Supplementary information

Highly sensitive g-C$_3$N$_4$ nanosheets as a potential candidate for the effective detection of NO$_2$ gas via langasite based surface acoustic wave gas sensor

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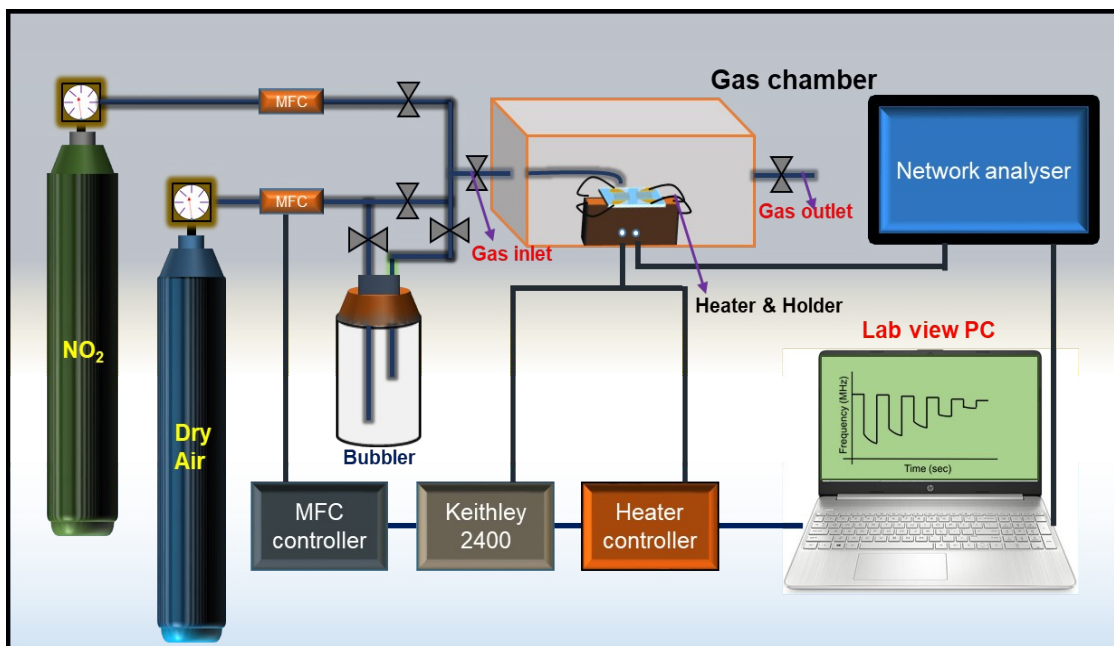
Tel: +82 42 821 5452, Fax: +82 42 822 8011

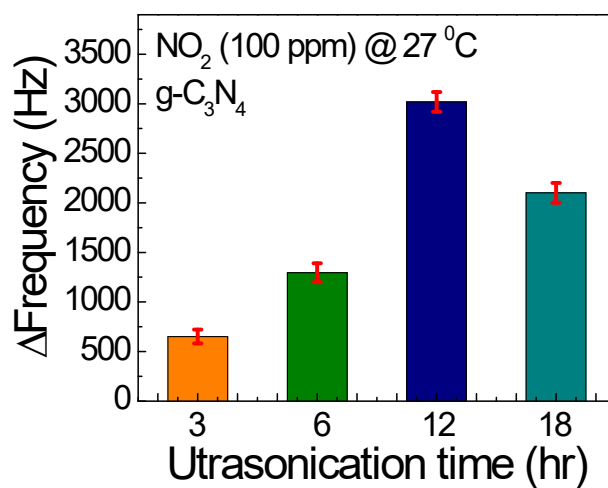**Fig. S1** Schematic illustration of g-C$_3$N$_4$/LGS SAW NO$_2$ gas sensing measurement system.

Fig. S2 Dynamic NO$_2$ gas (100 ppm) sensing frequency response characteristic of the g-C$_3$N$_4$

nanosheets sonicated at different time intervals at 3, 6, 12 and 18 h deposited on LGS SAW.

