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

Supporting Information

MOF-derived Synthesis of mesoporous In/Ga oxides and their ultra-sensitive ethanol-sensing properties

Y. F. Cui,[a] W. Jiang,[a] S. Liang, [a] L. F. Zhu[b] and Y. W. Yao *[a]

[a.] *Advanced Materials Institute, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China; E-mail:yaoyw@sz.tsinghua.edu.cn; Tel.: +86-755-2603-6796 .*

[b.] *Shenzhen Dovelet Sensors Technology Co. Ltd.*

Determine chemical moisture content

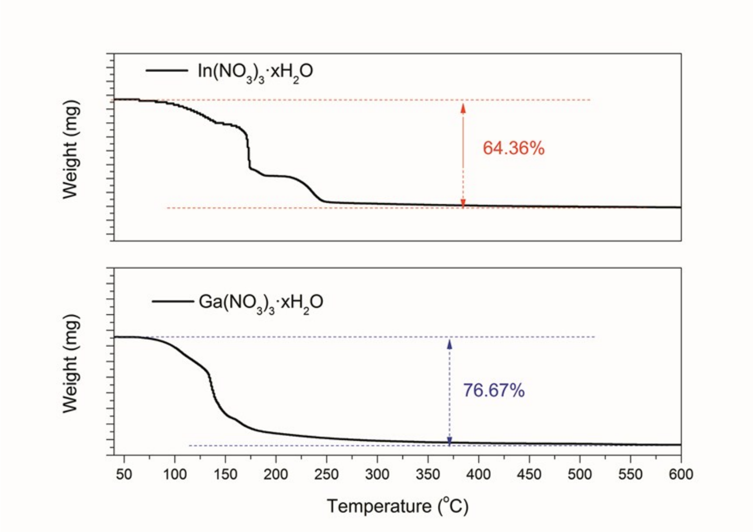

Fig. S1 TG curves of Indium nitrate hydrate and gallium nitrate hydrate

Solvothermal synthesis In/Ga oxides directly

0.6 mmol of indium nitrate, 0.4 mmol of gallium nitrate, and 3 mmol urea were dissolved in 12 ml absolute ethanol. The obtained mixture was sealed into a 20 mL Teflon-lined Parr autoclaves and maintained at the temperature of 100°C for 24 h, then cooled to room temperature naturally. The precipitates were washed by absolute ethanol for several times and dried at 60 °C. The resulting products were sintered at 500 °C for 3 h to obtain the In/Ga oxide powers, which were marked as IGO(3:2)-U.

Gas-Sensing Measurement

The Photo and scheme of gas sensing measurement system have been displayed in Fig S2.

According to Avo-gadro's law, vaporizing 1 mol C_2H_5OH in atmosphere generates 22.4 L of ethanol gas. The gas concentrations were determined by volume ratio of gasified ethanol to air in the chamber (volume of the chamber was 16 L). So, the amount of ethanol (liquid) could calcuated as follow.

$$Q = (16 \times C \times M) / (22.4 \times \rho) \times 10^{-6}$$

Here, Q is the volume of liquid ethanol (mL), M is the material molecular weight (g/mol), C is the concentration of the gas to be prepared(ppm), ρ is the liquid density (g/ml)

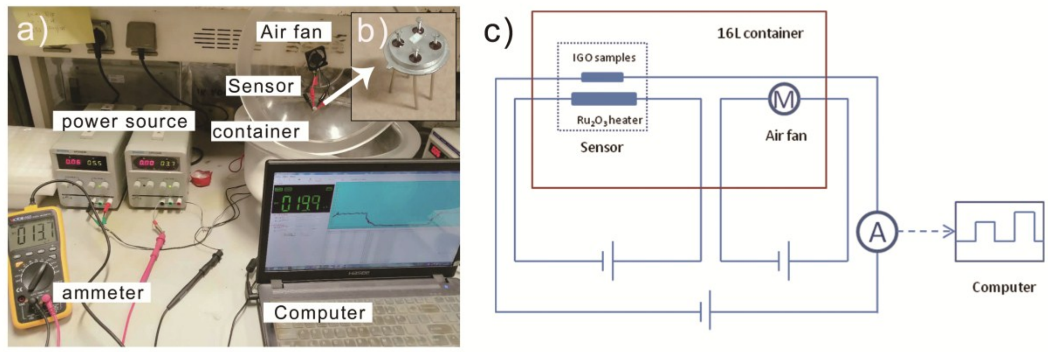

Fig. S2 Photo of a) gas sensing measurement system, b) sensor element based on the IGOs, and c) scheme of gas sensing measurement system

