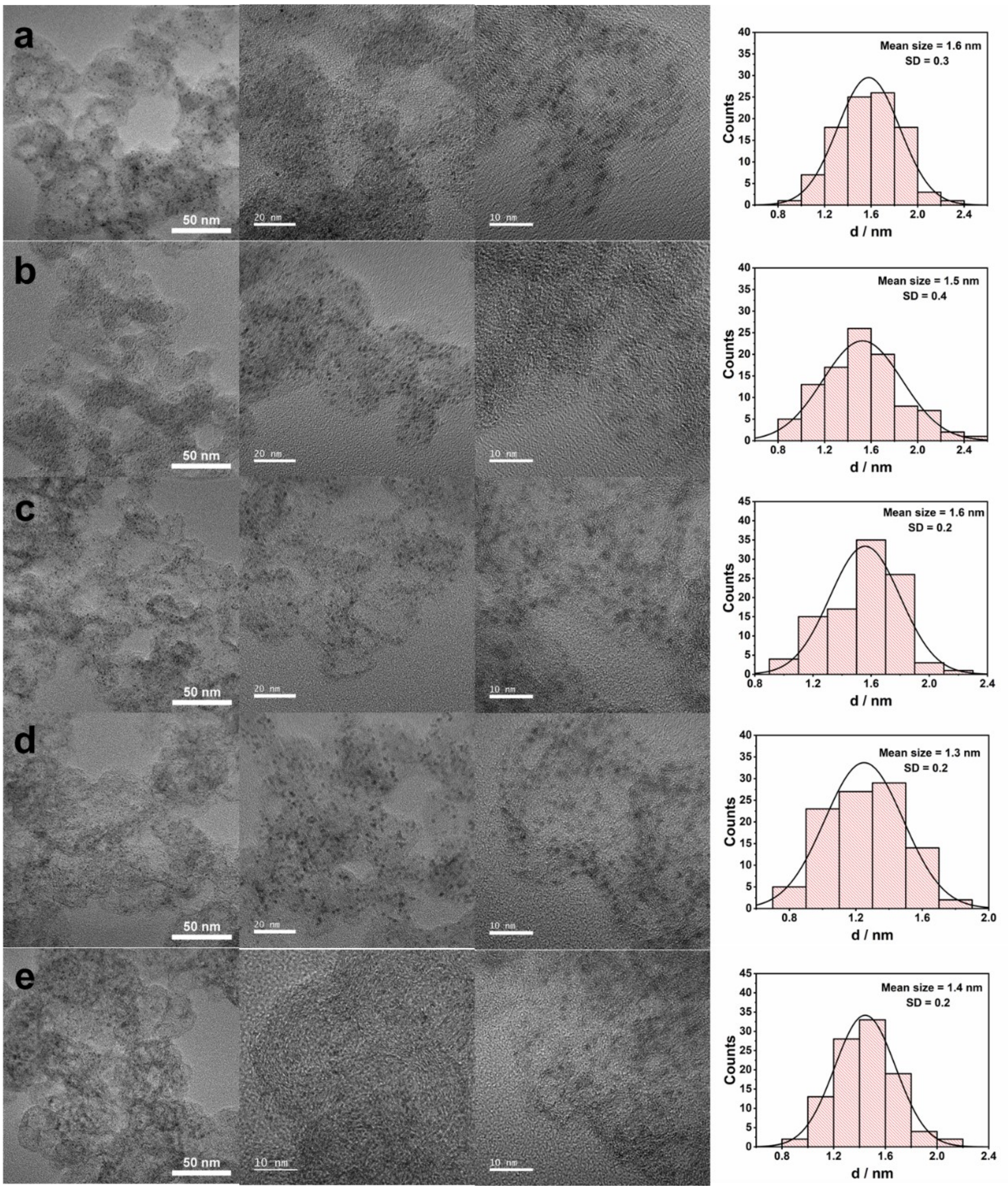


Fig. S6 TEM images and corresponding nanoparticle size distribution of (a) $IrGa_{0.5}$ (b) $IrGa_1$ (c)$IrGa_2$ (d) $IrGa_5$ and (e) $IrGa_{10}$.

