Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

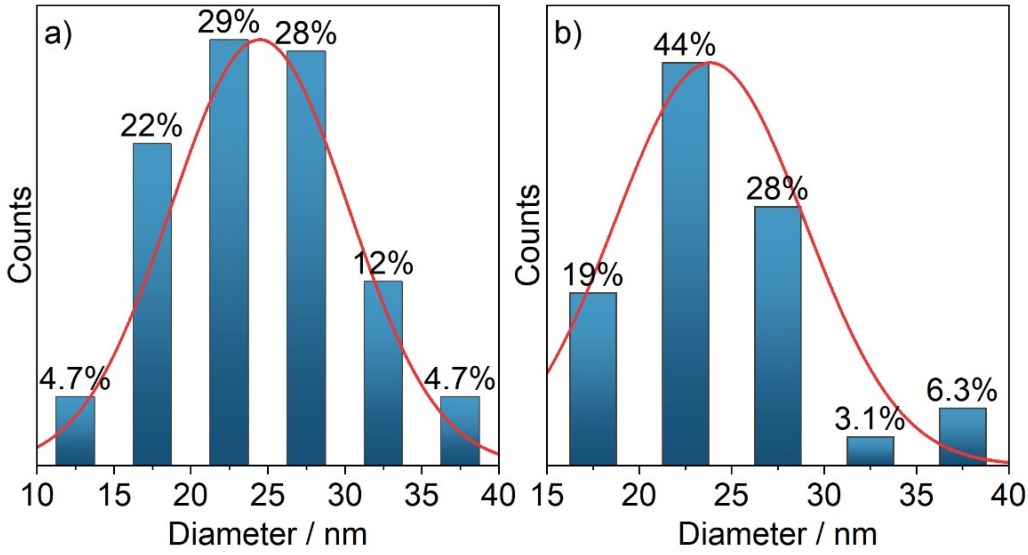

Figure S1. Size distribution of Bi_4Ir_2O particles obtained at a) 180 °C and b) 220 °C after 10 min.

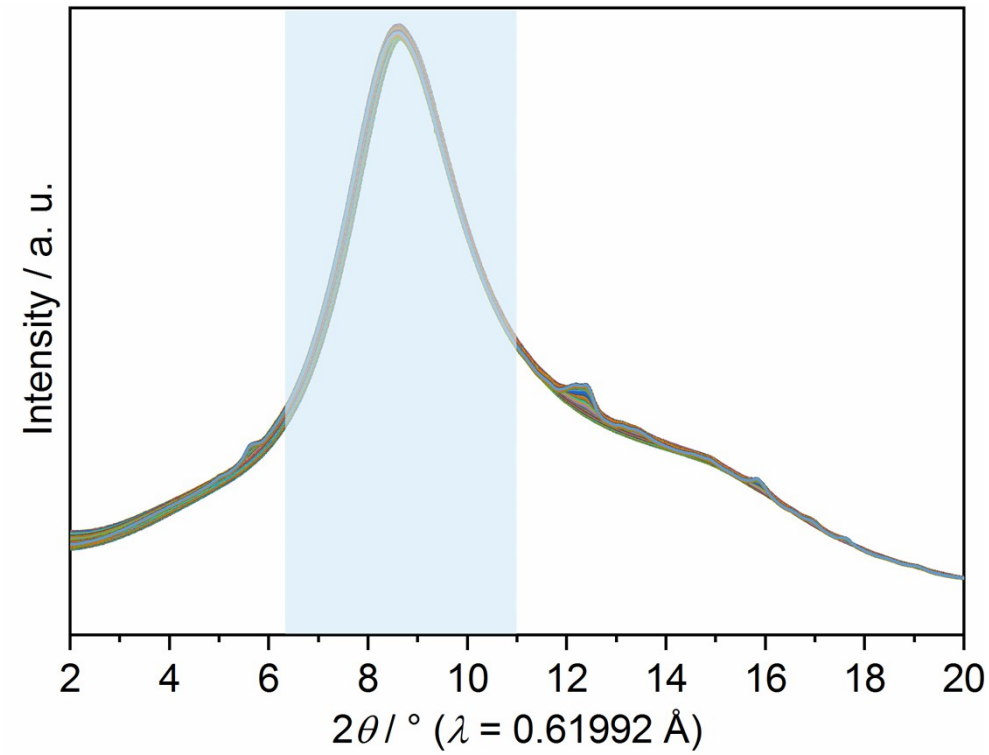

Figure S2. All *in-situ* obtained powder-patterns. Blue box shows amorphous background from the glass vessel omitted in Figure 5.

