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

Supplementary Information

UiO-66 metal-organic frameworks-derived ZrO_2/ZnO mesoporous material for high-efficiency detection towards NO_2 at room temperature

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Table S1 Comparison of gas-sensing performance of ZrO_2, ZnO and other hybrid materials to NO_2 gas with previous reports.

Sensor material	Gas	Operating temperature	Gas concentration	Response (s)	Response time	Recovery time	Detection limit	Ref.
SnO_2-ZrO_2	NO_2	150°C	10 ppm	24.7①	-	-	-	1
ZrO_2-Y_20_3(8%)	H_2	150°C	1000 ppm	7.3①	5 s	7 s	-	2
In_2O_3/ZrO_2	C_3H_6O	260°C	100 ppm	60.38①	1 s	38 s	10 ppm	3
SnO_2/ZrO_2	TEA	190°C	20 ppm	4①	1 s	1 s	-	4
NiO/ZnO	ethanol	260°C	100 ppm	61①	-	-	-	5
Ag/ZnO	NH_3	150°C	10 ppm	29.5①	13 s	20 s	10 ppm	6
MXene/GO/CuO /ZnO	NH_3	RT	200 ppm	96%②	-	-	4.1 ppm	7
ZnO/TiO_2	NO_2	500°C	50 ppm	7.5①	-	-	-	8
Al_2O_3/ZnO	acetylene	120°C	200 ppm	96.46%②	-	-	1 ppm	9
ZnO/rGO	NO_2	RT	50 ppm	9.61①	25	15	5 ppm	10
CuO/rGO	NO_2	RT	5 ppm	400.8%②	6.8	55.1	50 ppb	11
Pd-SnO_2/rGO	NO_2	RT	100 ppm	7.92①	56.9	22.1	37.8 ppb	12
CdS/CuO/rGO	NO_2	RT	10 ppm	7.25①	45.6	14.2	50 ppb	13
ZnO/ZrO_2	**NO_2**	**RT**	**100 ppm**	**40.35①**	**1.5 s**	**42.2 s**	**50 ppb**	**This work**

① :$S = R_a/R_g$ or $S = R_g/R_a$

② :$S = |R_a-R_g|/R_a \times 100\%$ or $S = |R_g-R_a|/R_a \times 100\%$

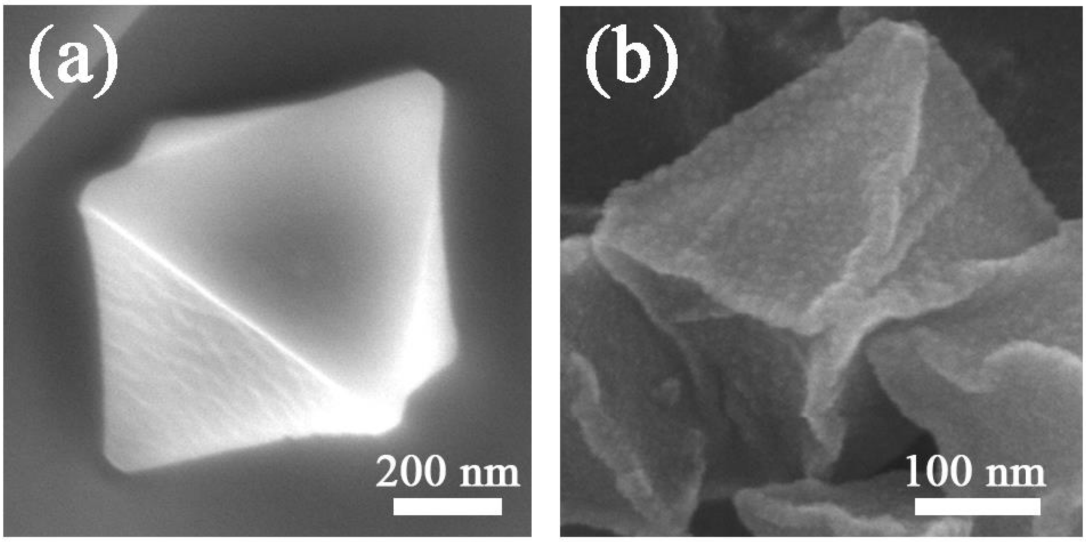

Fig. S1 (a) SEM images of UiO-66; (b) SEM images of ZrO_2.

