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

APTES-functionalized Thin-walled Porous WO_3 Nanotubes for Highly Selective Sensing of NO_2 in a Polluted Environment

Wei Liu, Lin Xu, Kuang Sheng, Cong Chen, Xiangyu Zhou, Biao Dong, Xue Bai, Shuang Zhang, Geyu Lu, Hongwei Song**

State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, 130012, People's Republic of China

*Email address: linxu@jlu.edu.cn, songhw@jlu.edu.cn;

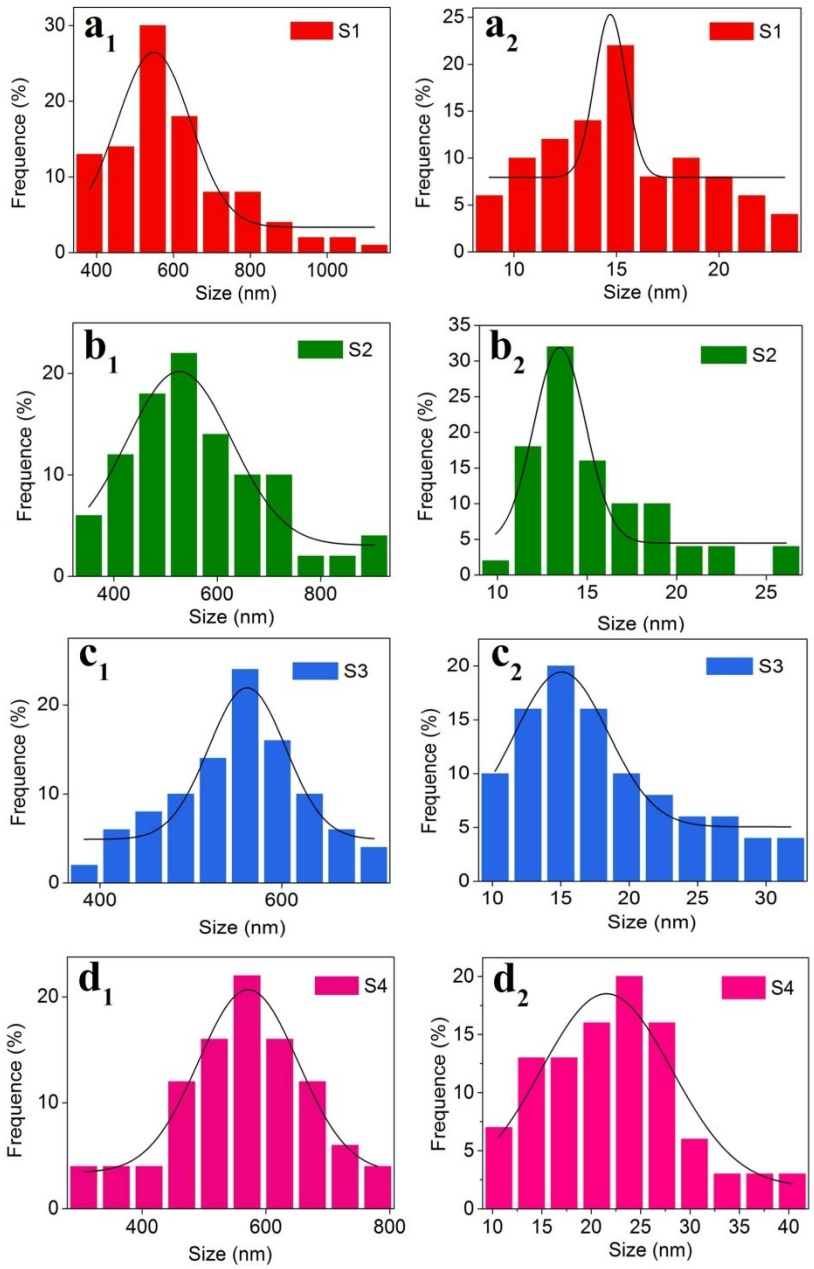

Fig. S1 The diameters and wall thickness distribution of (a_1) and (a_2) SiO_2/WO_3 NTs, (b_1) and (b_2) porous WO_3 NTs with 5 mol% SiO_2 removed, (c_1) and (c_2) porous WO_3 NTs with 10 mol% SiO_2 removed and (d_1) and (d_2) APTES functionalized porous WO_3 NTs based on the one with 10 mol% SiO_2 removed. The size distributions were obtained by measured the corresponding sizes from at least 100 NTs.