Morphology, structure and composition of IGO(3:2)-U

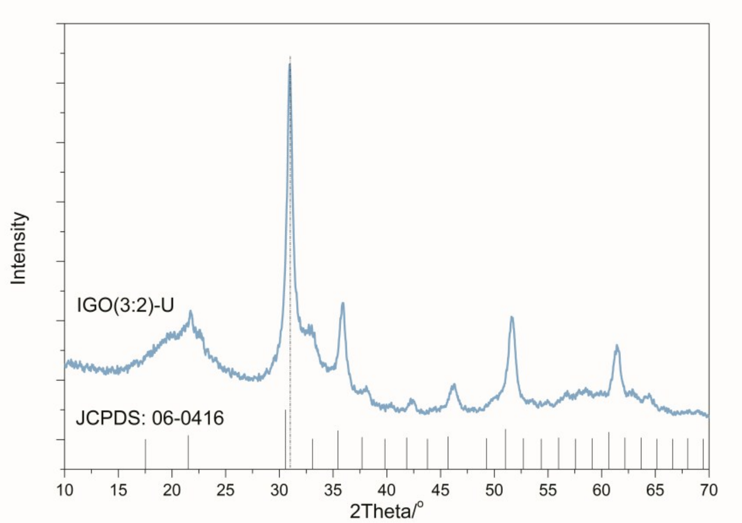

Fig. S3 XRD patterns of IGO(3:2)-U

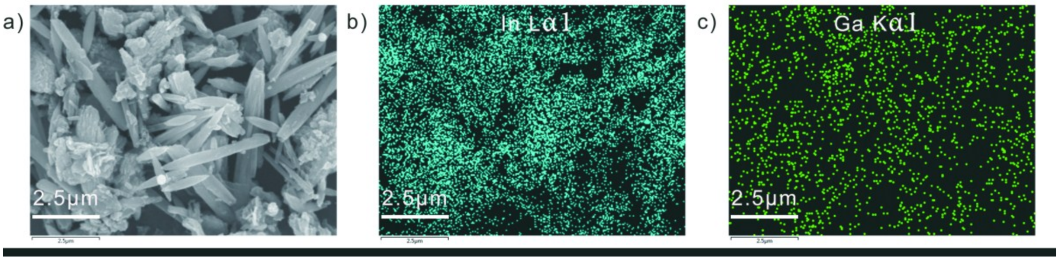

Fig. S4 a) SEM image and Elemental mapping images of b) In, c) Ga element of IGO(3:2)-Urea

Tab. S1 mole ratio of In and Ga in IGO(3:2)-U.

	Feed ratio	EDX ratio
In(III)	3.00	69.6%
Ga(III)	2.00	30.4%
In/Ga	1.50	2.29

Morphology and composition of IGOs

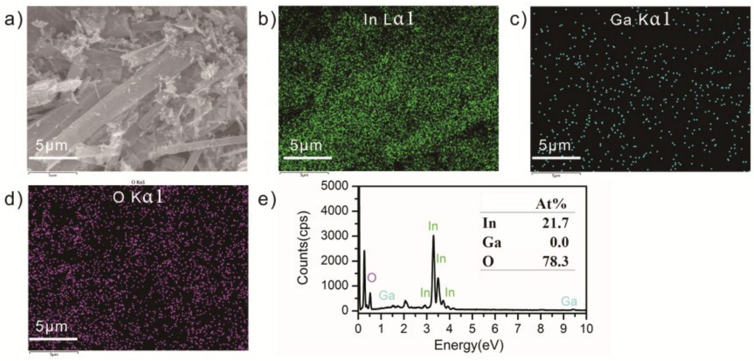

Fig. S5 a) SEM images of IGO(5:0); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDX spectrum of IGO(5:0).

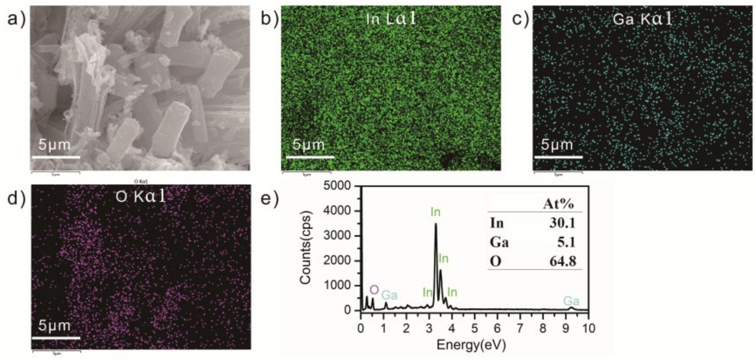

Fig. S6 a) SEM images of IGO(4:1); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDX spectrum of IGO(4:1).