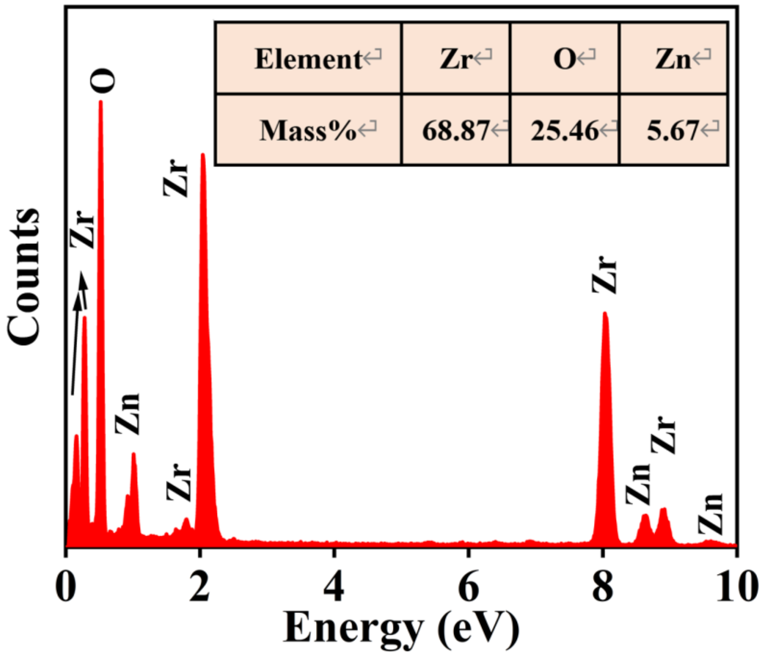

Fig. S2 EDS analysis of UZZ-2.

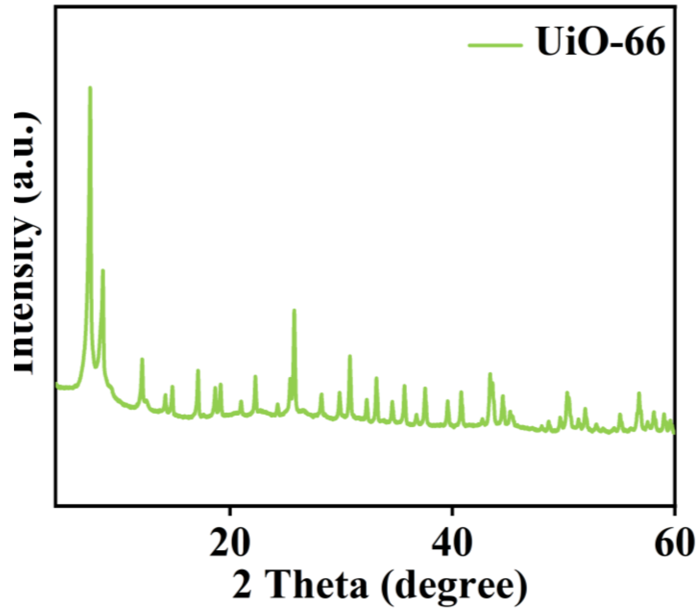

Fig. S3 PXRD diagram of UiO-66.

Fig. S3 shows the PXRD diagram of the metal-organic skeleton UiO-66. Various characteristic peaks of UiO-66 observed at 7.5°, 8.6°, 26° and 31°index to the (111), (200), (600) and (731) planes, respectively, consistent with reported literature.[14, 15]