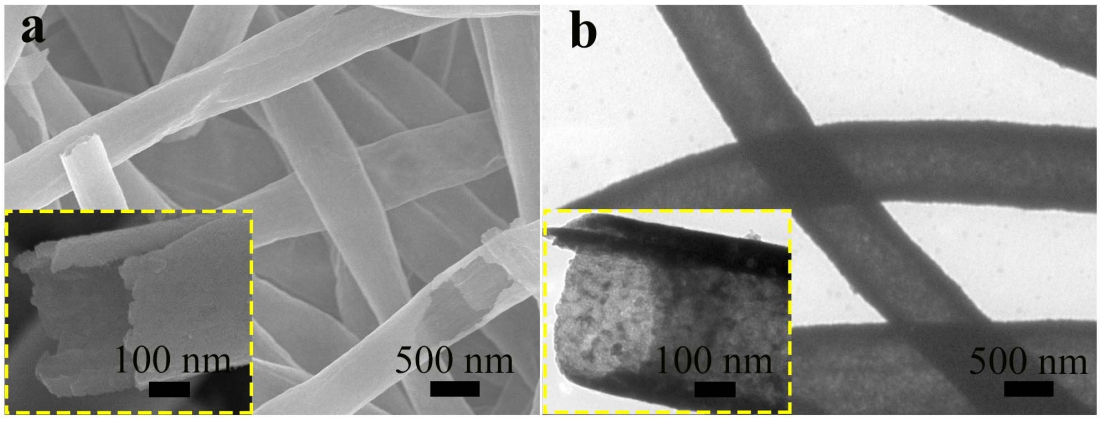

Fig. S2 (a) SEM image and (b) TEM image of pristine WO_3 NTs. The insert images are the enlarged SEM and TEM image of pristine WO_3 NTs.

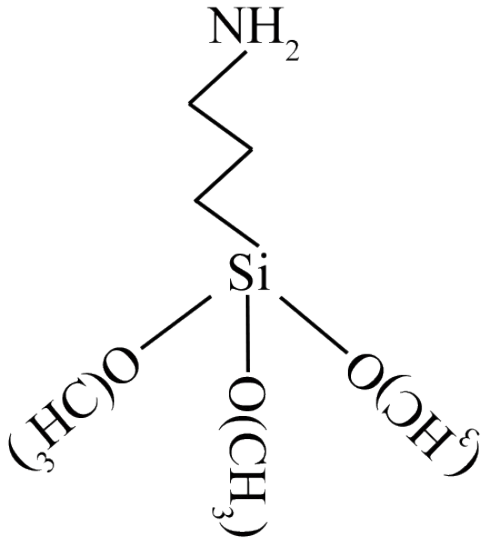

Fig. S3 The molecular structure of APTES.

