

Supporting Information (SI) for

Oxygen Vacancy Engineering of Self-Doped SnO_{2-x} Nanocrystals for Ultrasensitive NO₂ Detection

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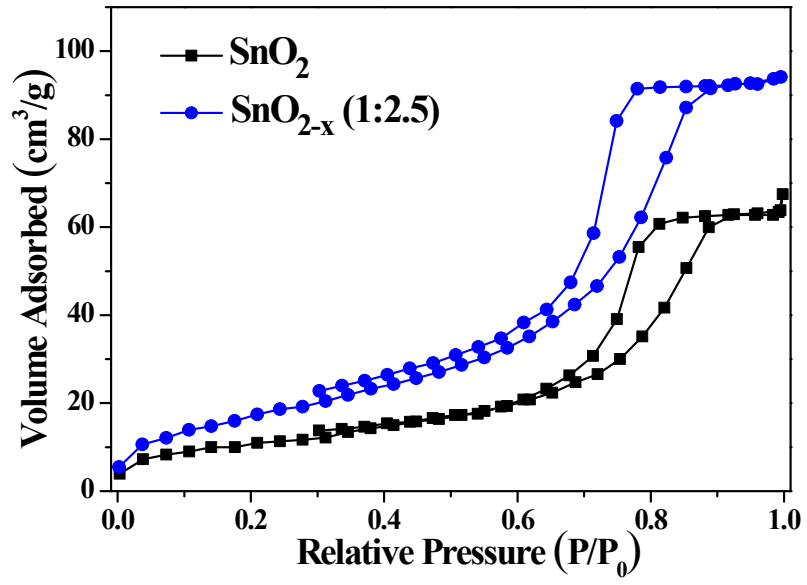


Figure S1. Nitrogen adsorption-desorption isotherms of the SnO₂ and SnO_{2-x} (1:2.5) NCs.

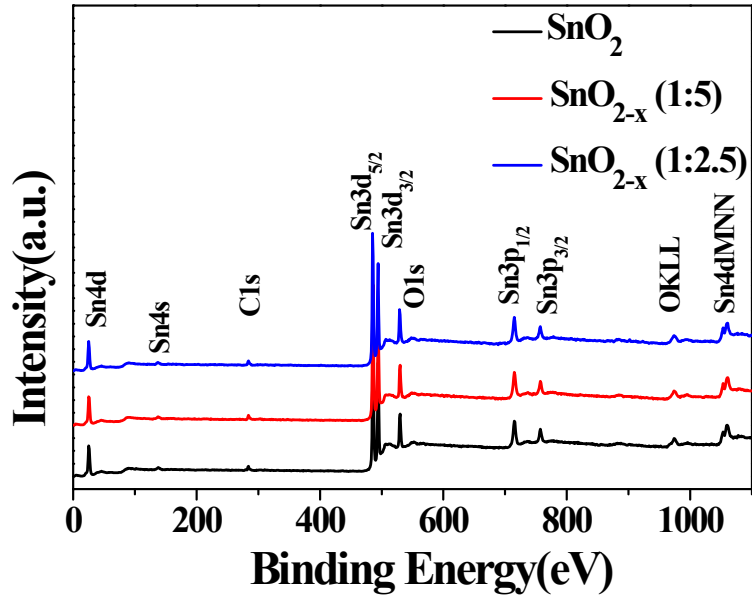


Figure S2. XPS survey spectra of SnO₂ and SnO_{2-x} (1:5) and SnO_{2-x} (1:2.5) NCs.

Table S1. Atomic compositions and atomic ratio (O/Sn) from XPS.

Samples	Atomic compositions (At.%)		Atomic ratio O/Sn
	Sn 3d	O 1s	
SnO ₂	33.38	66.62	1.996
SnO _{2-x} (1:5)	34.21	65.79	1.923
SnO _{2-x} (1:2.5)	35.63	64.37	1.807

