Supplementary Information

Role of graphene quantum dots with discrete band gap on SnO_2 nanodomes for NO_2 gas sensors with an ultralow detection limit

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Experimental section

Fabrication of GQD@SnO_2 nanodomes

Pt/Ti (thickness of 150 nm/30 nm) interdigitated electrode patterns (IDEs) consisting of 20 electrodes with 5 μm gap were fabricated on a SiO_2/Si substrate (thickness of 300 nm/550 μm). Nanodome-like structures were fabricated by the soft-templating method [1]. The polystyrene (PS) beads (700 nm, 5.0 wt%, Spherotech, USA) were dispersed in a water:ethanol = 1:1 (v:v) solution by a centrifuge process after the concentration reached 10 wt%. The PS bead solution was pipetted onto a glass slide positioned at an angle of 45° in a Petri dish with deionized water. The Pt/Ti IDEs patterned substrate and slide glass were treated by O_2-plasma treatment (CUTEMP, femtoscience) for 10 minutes before fabrication. The pipetted solution was dispersed onto the surface of deionized water and allowed to form a PS bead monolayer. The Pt/Ti IDEs patterned substrate were dipped into water and the PS bead monolayer was pulled out and dried at room temperature for 24 hours. SnO_2 was deposited onto the PS bead monolayer by using an electron-beam evaporator. A 150 nm thick SnO_2 layer was deposited at a rate of 1 Å s^{-1}. The deposited SnO_2 were annealed at 500 °C for 1 hour to simultaneously remove the PS templates and crystallize the SnO_2 nanodomes.

The GQDs were prepared from graphite intercalation compounds (GICs) through a previous method [2]. First, graphite and potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$) were vigorously mixed at a ratio of 1:15 (w:w) and then ground. The mixture was heated in a heating mantle at 250 °C for 24 hours, which led to the formation of GICs. The as-prepared GICs were immersed in DI water and sonicated to exfoliate and cut the graphite. The crude GQD solution was filtered using centrifugal microfilters (10,000 NMWL, Amicon Ultra-15), followed by dialysis using a dialysis membrane for 3 days to remove any impurities and obtain pure GQDs <5 nm in size.

The GQD solution (0.1 mg ml^{-1}) was repeatably drop cast (total 100 µl) onto SnO_2 nanodomes and allowed to dry at room temperature for 24 hours.

Characterization and gas response measurements

The morphology of the GQD@SnO_2 nanodomes was investigated by field-emission scanning electron microscopy (FE-SEM, SU 5000, Hitachi). The structures and fast Fourier transform (FFT) images of GQDs were investigated by transmission electron microscopy (TEM, Tecnai F20, FEI Company). The crystallinity of the sensors was measured by X-ray diffraction (XRD, Ultima IV, RIGAKU) with a Cu-Kα radiation source (wavelength 1.5418 Å). The chemical bonding and binding energies of the sensor materials were investigated by X-ray photoelectron spectroscopy (XPS) using a K-alpha system (Thermo VG Scientific) with an Al-Kα X-ray source. The surface charging effect was corrected with C 1s peak at 284.7 eV as a reference. The Raman spectra were collected by Senterra system (Bruker) with 532 nm laser. The samples for XPS analysis and Raman analysis were prepared by annealing for 1 hour on a hot plate at room temperature, 50 °C, 100 °C, and 150 °C. The oxygen content in the GQDs was estimated using Auger electron spectroscopy (AES) with a source electron beam energy of >10 kV.

The responses of target gases were measured in a quartz tube with a 1-inch furnace (Lindberg, blue M). The operating temperature was controlled by a 1-inch furnace at room temperature, 50 °C, 100 °C, and 150 °C to evaluate the gas response mechanism at different operating temperatures. The gas flows were controlled to give a constant flow rate of 1000 sccm under dry condition (RH 0) using a mass-flow controller. The sensor resistance was measured using a Keithley 2401 instrument with a DC bias voltage of 0.5 V.

Supplementary Figures

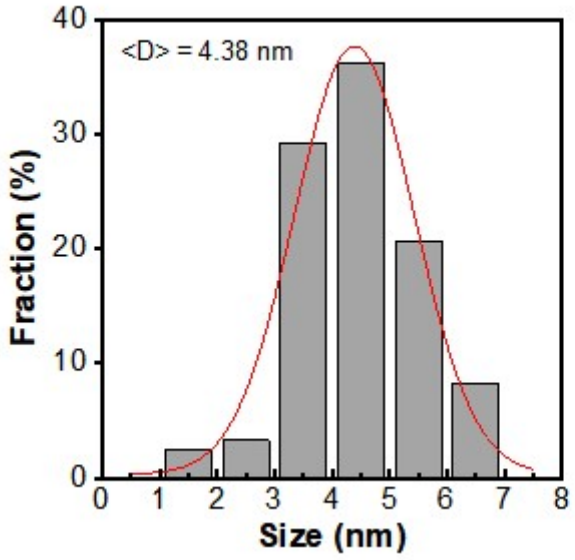

Fig. S1. Size distribution of pristine GQDs. <D> indicates average size.