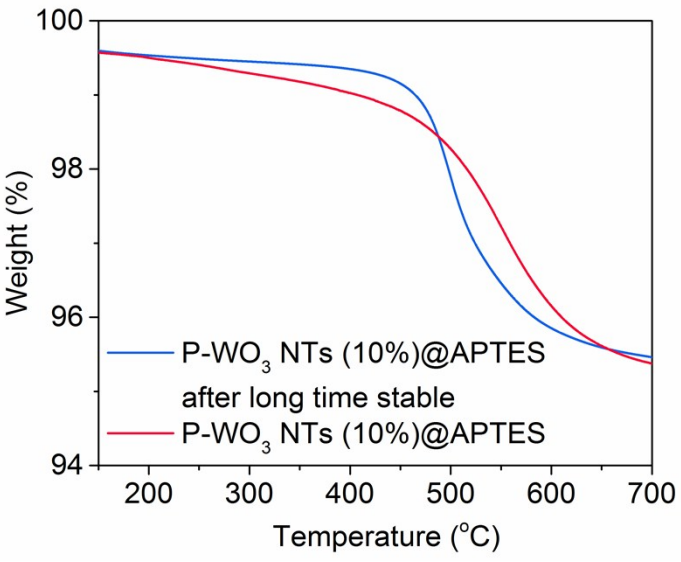

Fig. S4 The TGA of the P-WO_3 NTs (10%)@APTES and P-WO_3 NTs (10%)@APTES after long time stable.

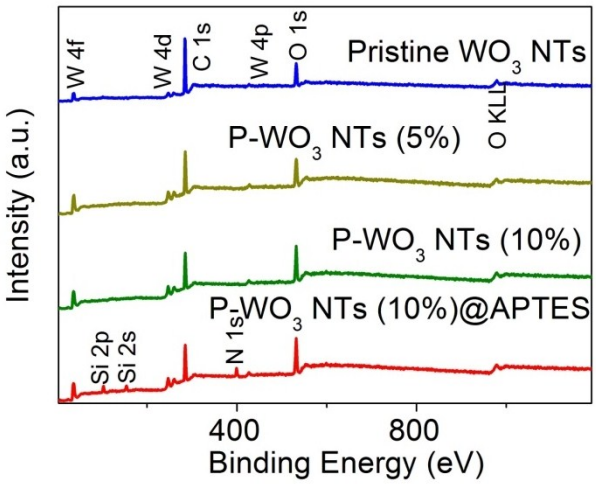

Fig. S5 The survey of X-ray photoelectron spectra of the pristine WO_3 NTs, P-WO_3 NTs (5%), P-WO_3 NTs (10%) and P-WO_3 NTs (10%)@APTES.

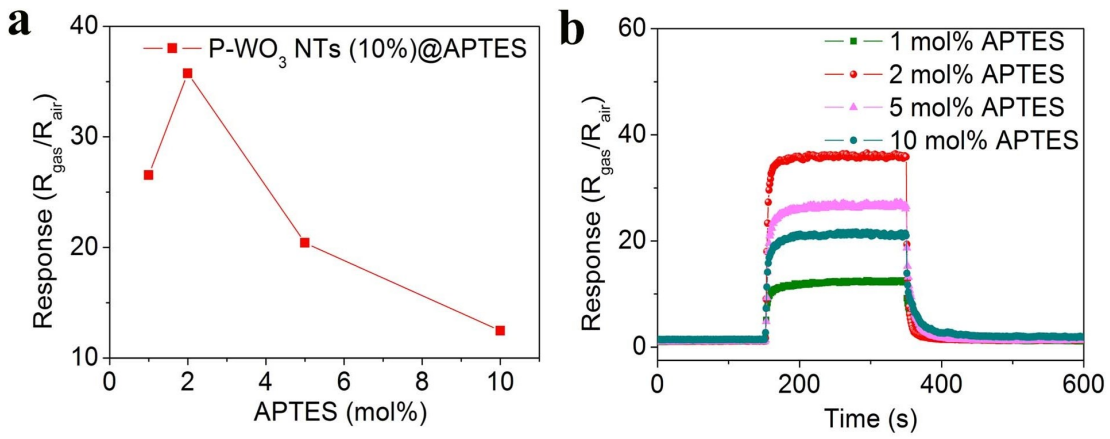

Fig. S6 (a) The response of 1 ppm NO_2 concentration with different amounts of APTES, (b) the dynamic response curve of P-WO_3 NTs (10%) modified with different amounts of APTES exposed to 1 ppm NO_2.