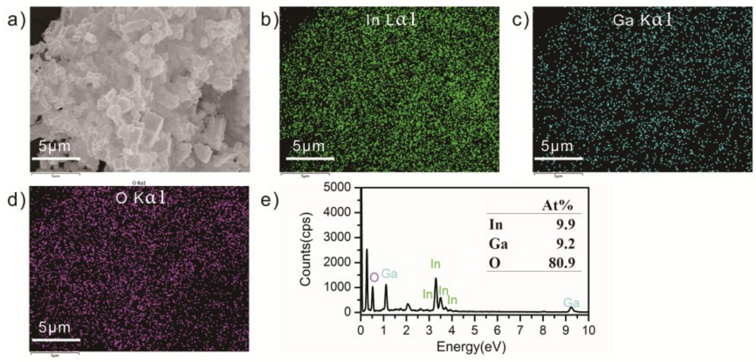

Fig. S7 a) SEM images of IGO(3:2); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDX spectrum of IGO(3:2).

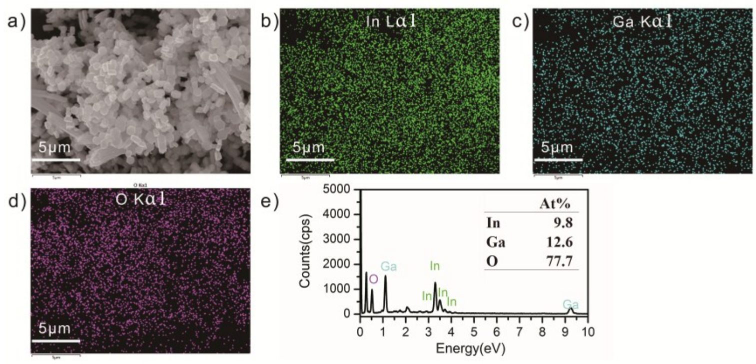

Fig. S8 a) SEM images of IGO(1:1); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDX spectrum of IGO(1:1).

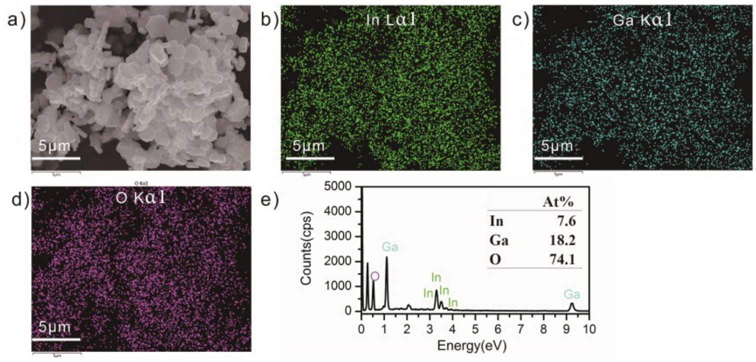

Fig. S9 a) SEM images of IGO(2:3); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDS spectrum of IGO(2:3).

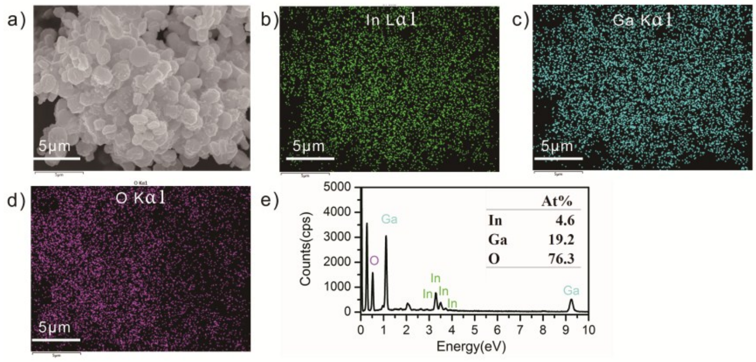

Fig. S10 a) SEM images of IGO(1:4); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDX spectrum of IGO(1:4).