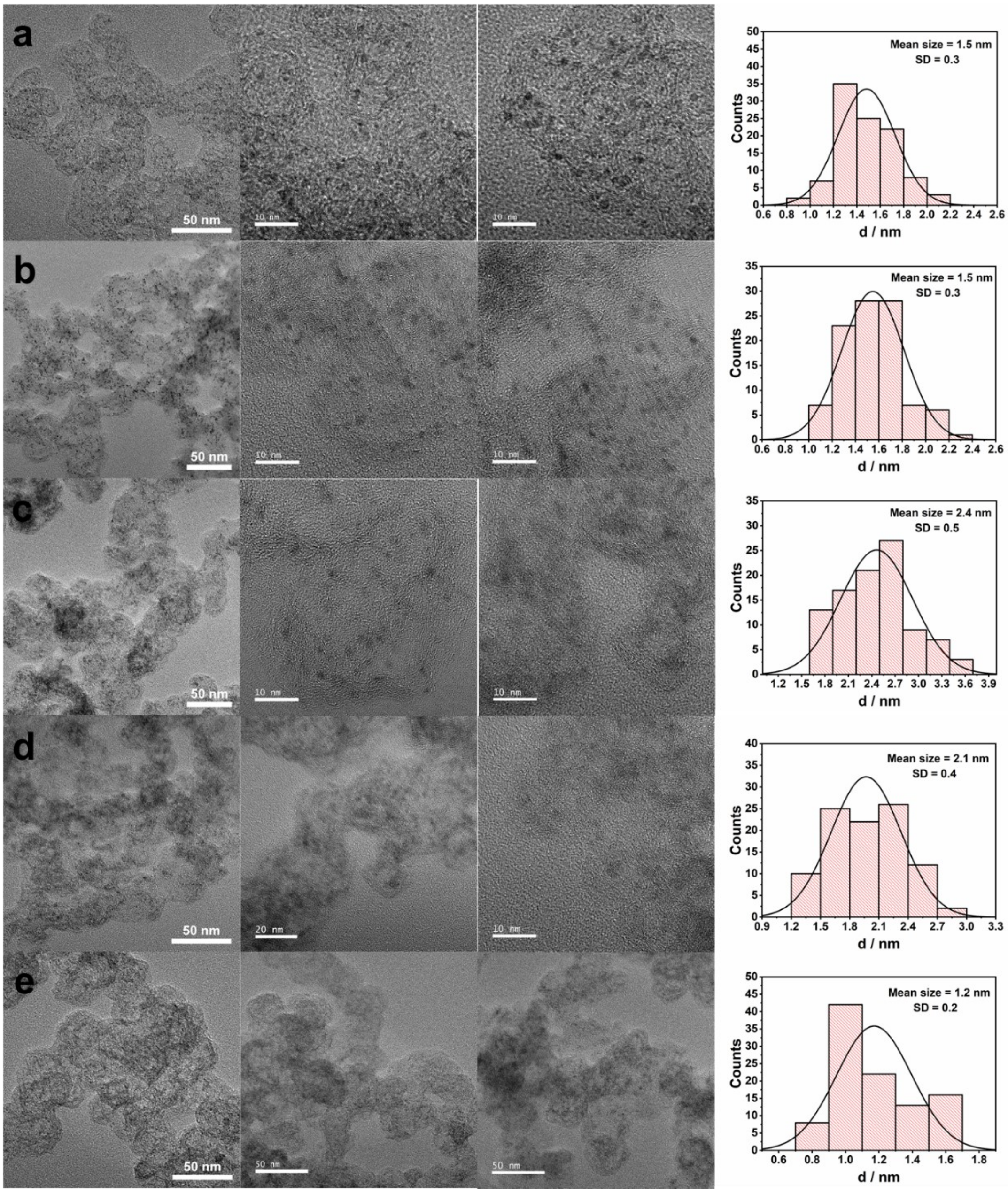


Fig. S7 TEM image and corresponding nanoparticle size distribution of (a) $IrSn_{0.05}$, (b) $IrSn_{0.5,}$ (c) $IrSn_1$ and (d) $IrSn_2$ and (e) $IrSn_5$.