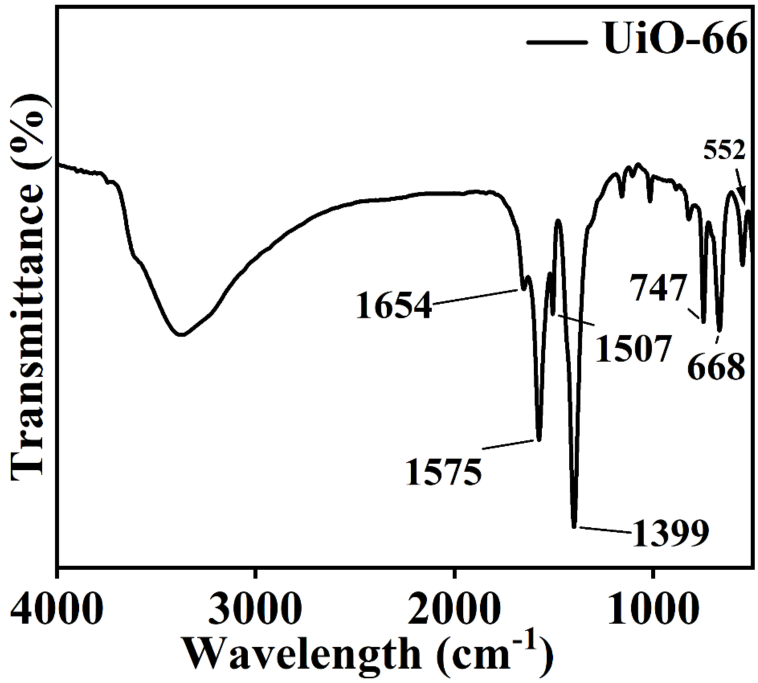

Fig. S4 FT-IR spectrum of UiO-66.

For the original UiO-66 sample, the strong characteristic peak at 3400^{-1} comes from the hydroxyl vibrations of the adsorbed H_2O molecules. The peak at 1654 cm^{-1} is attributed to the bending vibration of -OH, and the two characteristic peaks at 1575 and 1399 cm^{-1} are the symmetric stretching vibration and the asymmetric stretching vibration of the organic ligand O-C=O. The characteristic peak at 1507 cm^{-1} is the vibrational peak of C=C in the benzene ring, and at about 747 and 668 cm^{-1} are the vibrational peaks typical of C-H aromatic organic compounds. In addition, the asymmetric stretching vibration peak of Zr-(OC) is at about 552 cm^{-1}.[16, 17]

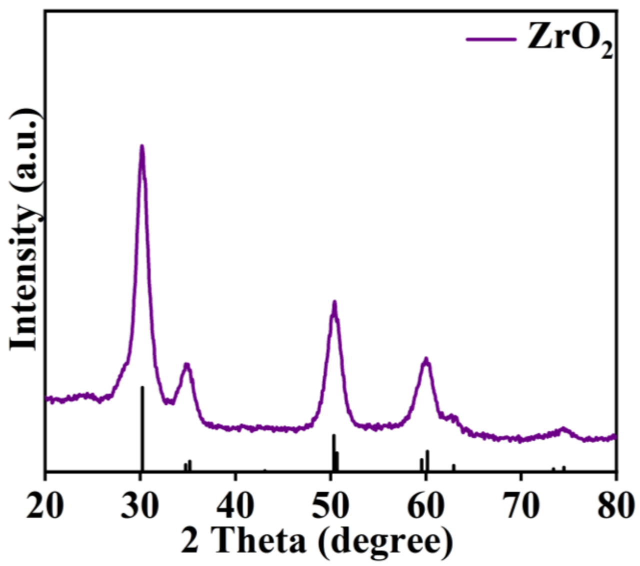

Fig. S5 XRD diagram of ZrO_2.

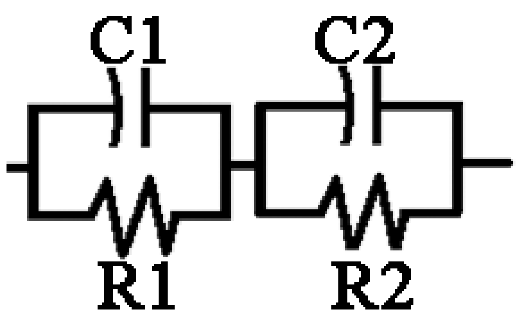

Fig. S6 Equivalent circuit model for interpreting EIS data.

Table S2 Parameters obtained by fitting the experimental curve to the equivalent circuit.

Raw materials	**R_1 (Ω)**	**C_1 (F)**	**R_2 (Ω)**	**C_2 (F)**
UZZ-2	8.367×10^{4}	9.521×10^{-11}	1.874×10^{6}	1.792×10^{-10}
UZZ-1	2.062×10^{5}	6.693×10^{-11}	1.101×10^{7}	2.341×10^{-10}
UZZ-3	2.436×10^{5}	6.447×10^{-11}	9.455×10^{6}	3.131×10^{-10}
ZrO_2	2.436×10^{5}	6.447×10^{-11}	9.454×10^{6}	3.131×10^{-9}

Where R_1 is the resistance at the electrode/sample interface, C_1 is the associated capacitance. R_2 is mainly derived from the conductivity of the sample itself, and C_2 is the corresponding associated capacitive property of the material itself.