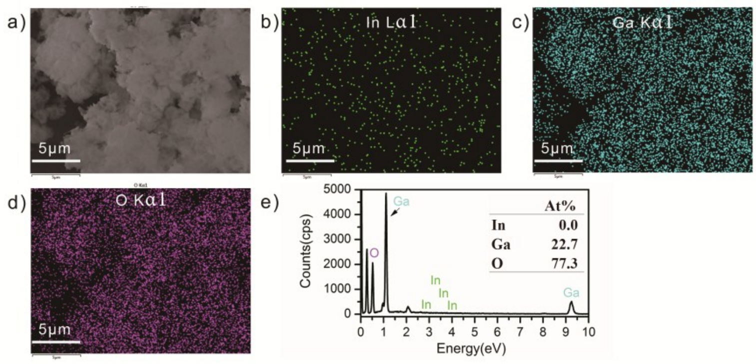

Fig. S11 a) SEM images of IGO(0:5); b–d) Elemental mapping images of In, Ga, and O element, respectively; And e) EDX spectrum of IGO(0:5).

Tab. S2 mole ratio of In and Ga in the IGOs using EDX method

	IGO(4:1)		**IGO(3:2)**		**IGO(1:1)**		**IGO(2:3)**		**IGO(1:4)**	
	Feed	EDX	Feed	EDX	Feed	EDX	Feed	EDX	Feed	EDX
	mmol	%	mmol	%	mmol	%	mmol	%	mmol	%
In(III)	0.80	30.10	0.60	9.90	0.50	9.80	0.40	7.60	0.20	4.60
Ga(III)	0.20	5.10	0.40	9.20	0.50	12.60	0.60	18.20	0.80	19.20
In/Ga	4.00	5.90	1.50	1.08	1.00	0.78	0.67	0.42	0.25	0.24

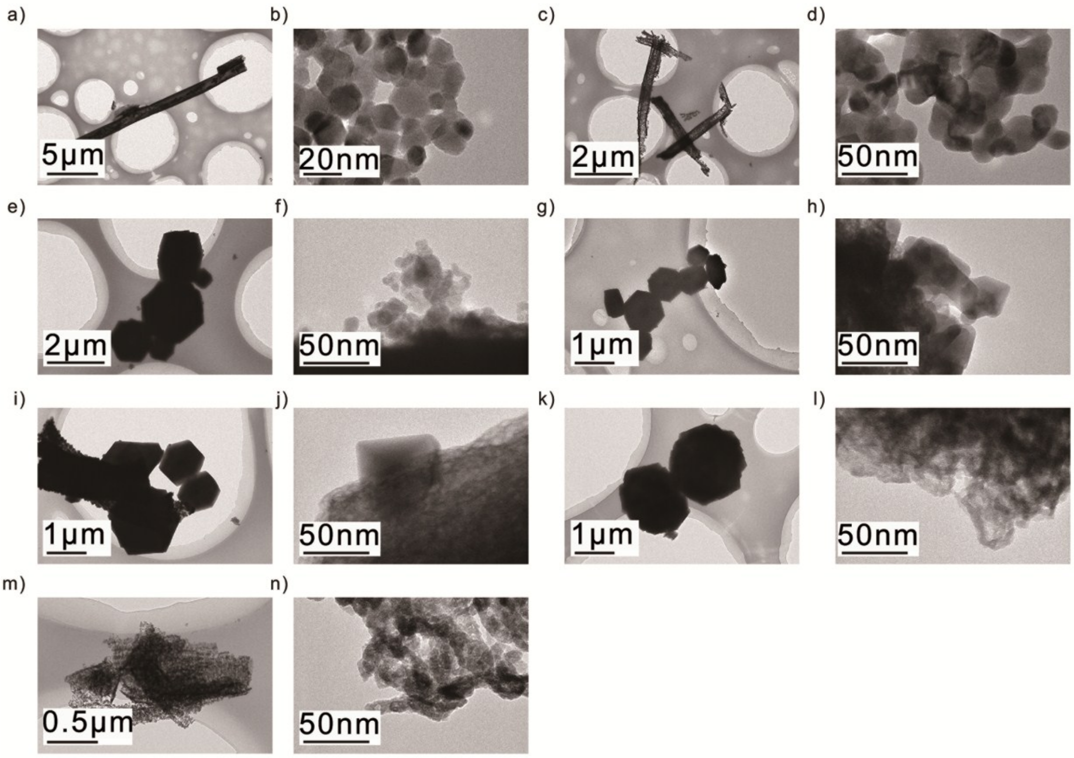

Fig. S12 TEM images and HRTEM images of a-b) IGO(5:0); c-d) IGO(4:1); e-f) IGO(3:2); g-h) IGO(1:1); i-j) IGO(2:3); k-l) IGO(1:4); m-n) IGO(0:4).