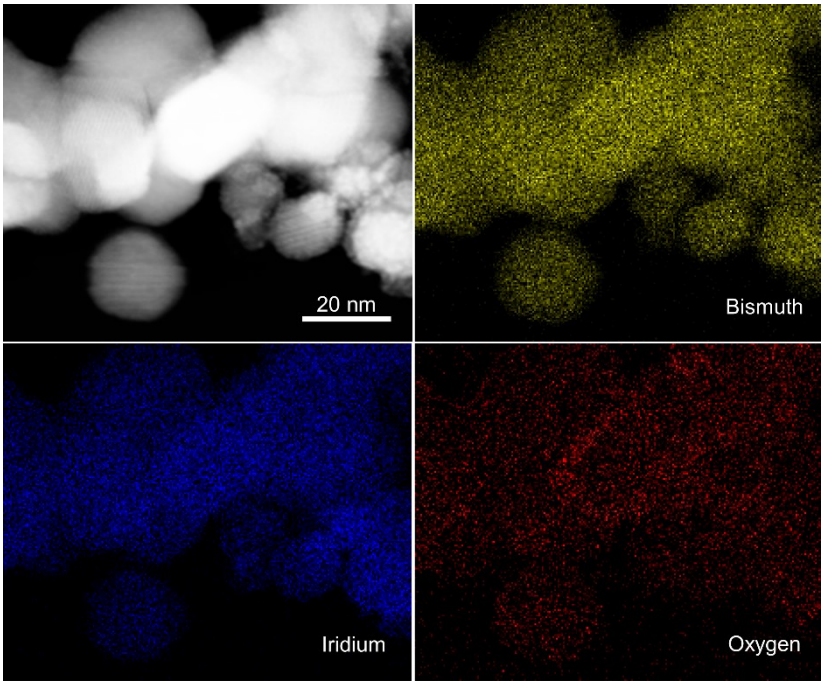

Figure S3. EDX measurement and the resulting elemental distribution of bismuth, iridium and oxygen in the particles.