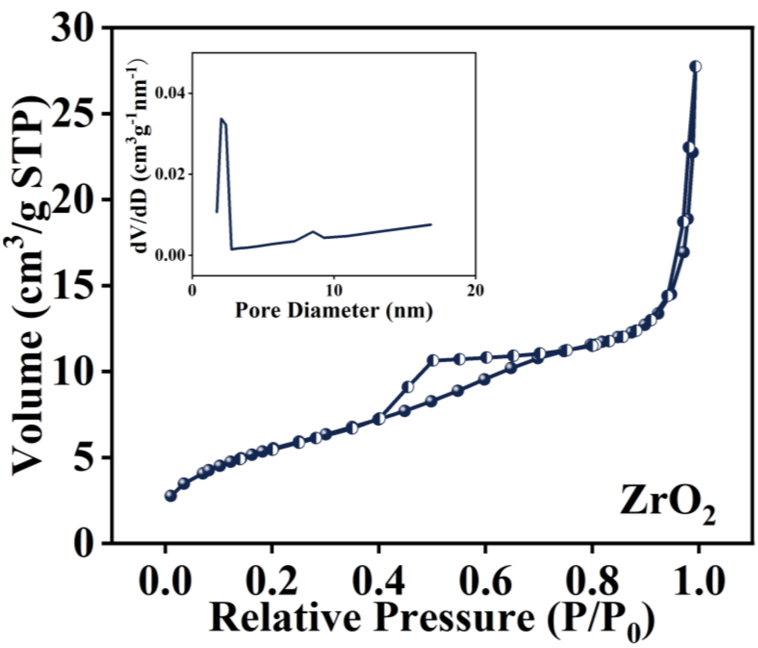

Fig. S7 N_2 adsorption-desorption isotherms for pure samples of ZrO_2 (inset shows the pore size distribution curve).

Table S3 Sample BET surface area, average pore size and pore volume.

Sample	S_{set} (m^2 g^{-1})	Pore Size (nm)	Pore Volume (cm^{-3} g^{-1})
ZrO_2	20.4676	9.5330	0.0429
UZZ-1	42.0633	4.4520	0.0606
UZZ-2	43.3205	5.8679	0.0801
UZZ-3	28.4719	6.2261	0.0511