The In/Ga ratios of the samples were measured using ICP-OES. Each sample was dissolved in 5 ml HCl solution (ρ = 1.19 g/ml). After the powder was completely dissolved, those clear solutions were diluted with deionised water to a given volume ($V_{1)}$ and if the concentration of some sample exceeds the working curve concentration range, the solution should be re-diluted. The details of the experiments were listed in Tab. S3 and Tab. S4.

Tab. S3 the first experiment details of ICP-OES

Samples		**Dilution**	**Re-dilution**			**Results**
	M_1（g）	**V_1（ml）**	**M_2（g）**	**V_2（ml）**	**element**	**(mmol/g)**
I4G1	0.0539	100	0.6328	10	In	6.18
					Ga	1.53
I3G2	0.0566	100	0.7266	10	In	4.74
					Ga	3.37
I1G1	0.0778	100	0.5999	10	In	4.05
					Ga	4.46
I2G3	0.0457	100	0.6461	10	In	3.50
					Ga	5.21
I1G4	0.0331	100	0.8089	10	In	1.87
					Ga	7.58

Tab. S4 the second experiment details of ICP-OES

Samples		**Dilution**	**Re-dilution**			**Results**
	M_1（g）	**V_1（ml）**	**M_2（g）**	**V_2（ml）**	**element**	**(mmol/g)**
I4G1	0.0131	250	_	_	In	6.65
					Ga	1.58
I3G2	0.0137	250	_	_	In	5.17
					Ga	3.38
I1G1	0.0163	250	_	_	In	4.28
					Ga	4.49

I2G3	0.0145	250	_	_	In	3.16
					Ga	5.29
I1G4	0.0160	250	_	_	In	1.95
					Ga	7.35

Gas-Sensing performance

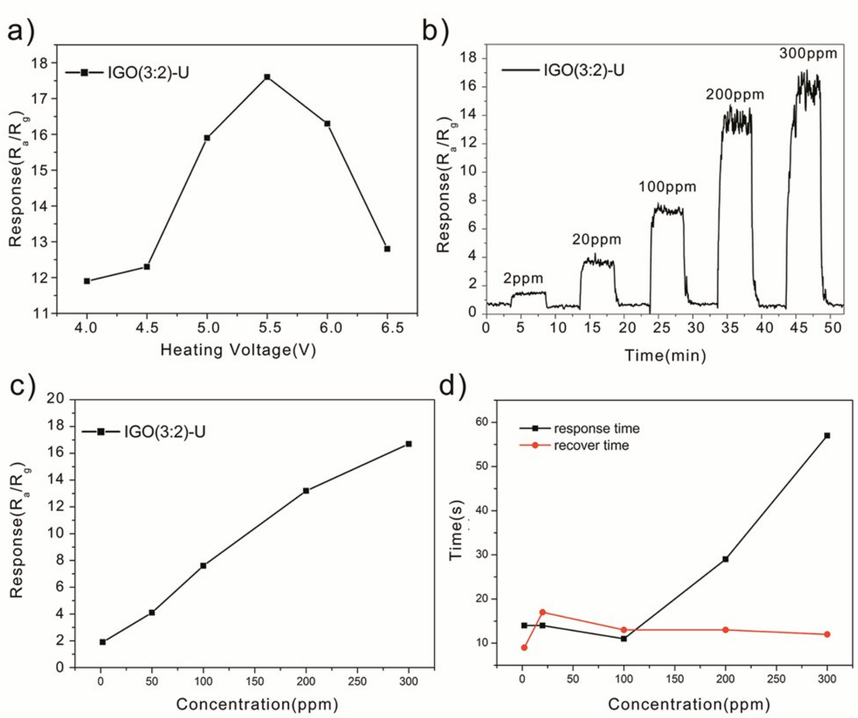

Fig. S13 a) Gas responses of the sensors based on IGO(3:2)-U at different operating voltages to 300 ppm ethanol; b) Dynamic sensing transients of the sensor to different ethanol concentrations; c) Concentration dependent response curves of IGO(5:0), IGO(3:2) and IGO(1:1); d) tres/trec curves of IGO(3:2)-U.