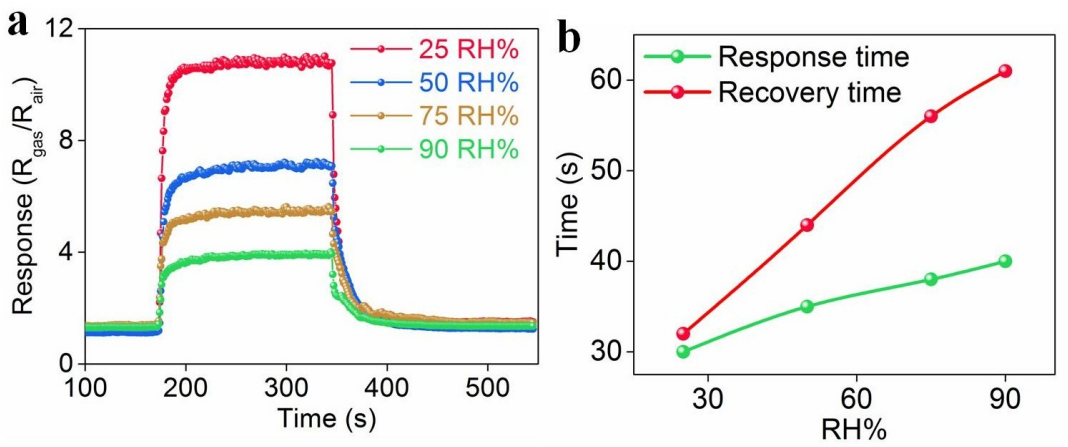

Fig. S7 (a) The dynamic curves and of P-WO_3 NTs (10%) sensor under different RH% (25~90%) for 1 ppm NO_2. (b) The corresponding response and recovery times of P-WO_3 NTs (10%) sensor under different RH% (25~90%) for 1 ppm NO_2.

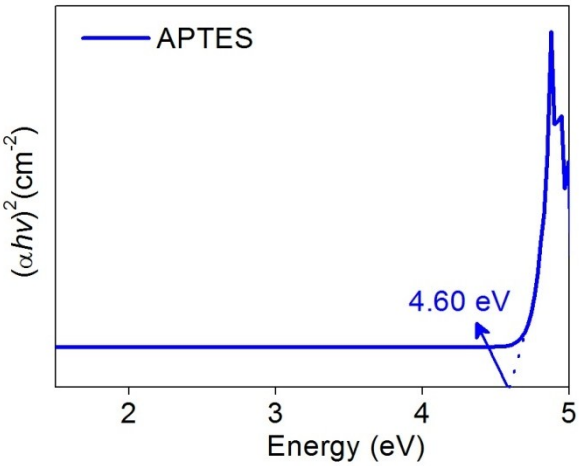

Fig. S8 Plot of $(\alpha hv)^2$ versus hv of APTES.

Table S1. A comparison of WO_3 based NO_2 gas sensors in the literature to P-WO_3 NTs (10%)@APTES sensor in this work.