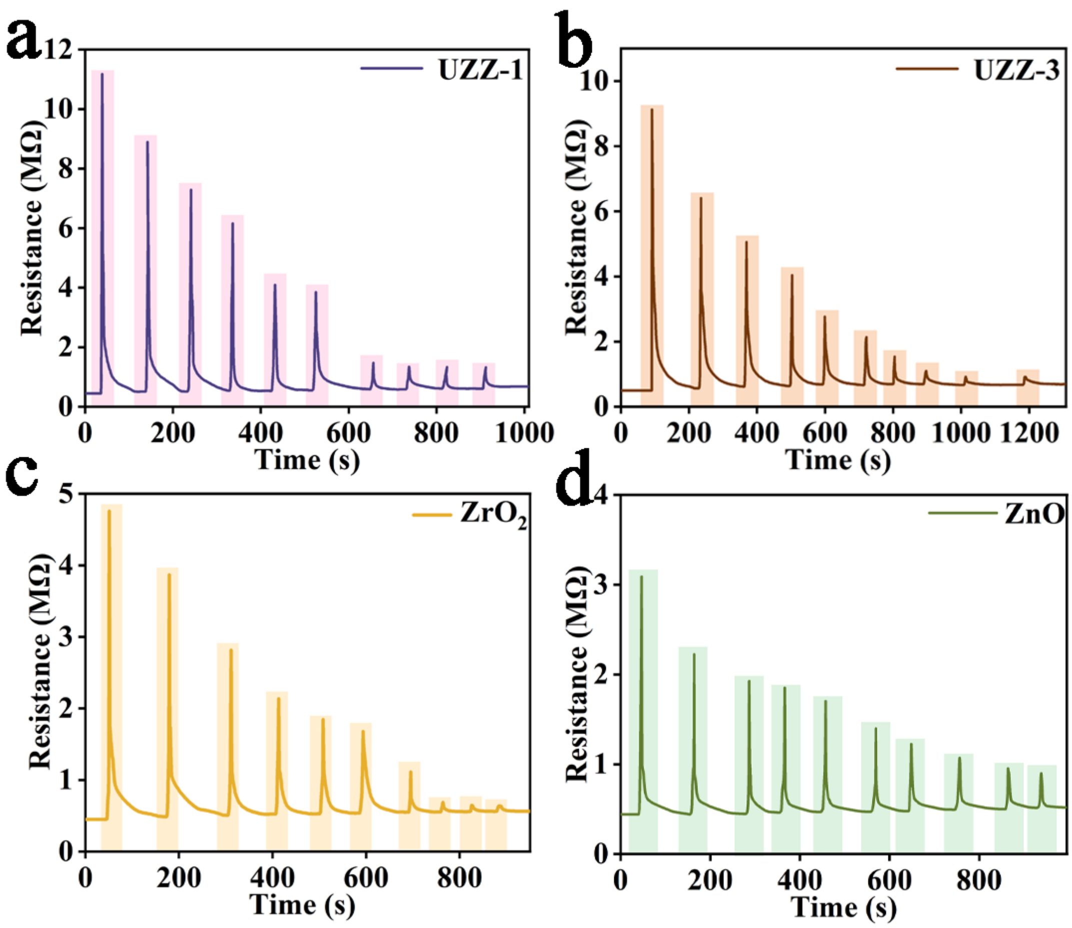

Fig. S8 Response curves of (a) UZZ-1; (b) UZZ-3; (c) ZrO_2; (d) ZnO sensors at room temperature for different concentrations of NO_2.

Table S4 Response, response time and recovery time of samples at different NO_2 concentrations at room temperature.

Sample	UZZ-2			UZZ-1			UZZ-3			ZrO_2			ZnO		
NO_2(ppm)	**S**	**Tres/s**	**Trec/s**	**S**	**Tres/s**	**Trec/s**	**S**	**Tres/s**	**Trec/s**	**S**	**Tres/s**	**Trec/s**	**S**	**Tres/s**	**Trec/s**
100	**40.35**	1.40	42.20	**24.84**	4.80	77.50	**18.25**	6.40	89.40	**10.57**	7.20	98.00	**6.99**	5.30	59.20
50	**37.39**	2.30	38.50	**17.31**	5.50	70.80	**11.07**	6.80	60.60	**7.96**	8.10	95.10	**5.02**	6.20	56.80
30	**34.39**	3.20	36.30	**14.16**	6.90	67.20	**8.21**	7.50	54.20	**5.62**	9.20	48.30	**4.17**	7.40	38.00
10	**27.97**	4.70	32.80	**11.31**	7.60	51.30	**6.34**	7.80	43.50	**4.04**	10.20	32.40	**3.99**	8.50	36.40
5	**22.14**	6.10	29.60	**7.20**	8.20	39.80	**3.86**	9.50	28.80	**3.49**	15.20	30.20	**3.43**	9.20	28.50
3	**17.63**	7.30	28.30	**6.79**	10.40	36.40	**3.05**	10.60	23.50	**3.12**	16.10	21.30	**2.92**	10.20	25.00
1	**13.14**	10.80	22.40	**2.49**	11.60	15.00	**2.20**	13.20	21.20	**2.01**	23.30	15.40	**2.53**	10.80	23.60
0.5	**9.19**	11.90	20.00	**2.24**	13.40	11.40	**1.56**	15.40	19.30	**1.24**	24.80	5.80	**2.12**	11.20	21.40
0.3	**7.01**	12.80	17.00	**2.11**	15.20	7.60	**1.35**	17.50	6.20	**1.14**	25.50	3.60	**1.90**	15.40	18.10
0.1	**4.59**	13.00	13.80	**1.47**	17.30	3.30	**1.13**	19.20	4.30	**1.09**	25.80	3.20	**1.73**	16.20	13.40
0.05	**2.69**	14.70	8.50												