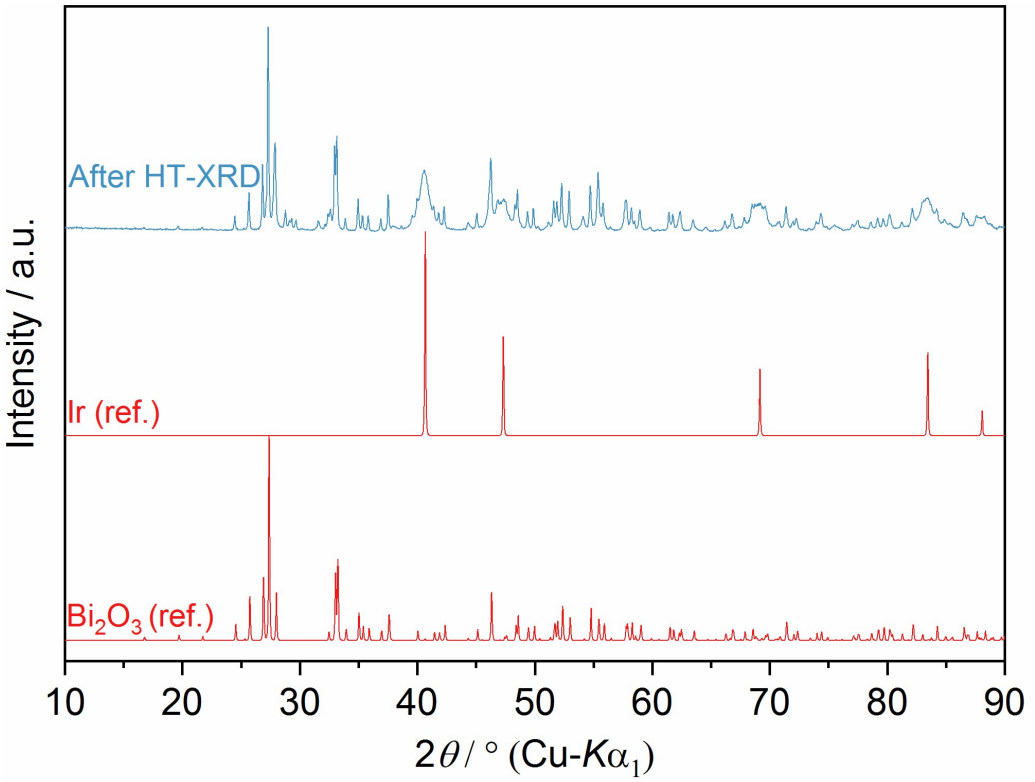

Figure S4. PXRD pattern of the powder obtained after the HT-XRD measurement. Ir (ref.) and Bi_2O_3 (ref.) are the calculated diffractograms based on the crystal structure of Ir (CSD-640730) and Bi_2O_3 (CSD-15072)

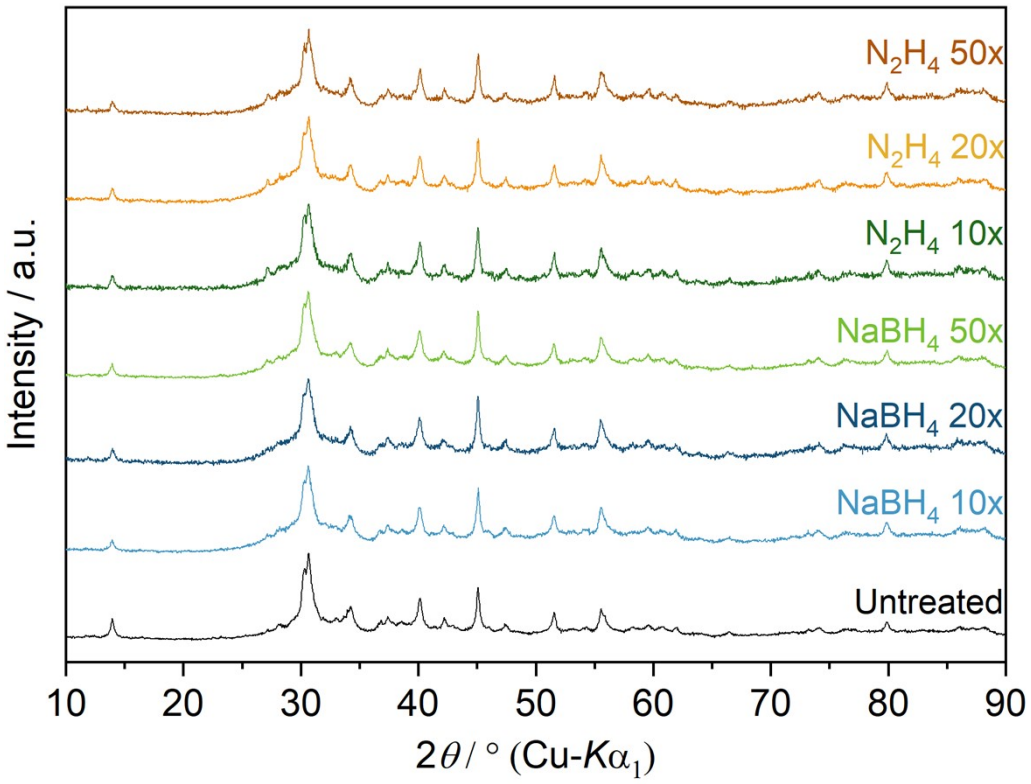

Figure S5. PXRD patterns obtained after treatment of freshly synthesized Bi_4Ir_2O with solutions of $NaBH_4$ and N_2H_4 in molar ratios of 1:10, 1:20 and 1:50 at 60 °C for 30 min.