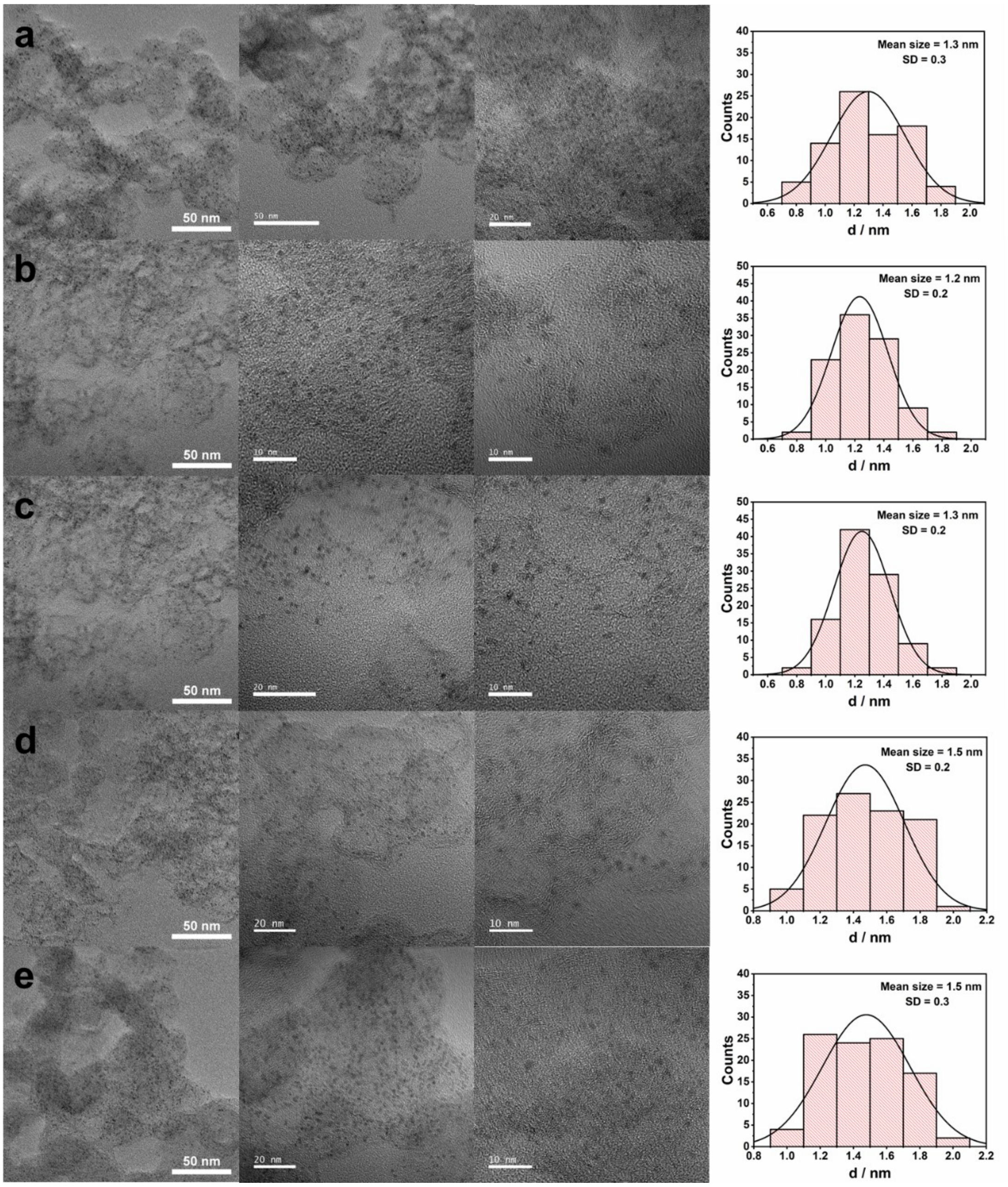


Fig. S8 TEM image and corresponding nanoparticle size distribution of (a) $IrZn_{0.5}$ (b) $IrZn_1$ (c)$IrZn_2$ (d) $IrZn_5$ and (e) $IrZn_{10}$.