***S:Response** **T_{res}: Response time** **T_{rec}: Recovery time**

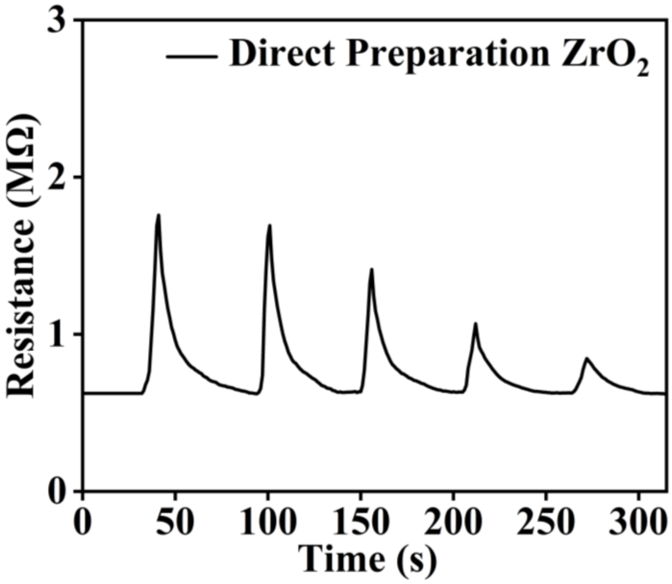

Fig. S9 The response curves of directly prepared ZrO_2 sensors towards different concentrations of NO_2 at room temperature.

Table S5 Peak position and peak area ratio of XPS O1s for UZZ-2 and UZZ-2+NO_2 samples (%).

Sample	**UZZ-2**			**UZZ-2+NO₂**		
Peak	O_l	O_V	O_C	O_l	O_V	O_C
Binding energy （eV）	530.7	531.5	532.7	530.8	531.7	532.8
Peak area ratio (%)	41.2	33.2	25.6	22.7	30.1	47.2

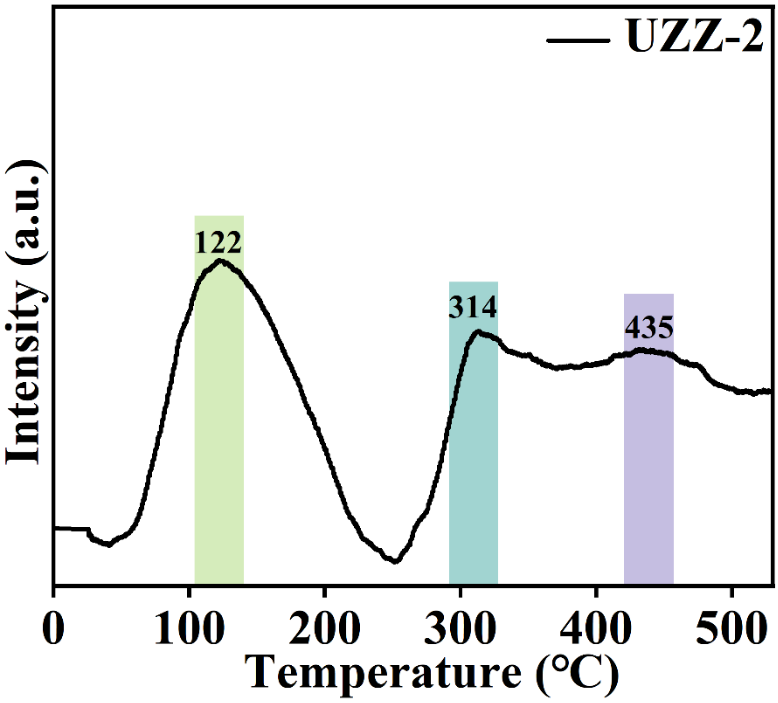

Fig. S10 NO_2-TPD of UZZ-2.

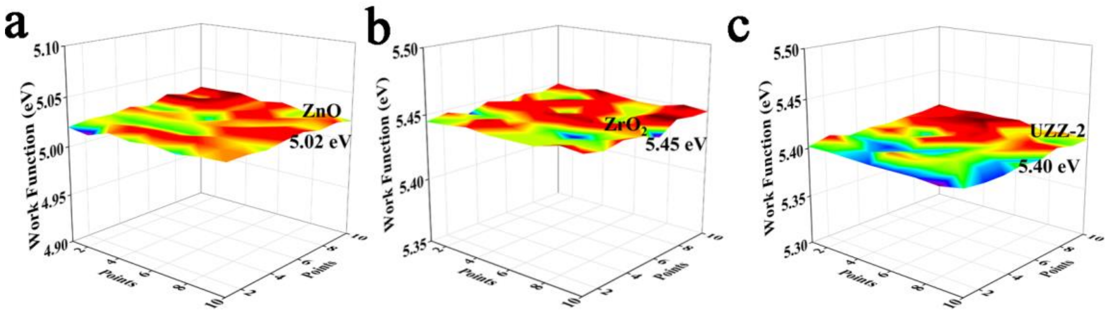

Fig. S11 Kelvin probe test of (a) ZnO; (b) ZrO_2; (c) UZZ-2.