Moisture testing

In order to measure the relationship between the electric conductivity of the sensors and the relative humidity, we placed the sensors into the standard humidity field of saturated sodium solution and record current signal (Fig S14a). The saturated NaCl solution, saturated KCl solution and saturated K_2SO_4 solution were prepared for the saturated humidity fields, and the humidity fields were maked as “NaCl”, “KCl” and “K_2SO_4”, respectively. The humidity response (R_h) was defined as C_h/C_{am}, where Ch and Cam represented currents of the sensors in target humidity and ambient humidity, respectively. Standard testing conditions: 40% ambient humidity and 21°C ambient temperature.

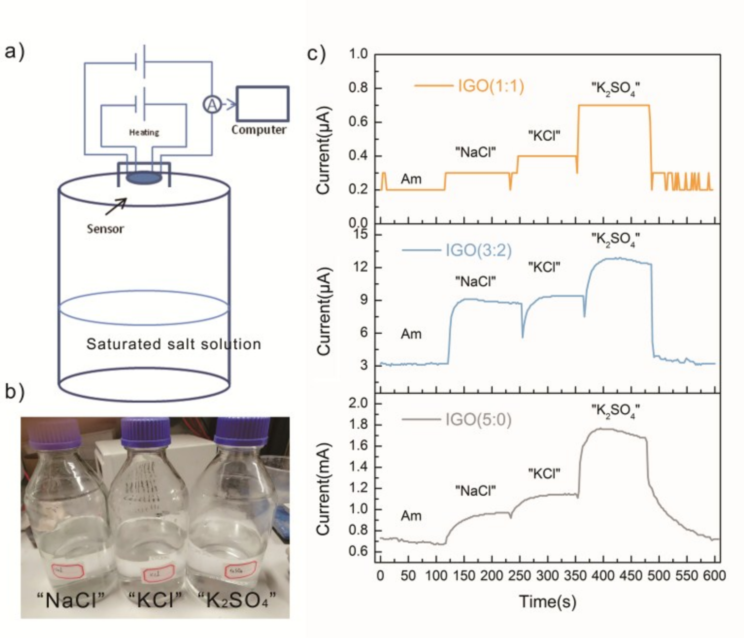

Fig. S14 a)scheme of humidity sensing measurement system; b) photo of aqueous salt solution; c) dynamic sensing transients of the their sensors to humidity.

Tab. S5 The humidity responses of IGOs.

	"NaCl"	"KCl"	"K_2SO_4"
saturated humidity[1]	75% ± 1%	85% ± 3%	98% ± 1%
IGO(5:0)	$R_h = 1.4$	$R_h = 1.6$	$R_h = 2.4$
IGO(3:2)	$R_h = 2.7$	$R_h = 2.9$	$R_h = 3.0$
IGO(1:1)	$R_h = 1.5$	$R_h = 2.0$	$R_h = 3.5$

1. L. Greenspan, *JOURNAL OF RESEARCH of the National Bureau of Standards - A. Phys ics and Chemistry*, 1977, **Vol. 81 A, No.1**.

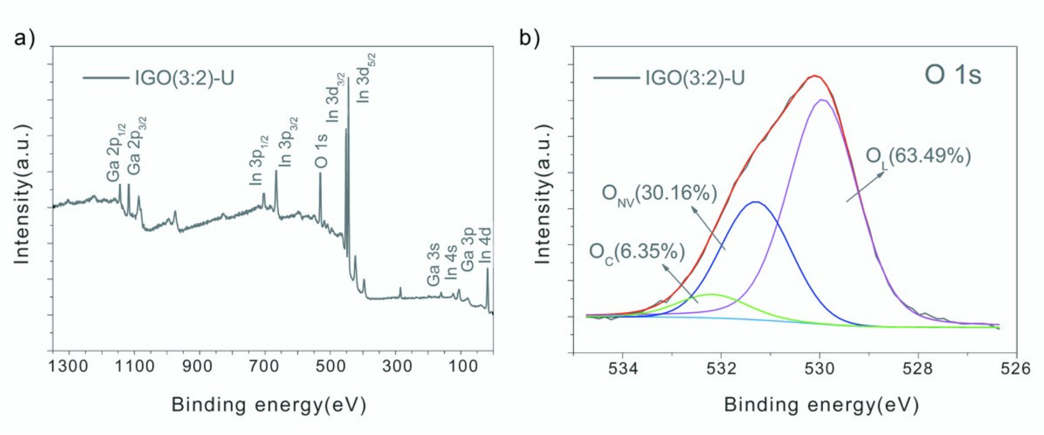

Fig. S15 a) XPS spectra of IGO(3:2)-U; and b) O 1s spectrum of IGO(3:2)-U.