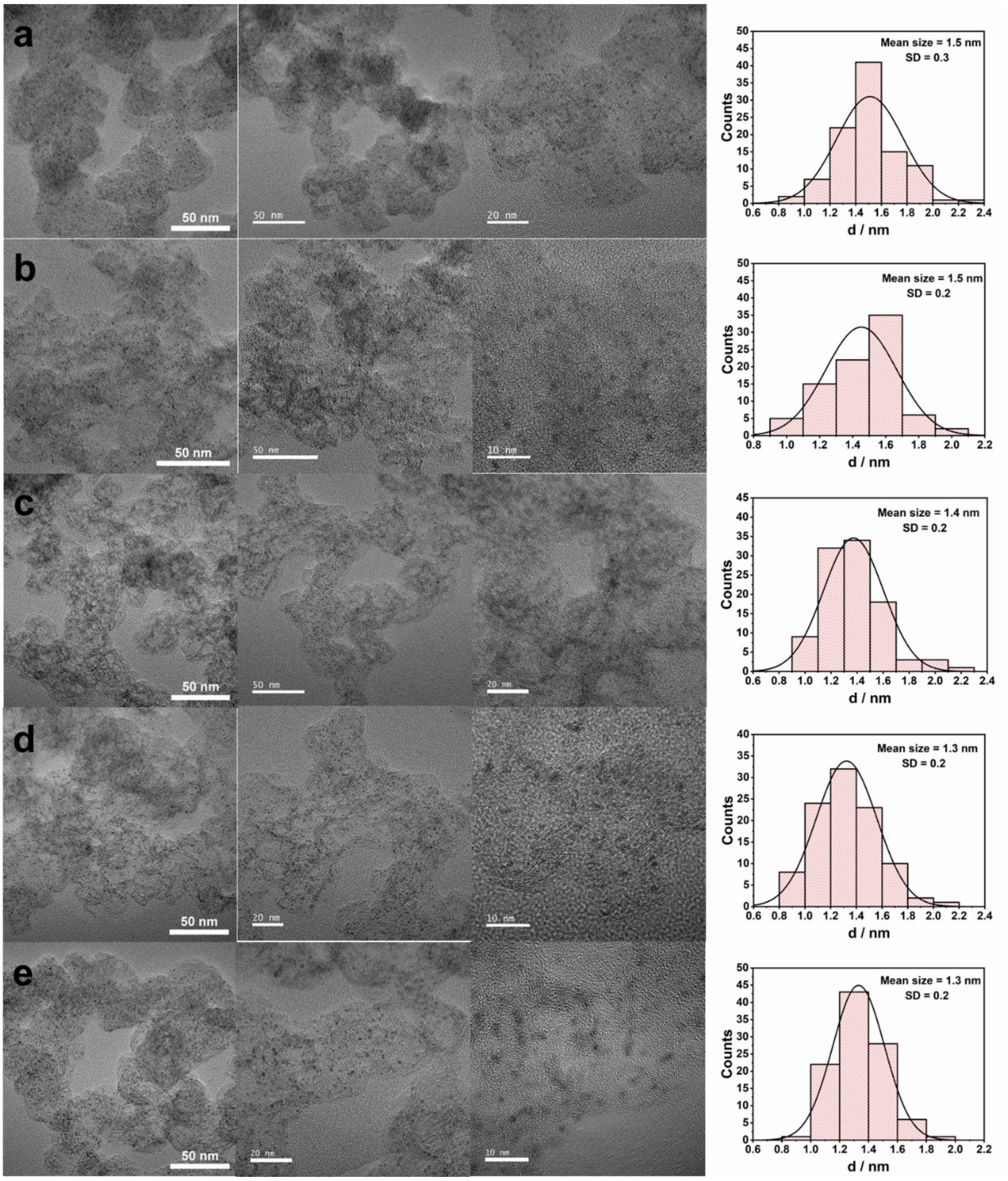


Fig. S9 TEM image and corresponding nanoparticle size distribution of (a) $IrIn_{0.5}$ (b) $IrIn_1$ (c)$IrIn_2$ (d) $IrIn_5$ and (e) $IrIn_{10}$.

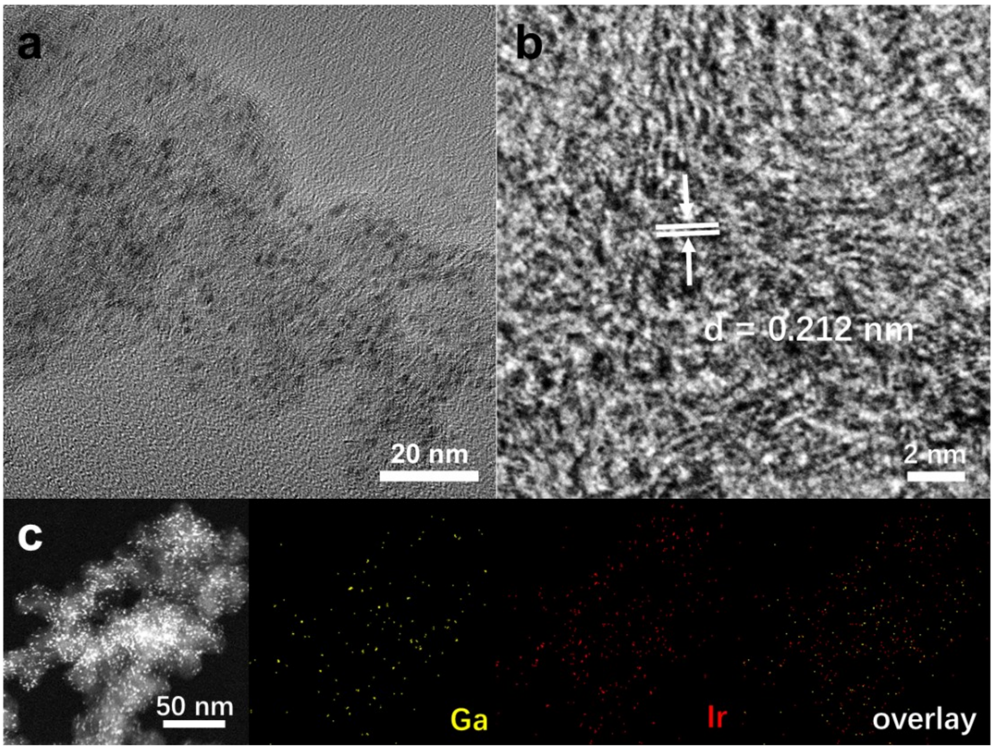


Fig. S10 (a) TEM (b) HRTEM image (c) HAADF-STEM-EDS element mappings of $IrGa_1$.