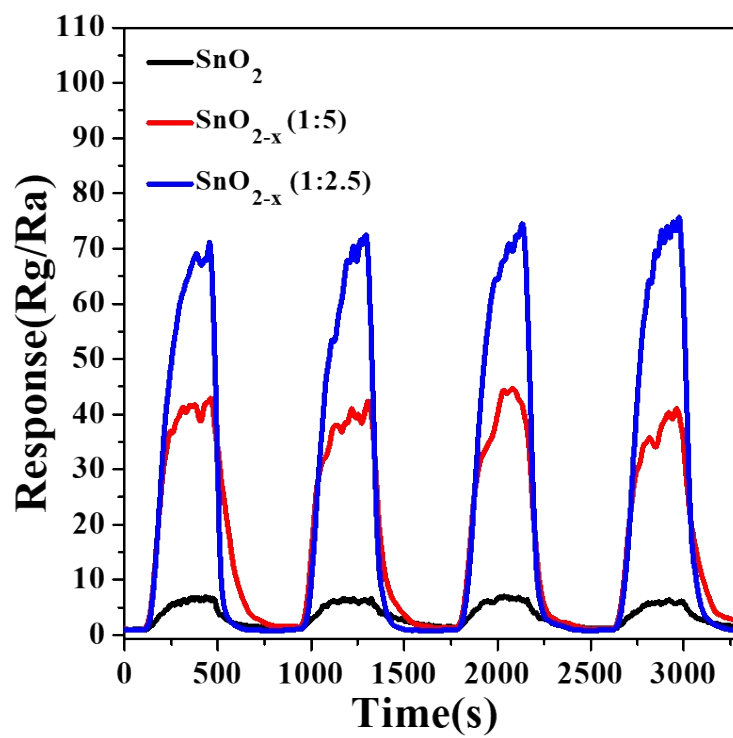


Figure S3. Dynamic response/recover curves of four repeated cycles at NO₂ concentration of 500 ppb.

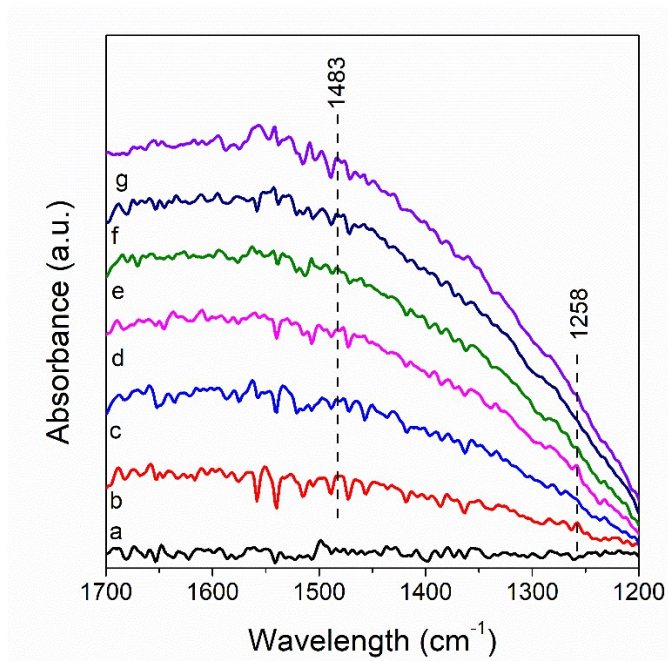


Figure S4. Time-resolved DRIFS spectra of SnO_{2-x} (1:5). (a: background in 100 ml/min helium at 100 °C; after adsorption of NO₂ (1.5ppm NO₂ in oxygen and helium) at 100 °C for 0.5, 1, 2, 3, 4, 5 min (b, c, d, e, f, g).)

Table S2. Comparison of other SnO₂-based sensing performance of NO₂

Materials	NO ₂ concentration (ppm)	Operating temperature (°C)	Response	Response Time(s)	Recovery Time(s)	Reference
NiO/SnO ₂	5	250	4	-	-	¹
graphene oxide/SnO ₂	6	150	10.5	360	780	²
SnO ₂ nanowires	2	150	14.2	292	228	³
Ni-doped SnO ₂ nanofiber	20	250	90.3	24s	35s	⁴
Ln-doped SnO ₂	500	150	72	<2s	-	⁵
Sn ²⁺ Self-Doped SnO _{2-x}	0.5	100	70	230	88	This work

Table S3. Assignment of vibrational frequencies of adsorbed surface products following the absorption of NO₂ on SnO₂ NCs.

Surface species description	ν_3 (cm ⁻¹)	ν_1 (cm ⁻¹)	Refs
NO ₂ (gas)	1628, 1595		6
NO ₂ (ads)	1390, 1348		6
Free NO ₃ ⁻ ion	1380		7
Monodentate nitrate (M–O–NO ₂)	1530-1480 1290-1250	1035-970	7
	1500-1045 1305-1270	1025-990	8
Bidentate nitrate (M–O ₂ NO)	1565-1500 1300-1260	1040-1010	7
	1630-1475 1300-1160	1040-960	8
	1545-1580 1280	1045	9
Bridging nitrate ((M–O) ₂ =NO)	1650-1600 1225-1170	1030-1000	7
	1520 1290	1008	8
Free NO ₂ ⁻ ion	1260	1330	7
Bridging bidentate nitrite ((M–O) ₂ =N)	1230-1200	~1330	10,11
Nitro compound (M–NO ₂)	1440-1335	1350-1315	7
Monodentate nitrite (M–O–N–O)	~1479		10
	~1463		11
Chelating nitro compound (M–O M–N–O)	1520-1390	1260-1180	7
	1510	1175	9

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