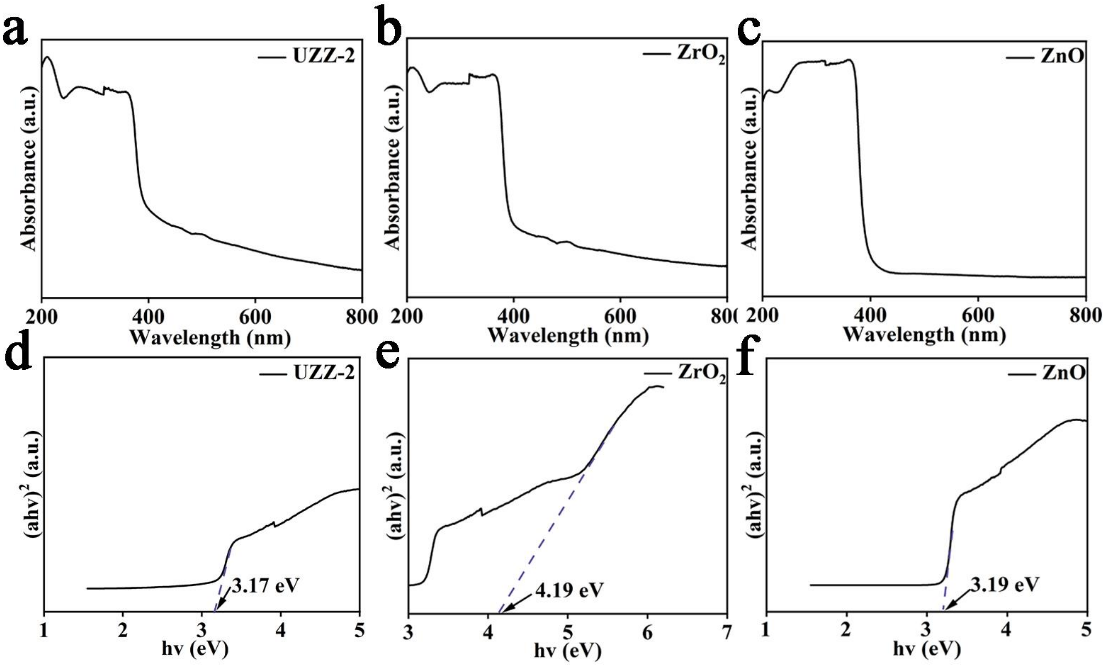

Fig. S12 (a-c) UV-vis absorption spectra of UZZ-2, ZrO_2 and ZnO; (d-f) Tauc plots of UZZ-2, ZrO_2 and ZnO. (The energy value at the intersection of the tangent line and the horizontal axis is the band gap width).

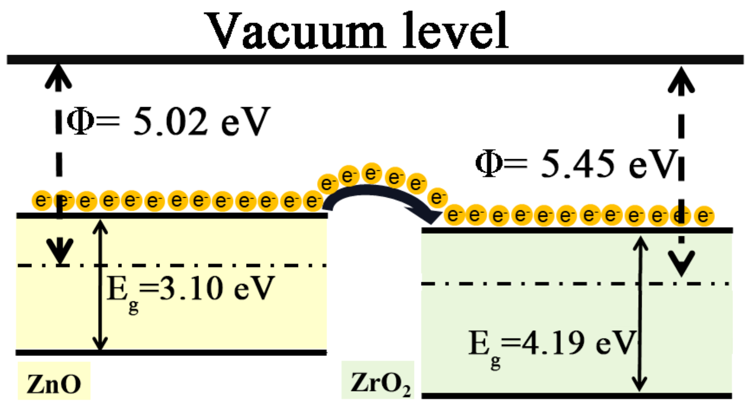

Fig. S13 Sche matic diagram of the work function of ZnO and ZrO_2.

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