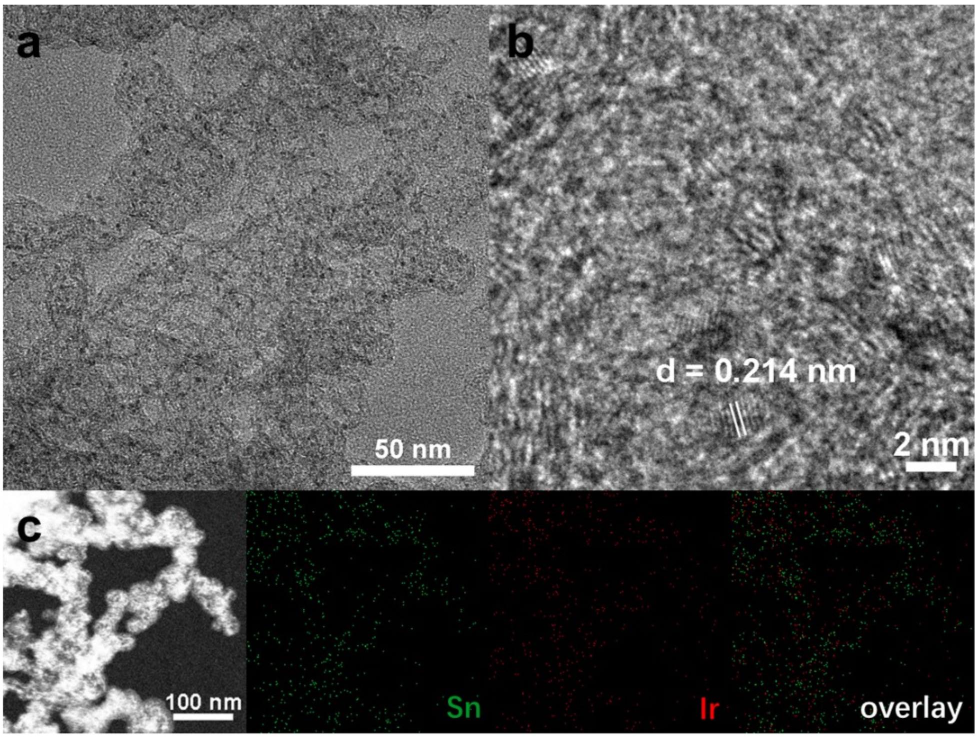


Fig. S11 (a) TEM (b) HRTEM image (c) HAADF-STEM-EDS element mappings of of $IrSn_{0.05}$.

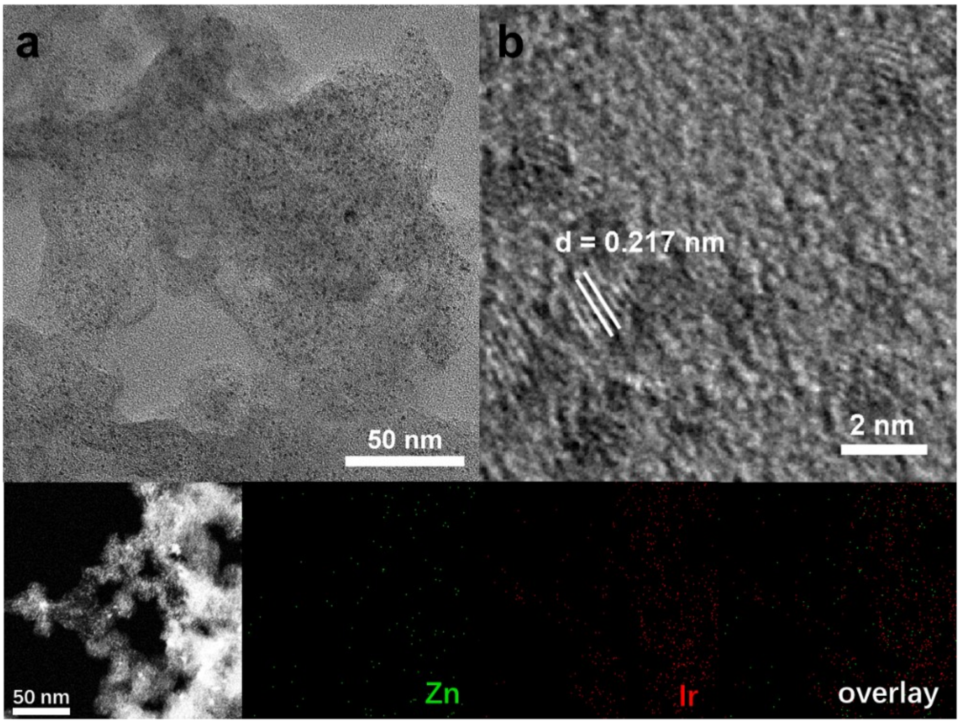


Fig. S12 (a) TEM (b) HRTEM image (c) HAADF-STEM-EDS element mappings of of $IrZn_{10}$.