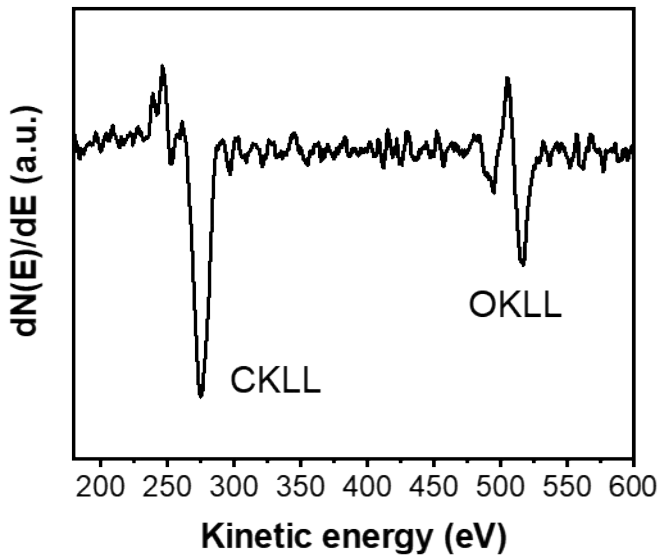

Fig. S2. Spectrum of magnified Auger electron spectroscopy (AES) for GQDs.

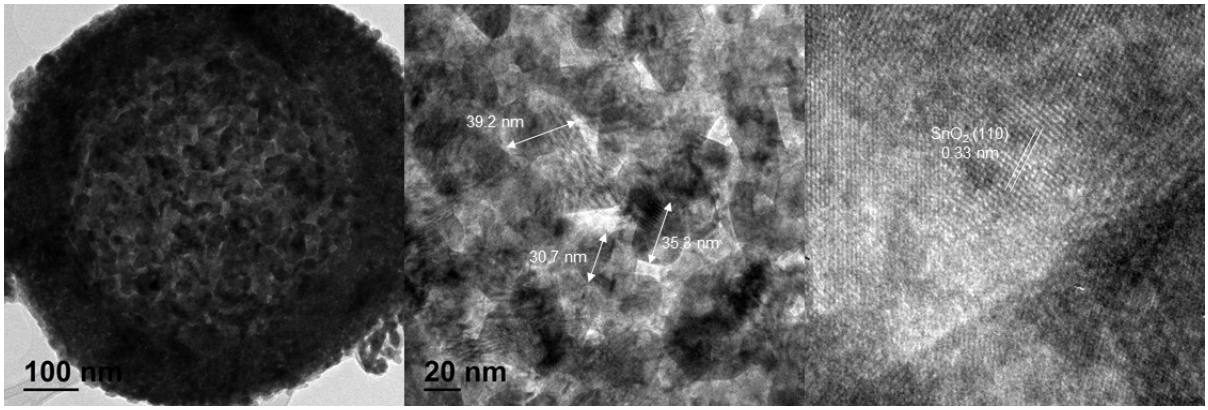

Fig. S3. HR-TEM image of individual SnO_2 nanodomes.

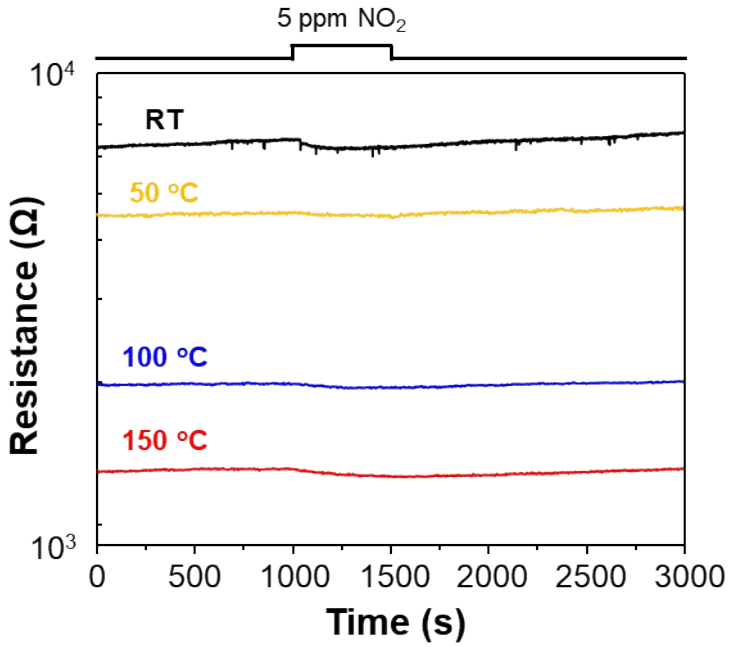

Fig. S4. Resistance curves for 5 ppm NO_2 as a function of operating temperature for a GQD@SnO_2 nanodomes under humid condition (relative humidity: 50 %).