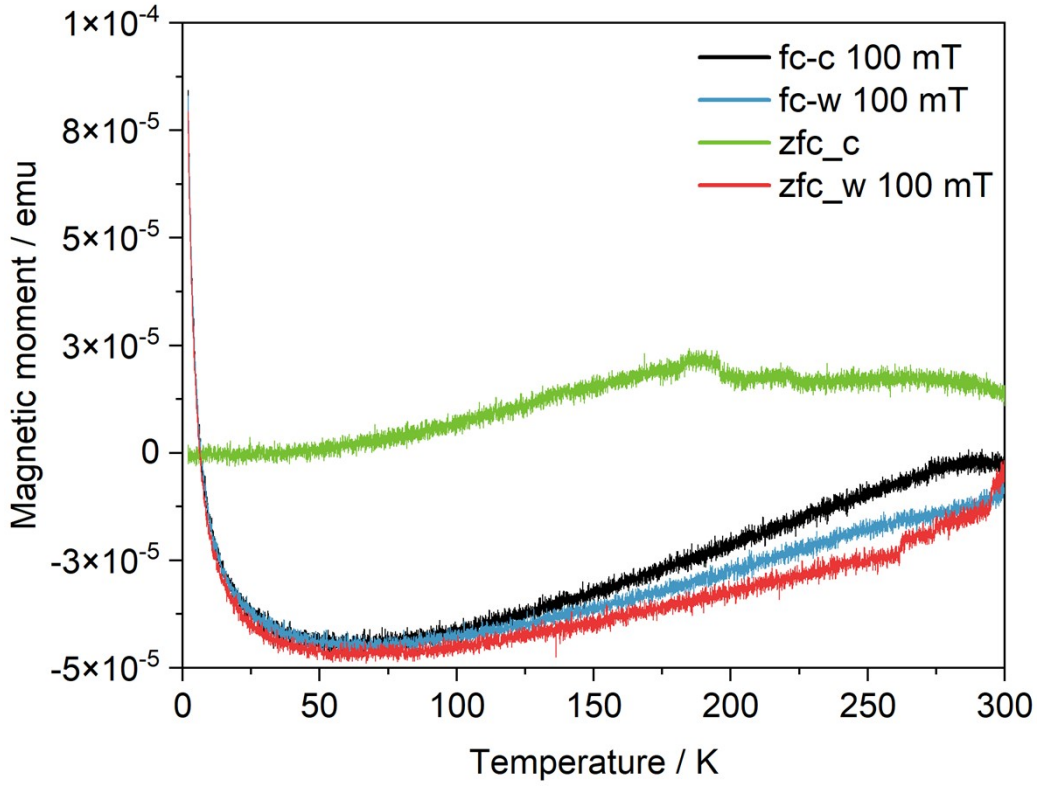

Figure S6. Magnetic moment of Bi_4Ir_2O measured against temperature in the range of 2 to 300 K. The applied field during cooling and warming was 100 mT.