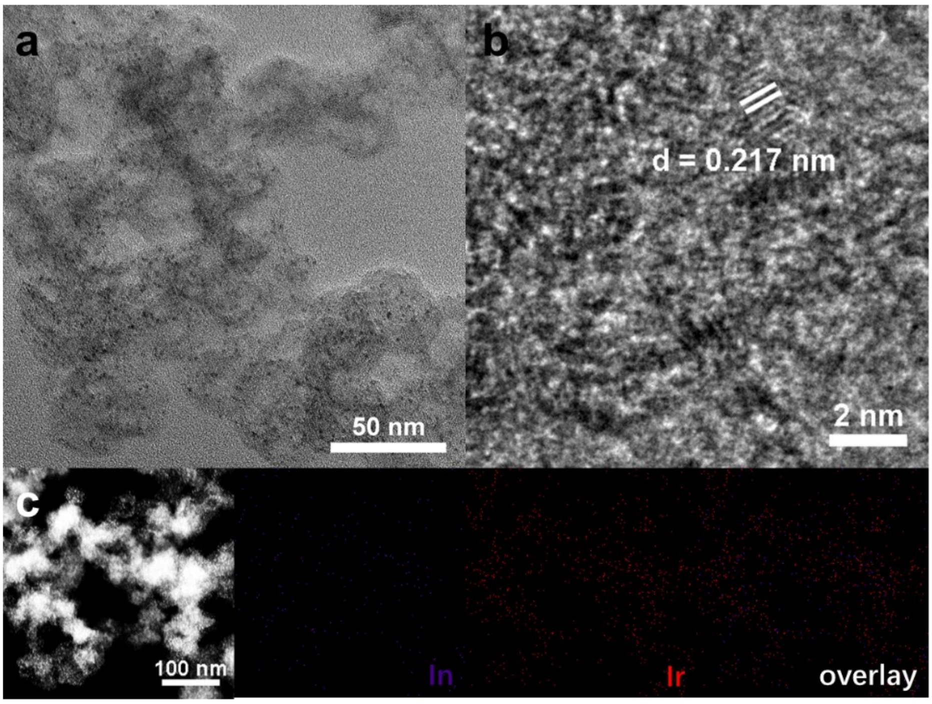


Fig. S13 (a) TEM (b) HRTEM image (c) HAADF-STEM-EDS element mappings of $IrIn_1$.

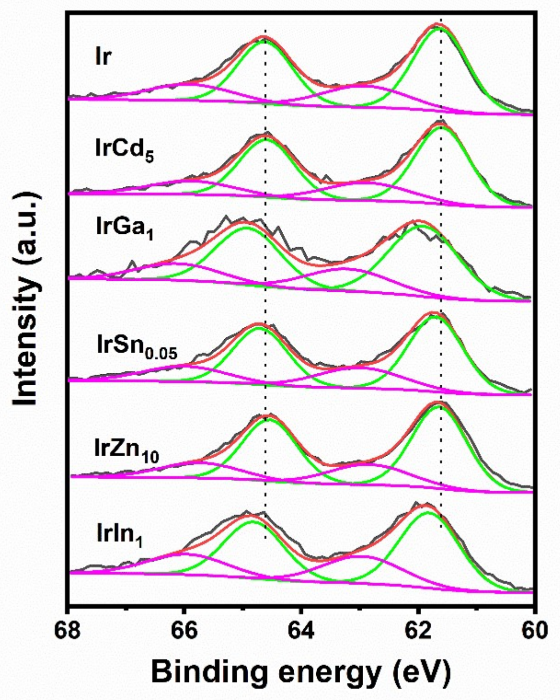


Fig. S14. (a) XPS spectra of Ir 4f in Ir and Ir-M alloy catalysts.

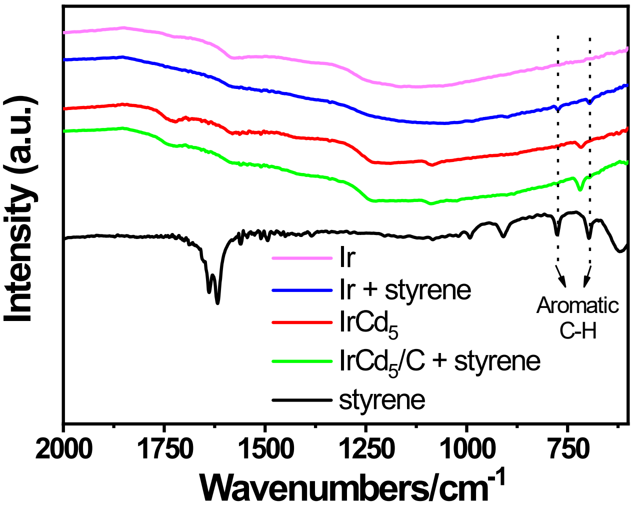


Fig. S15 IR spectra of the catalysts treated with styrene. The doublet 770 and 690 cm^{-1} associate with the Aromatic C-H, and the signal at 720 cm^{-1} assigns to C-Cl bond.