Sensing material	Sensing performance	Response in this work	Temperature	Detection limit	Response/Recovery time	Reference
WO_3 NRs/graphene	61/1 ppm	45	300°C	25 ppb	-	[1]
WO_3 nanorods	209/10 ppm	184	200°C	700 ppb	-	[2]
WO_3 nanoparticles	48/1 ppm	45	50°C	-	-/~10 min	[3]
NiO/WO_3 nanocomposites	4.8/10 ppm	184	room temperature	-	2.5/1.1 s	[4]
WO_3–rGO porous nanocomposite	4.3/10 ppm	184	90°C	-	5.8/8.7 s	[5]
WO_3 thin film	20/10 ppm	184	200°C	-	3/151 s	[6]
WO_3 thin film	511/10 ppm	184	200°C	500 ppb	5.9/8.0 min	[7]
Ag-loaded mesoporous WO_3	44/1 ppm	45	75°C	100 ppb	5.05/2.46 min	[8]
WO_3 nanowires	4.49/1 ppm	45	250°C	250 ppb	9/7 s	[9]
Au-functionalized WO_3 microspheres	16/5 ppm	112	50°C	-	75/9 s	[10]
WO_3 nanowires/porous silicon	6.75/5 ppm	184	100°C	-	175/44 s	[11]
WO_3 NPs/porous silicon	3.4/2 ppm	56	150°C	50 ppb	2/20 min	[12]
Graphene oxide/WO_3	7.69/5 ppm	112	room temperature	-	10/18 min	[13]
Porous silicon/WO_3 nanorods	3.38/1 ppm	45	room temperature	100 ppb	92/398 s	[14]
WO_3 thin films	4.1/2 ppm	56	300°C	200 ppb	4.5/4.5 min	[15]
WO_3 nanorod bundles	111/5 ppm	112	250°C	-	230/42 s	[16]
Graphene oxide-Fe doped WO_3	4.5/1 ppm	45	25°C	-	4.9/5.47 min	[17]
WO_3-TiO_2 thick film	2.5/500 ppm	-	600°C	-	-	[18]
WO_3 thin-film	5/1 ppm	45	370°C	100 ppb	-	[19]
P-WO_3 NTs (10%)@APTES	45/1 ppm	45	340°C	10 ppb	10/11 s	This work

Table S2. A comparison of some typical semiconductor oxide based NO_2 gas sensors with that of P-WO_3 NTs (10%)@APTES sensor in this work.

Sensing material	Sensing performance	Response in this work	Temperature	Detection limit	Response/Recovery time	Reference
rGO-Cu_2O	1.68/2 ppm	56	room temperature	64	-	[20]
Co_3O_4-SnO_2 nanowires	3.47/10 ppm	184	350°C	2 ppm	>100/100 s	[21]
ZnO-rGO	1.25/5 ppm	112	room temperature	-	165/499 s	[22]
SnS_2 materials	14.9/10 ppm	184	250°C	500 ppb	6/40 s	[23]
ZnO microspheres	4/1 ppm	45	400°C	500 ppb	-	[24]
In_2O_3 microspheres	1.5/5 ppm	112	250°C	5 ppm	5/20 s	[25]
Ag-SnO_2 microrods	24/50 ppm	541	300°C	100 ppb	-	[26]
CuO/p-porous silicon	7.8/1 ppm	45	300°C	125 ppb	257/374 s	[27]
NiO nanosheets	1.5/10 ppm	184	250°C	1 ppm	-	[28]
Cr-doped TiO_2-NT	2.9/50 ppm	541	500°C	-	3/6 min	[29]
P-WO_3 NTs (10%)@APTES	45/1 ppm	45	340°C	10 ppb	10/11 s	This work

Table S3. The anti-interference test of P-WO_3 NTs (10%)@APTES sensor to 10 ppm interfering gases in the existence of 1 ppm NO_2.

Gas species	Response of P-WO_3 NTs (10%)@APTES sensor
1 ppm NO_2	45.5
1 ppm NO_2 + 10 ppm NH_3	44.5
1 ppm NO_2 + 10 ppm H_2S	43.7
1 ppm NO_2 + 10 ppm ethanol	45.3
1 ppm NO_2 + 10 ppm toluene	44.9
1 ppm NO_2 + 10 ppm methanol	45.2
1 ppm NO_2 + 10 ppm acetone	44.2
1 ppm NO_2 + 10 ppm CO	43.4
1 ppm NO_2 + 10 ppm O_3	44.8
1 ppm NO_2 + 10 ppm NO	43.9
1 ppm NO_2 + 10 ppm SO_2	45.1

Table S4. The pollution data came from the real-time air quality information of Changchun environmental protection bureau.

Air pollution species	Satisfied	Light pollution	Moderate pollution	Heavy pollution
SO_2 (ppb)	9	11	17	19
PM 10 (ppb)	75	89	92	152
CO (ppb)	15	17	18	22
O_3 (ppb)	5	10	13	41

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