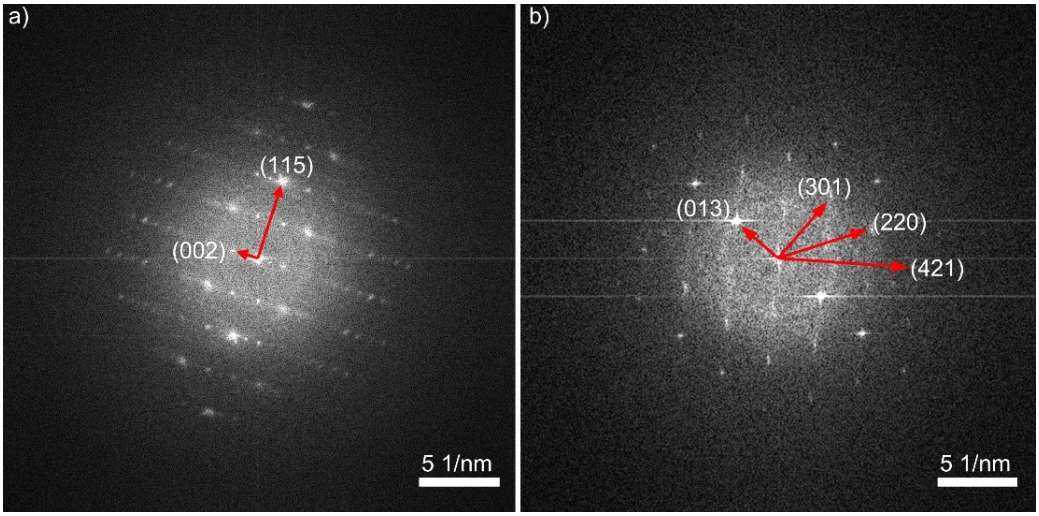

Figure S7. Selected area diffraction patterns of Bi_4Ir_2O.

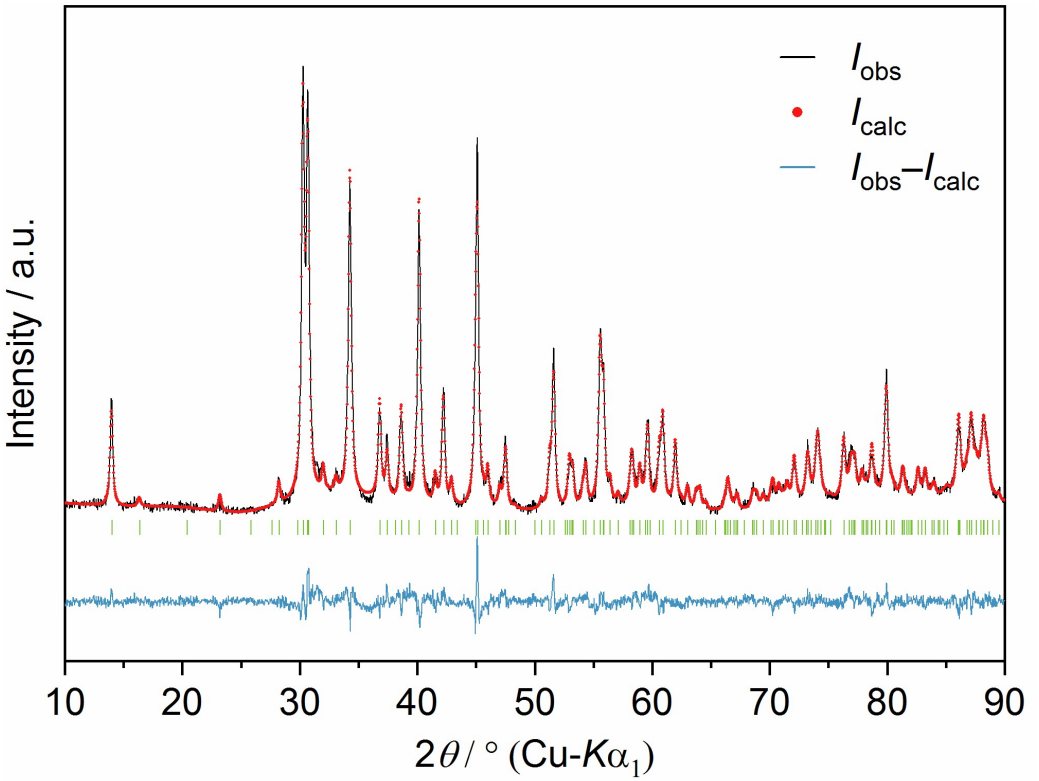

Figure S8. Rietveld refinement plot of Bi_4Ir_2O. Peak positions are marked by green vertical bars. R_p= 0.05959, R_{wp}= 0.07595, R_{exp}= 0.06648, GOF= 1.14.

Table S1. Crystallographic and Rietveld refinement data of Bi_2IrO. *R* values as defined by the *TOPAS Academic V5* manual.