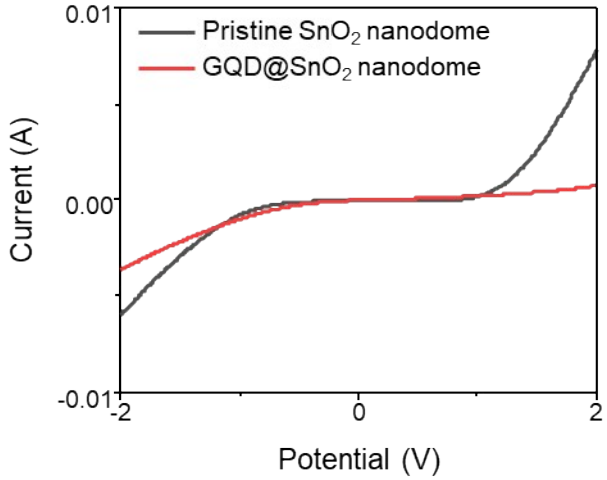

Fig. S5. *I-V* curve of SnO_2 nanodomes and GQD@SnO_2 nanodomes

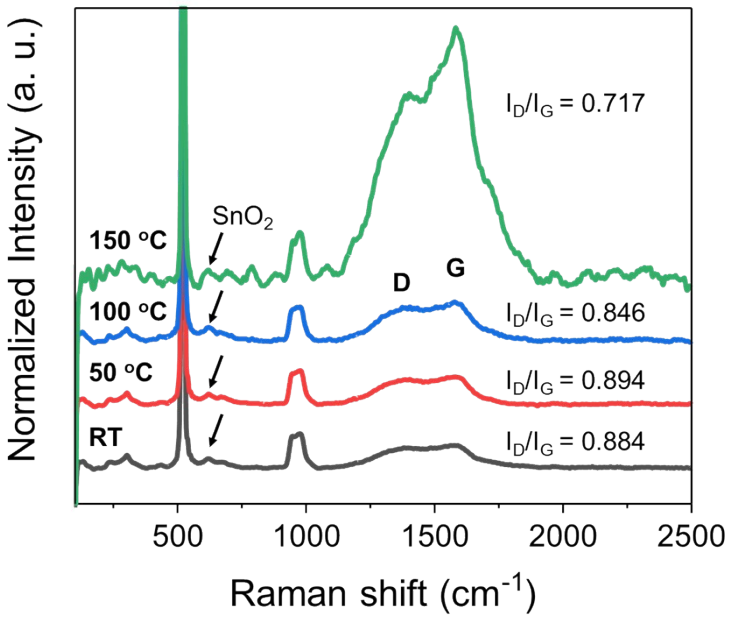

Fig. S6. Raman spectrum of the GQDs@SnO_2 nanodomes.

Table S1. Comparison of gas sensing performance of GQDs/graphene-based gas sensors.

Year	Material	Temp. (°C)	t_{res}[g)]/t_{rec}[h)] (s)	Response $((R_a-R_g)/R_g)$ or $((R_g-R_a)/R_a)$	LOD[i)] (ppb)	Refs.
2022	GQD@SnO_2 nanodomes	150	322/105	39.1 (5 ppm)	1.1	*This work*
2021	N-GQDs[a)]-SnO_2 hollow cube	130	59/33	417 (1 ppm)	-	3
2021	GQD-metal phthalocyanine hybrid	RT	100/100	15.8 (50 ppm)	50	4
2020	N-GD[b)]-SnO_2-0D heterostructure	50	528/384	4336 (100 ppb)	20	5
2020	N-GQDs-3D ordered macroporous In_2O_3	100	95/36	81.7 (1 ppm)	100	6
2020	$BiVO_4$/Cu_2O/rGO[c)]	60	51.3/87.5	8.1 (1 ppm)	-	7
2020	$CuWO_4$/rGO	RT	38/22	9.45 (50 ppm)	500	8
2019	rGO/ZnO-CT[d)]	RT	140/630	1.15 (15 ppm)	43.5	9
2018	rGO-Co_3O_4	RT	90/2400	1.27 (5 ppm)	50	10
2018	CuO/rGO	RT	66/34	14 (1 ppm)	60	11
2018	WO_3/S-rGO[e)]	RT	6/56	2.50 (20 ppm)	-	12
2017	SnO_2/N-RGO[f)]	RT	45/168	1.38 (5 ppm)	-	13
2017	rGO-In_2O_3	RT	208/39	109 (1 ppm)	10	14
2016	ZnO/rGO	RT	75/132	2.19 (1 ppm)	50	15

[a)] nitrogen-doped graphene quantum dots; [b)] nitrogen-doped graphene dot; [c)] reduced graphene oxide; [d)] cotton thread; [e)] sulfonated reduced graphene oxide; [f)] nitrogen-doped reduced graphene oxide; [g)] response time; [h)] recovery time; [i)] limit of detection

Table S2. Response/recovery times of bare SnO_2 and GQD@SnO_2 nanodome gas sensors at different operating temperatures.

	Bare SnO_2 nanodome		**GQD@SnO_2 nanodome**	
	Response time (s)	Recovery time (s)	Response time (s)	Recovery time (s)
RT	-	-	452	> 1500
50 °C	-	-	450	> 1500
100 °C	315	> 1500	459	1322
150 °C	59	1247	322	105

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