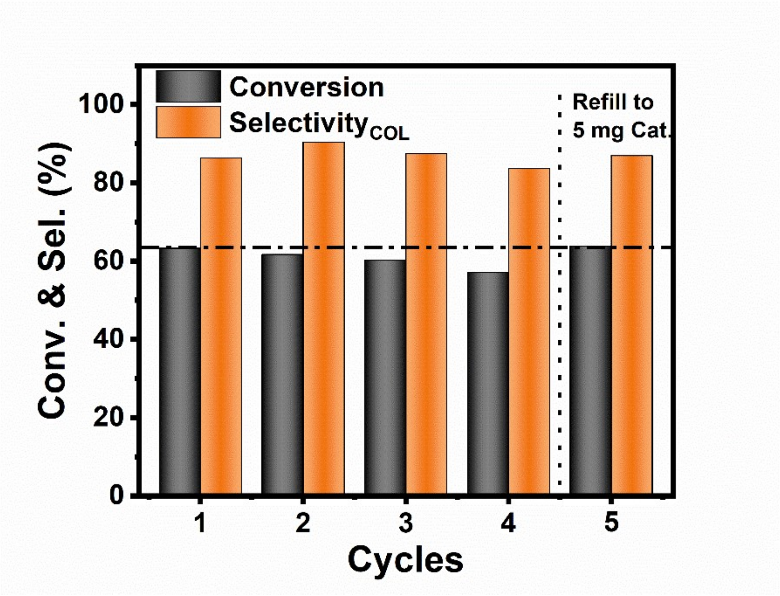


Fig. S16 Recycle test of $IrCd_5$. Reaction condition: 5 mg $IrCd_5$, 50 μL CAL, 1 mL isopropanol, 1 mL DIW, RT, 1 MPa H_2, 6 h. After 4 cycles reaction, the amount of catalyst was refilled to 5 mg, and then carried out the fifth cycle test. Fortunately, the catalytic performance recovered to a level comparable to that of the first cycle, demonstrating the impressive stability of $IrCd_5$ catalyst.

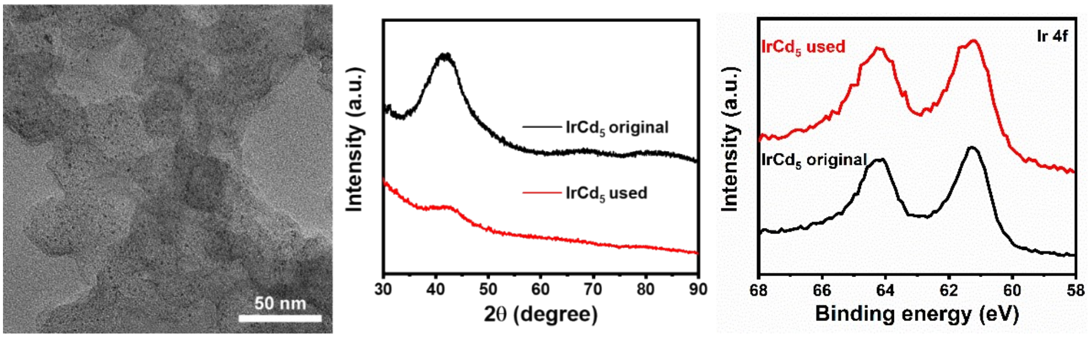


Fig. S17 TEM image, XRD and XPS pattern of used $IrCd_5$.

Table S1 Metal loading of the different samples determined by ICP-MS.