Empirical formula	Bi_4Ir_2O
Formula weight	1236.36
T / K	296(1)
Crystal system	orthorhombic
Space group	*Pnma*
a / Å	5.9826(7)
b / Å	4.0121(5)
c / Å	12.6253(5)
V / Å^3	303.04(6)
Z	2
ρ_{calc} / g cm^{-3}	13.72
Radiation	Cu-*K*α$_1$ (λ = 1.5406 Å)
2θ range / °	5 to 90
Step width / °	0.026
Scan time / h	1
Data points	3269
R_{Bragg}	0.02434
R_p	0.05959
R_{wp}	0.07595
R_{exp}	0.06648
Goodness of fit (χ)	1.14

Table S2. Wyckoff positions, coordinates and displacement parameters (/Å) for the atoms in Bi_4Ir_2O. All atoms reside on Wyckoff positions 4*c*.

Atom	*x*	*y*	*z*	B_{eq}
Bi1	0.1121(6)	3/4	0.1573(3)	1.8(1)
Bi2	0.1051(6)	1/4	0.4012(2)	2.1(1)
Ir	0.1674(6)	1/4	0.0119(3)	2.8(1)
O	0.254(9)	3/4	0.3127(5)	3

Table S3. Interatomic distances in Bi_4Ir_2O.

Atom #1	Atom #2	Symmetry code	*d* / Å
Bi1	Bi1	x, 1+y, z	4.01(1)
Bi1	Bi1	-1/2+x, 3/2-y, 1/2-z	3.80(1)
Bi1	Bi2	-1/2+x, 3/2-y, 1/2-z	3.71(1)
Bi1	Bi2	x, y, z	3.68(1)
Bi1	Bi2	1/2-x, 1-y, -1/2+z	3.65(1)
Bi1	Bi2	1/2+x, 1/2-y, 1/2-z	3.64(1)
Bi1	Ir	x, y, z	2.74(1)
Bi1	Ir	-x, 1/2+y, -z	2.71(1)
Bi1	O	-1/2+x, 3/2-y, 1/2-z	2.18(5)
Bi1	O	x, y, z	2.14(2)
Bi2	Bi2	x, 1+y, z	4.01(1)
Bi2	Bi2	-x, 1/2+y, 1-z	3.44(1)
Bi2	Ir	-1/2+x, 1/2-y, 1/2-z	2.84(1)
Bi2	Ir	1/2-x, 1-y, 1/2+z	2.80(1)
Bi2	O	x, y, z	2.52(2)
Ir	Ir	-x, 1/2+y, -z	2.81(1)

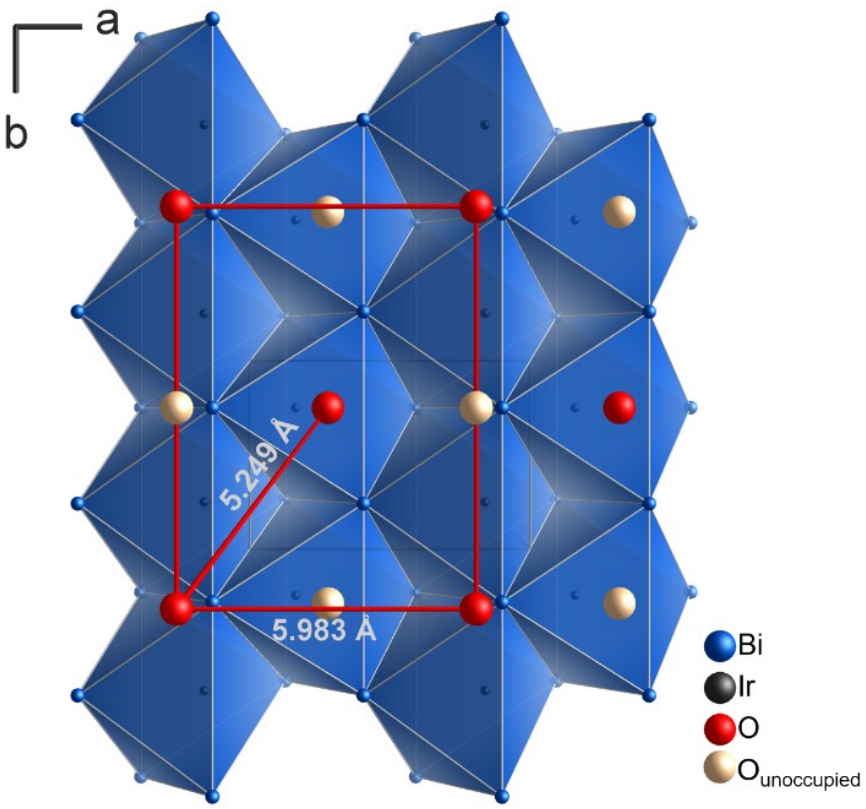

Figure S9. Hypothetical ordered structure model in unit cell with *b*' = 2*b*.

Table S4. Coordinates of the atoms of a hypothetical oxygen-ordered structure of Bi_4Ir_2O with maximum O···O distances. This superstructure in the monoclinic space group *P* 1 1 2_1/*n* (*a*' = *a* = 5.9826 Å; *b*' = 2*b* = 8.0242 Å; *c*' = *c* = 12.6253 Å; $\alpha = \beta = \gamma = 90°$) was derived from the refined structure model in *Pnma* by group-subgroup relationships. All atoms reside on Wyckoff positions 4*e*.

Atom	*x*	*y*	*z*
Bi1	0.1121	0.375	0.1573
Bi2	0.1121	0.875	0.1573
Bi3	0.1051	0.125	0.4012
Bi4	0.1051	0.625	0.4012
Ir1	0.1674	0.125	0.0119
Ir2	0.1674	0.625	0.0119
O	0.2540	0.375	0.3127

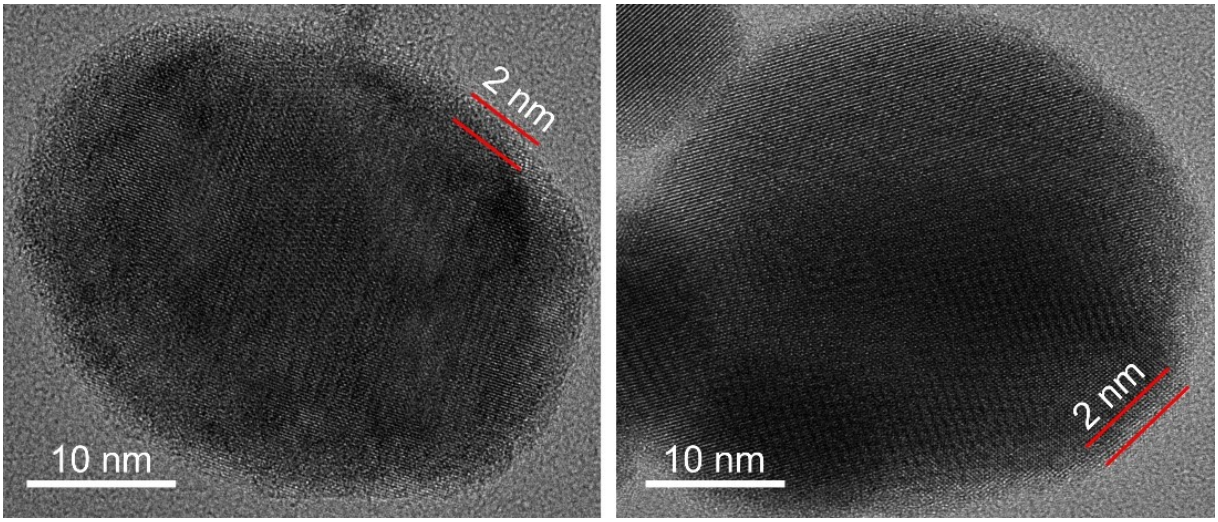

Figure S10. HR-TEM images of Bi_4Ir_2O particles encased in an amorphous shell of 2–4 nm of thickness.