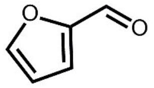
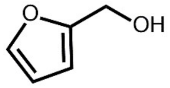
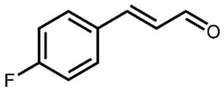
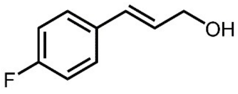
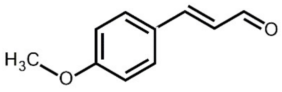
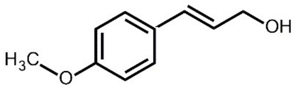
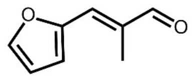
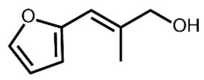
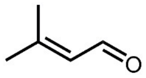
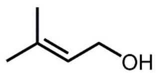
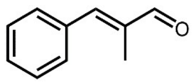
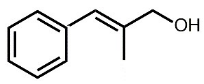
Catalysts	Mass Loading (wt%, ICP-MS)		Molar ratio M : Ir /at%
	Ir	Second metal	
Ir	4.71	-	-
$IrCd_{0.5}$	4.94	0.28	0.10
$IrCd_1$	2.56	0.17	0.11
$IrCd_2$	3.36	0.26	0.13
$IrCd_5$	3.46	0.42	0.21
$IrCd_{10}$	4.63	0.70	0.26
$IrGa_{0.5}$	5.96	0.92	0.42
$IrGa_1$	7.95	3.41	1.18
$IrGa_2$	7.39	5.92	2.21
$IrGa_5$	6.07	11.10	5.04
$IrGa_{10}$	3.35	16.86	13.85
$IrSn_{0.05}$	4.95	0.18	0.06
$IrSn_{0.5}$	4.86	1.76	0.59
$IrSn_1$	4.79	3.16	1.07
$IrSn_2$	3.98	4.99	2.03
$IrSn_5$	2.79	6.64	3.85
$IrZn_{0.5}$	7.02	0.03	0.01
$IrZn_1$	7.13	0.06	0.03
$IrZn_2$	7.60	0.09	0.03
$IrZn_5$	5.99	0.09	0.04
$IrZn_{10}$	3.20	0.26	0.24
$IrIn_{0.5}$	5.42	0.81	0.25
$IrIn_1$	3.75	0.62	0.28
$IrIn_2$	6.07	1.40	0.39
$IrIn_5$	7.19	1.61	0.37
$IrIn_{10}$	6.22	1.97	0.53

Table S2 Selective hydrogenation performance of different catalyst. [a]

Catalysts	Conv. /%	Sel$_{\mathrm{HCAL}}$ /%	Sel$_{\mathrm{HCOL}}$ /%	Sel$_{\mathrm{COL}}$ /%	TOF /h^{-1}
Ir	**70.0**	**14.3**	**4.8**	**80.9**	**23.8**
IrCd$_{0.5}$	91.9	1.0	8.2	90.8	29.8
IrCd$_{1}$	96.8	0.3	5.8	93.9	60.6
IrCd$_{2}$	96.7	0.2	6.3	93.5	46.1
IrCd$_{5}$	**96.7**	**0.3**	**5.4**	**94.3**	**44.8**
IrCd$_{10}$	96.6	0.3	3.5	96.2	33.4
IrGa$_{0.5}$	74.2	9.5	2.8	87.6	19.9
IrGa$_{1}$	**93.0**	**1.7**	**6.3**	**92.0**	**18.7**
IrGa$_{2}$	97.5	0.4	11.3	88.3	21.1
IrGa$_{5}$	87.4	2.3	4.2	93.5	23.1
IrGa$_{10}$	45.5	5.8	1.6	92.6	21.8
IrSn$_{0.05}$[b]	**93.8**	**4.8**	**4.9**	**90.3**	**30.4**
IrSn$_{0.5}$	82.1	2.8	6.8	90.3	27.1
IrSn$_{1}$	82.0	2.5	5.9	91.6	27.4
IrSn$_{2}$	25.2	5.3	0.1	94.6	10.1
IrSn$_{5}$	10.4	6.4	0.1	93.5	6.0
IrZn$_{0.5}$	93.0	4.9	13.0	82.1	21.2
IrZn$_{1}$	93.6	4.1	10.1	85.8	21.0
IrZn$_{2}$	90.5	4.4	11.3	84.2	19.1
IrZn$_{5}$	93.0	3.1	12.2	84.7	24.9
IrZn$_{10}$	**95.0**	**0.9**	**1.0**	**92.1**	**47.5**
IrIn$_{0.5}$	98.2	15.4	0.7	83.8	29.0
IrIn$_{1}$	**99.1**	**5.5**	**0.1**	**94.3**	**42.3**
IrIn$_{2}$	99.6	0.1	1.5	98.4	26.3
IrIn$_{5}$	99.8	0.1	1.7	98.2	22.2
IrIn$_{10}$	99.6	0.1	0.9	99.0	25.6

[a] Reaction condition: substrate (0.5 mmol), catalyst (5 mg), isopropanol (1 mL), water (1 mL), 1 MPa H_2, RT 12 h. [b] Reaction time: 7 h

Table S3 Hydrogenation of α,β-unsaturated aldehyde catalyzed by $IrCd_5$.

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			11	99.9	99.9
2			9	99.9	91.3
3			7	99.9	94.0
4			9	99.9	91.1
5			11	99.9	95.4
6			9	99.9	91.1

Reaction condition: substrate (0.1 mmol), catalyst (5 mg), isopropanol (1 mL), water (1 mL), 1 MPa H_2, room temperature.

Reference

1. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B - Condens. *Matter Mater. Phys.* 1996, **54**, 11169–11186.

2. Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* 1994, **50**, 17953–17979.

3. Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B - Condens. *Matter Mater. Phys.* 1999, **59**, 1758–1775.