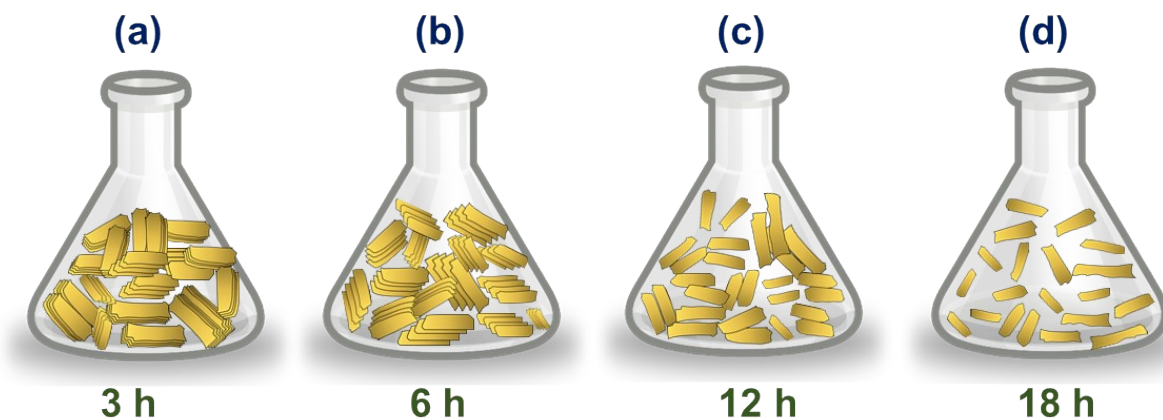**Fig. S3** Schematic illustration of the exfoliation of g-C₃N₄ nanosheets based on the ultrasonication time: (a) 3 h, (b) 6 h, (c) 12 h and (d) 18 h, at room temperature.
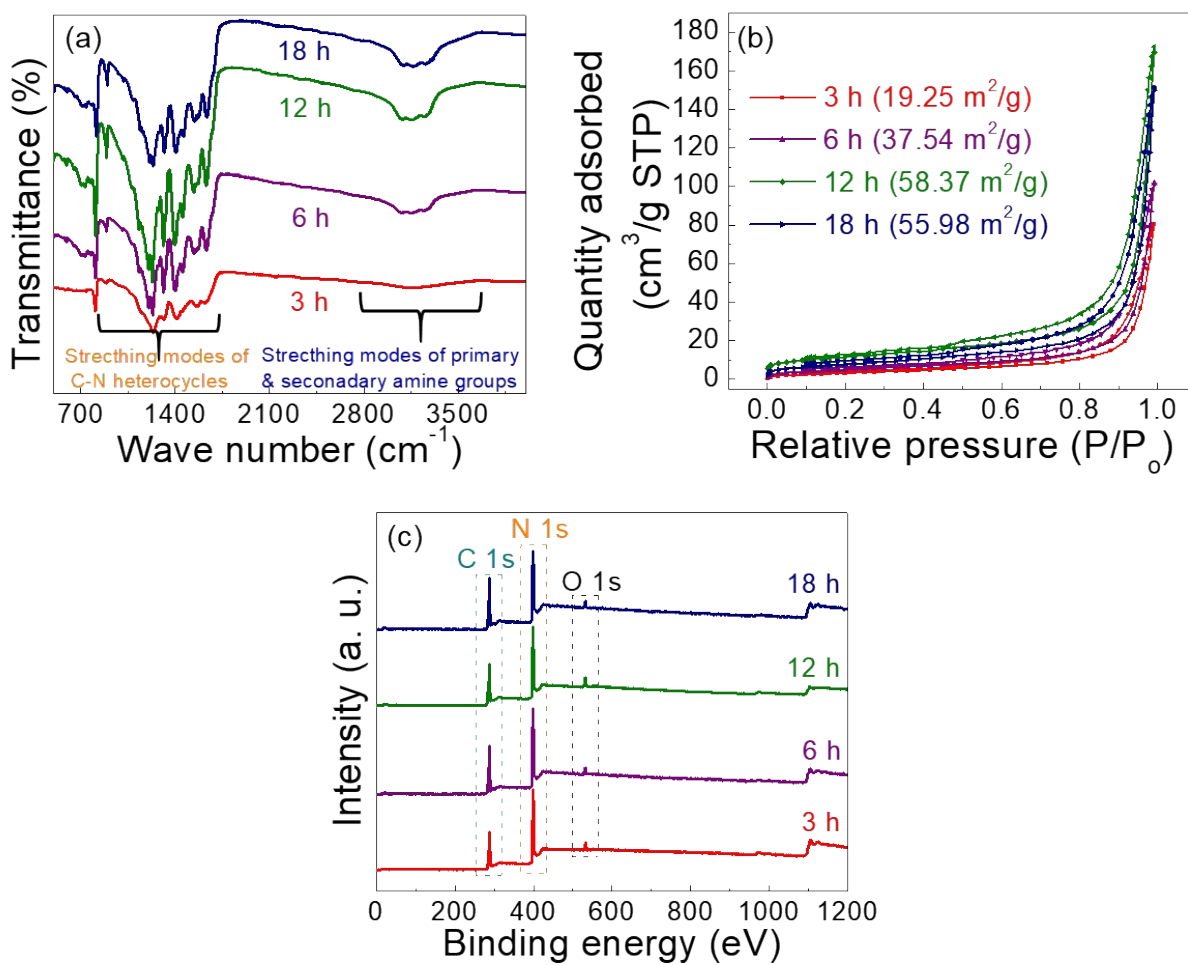
Fig. S4 (a) FTIR spectra of the ultrasonically exfoliated g-C$_3$N$_4$ nanosheets based on the sonication time intervals: 3, 6, 12 and 18 h, (b) BET adsorption/desorption characteristics of g-C$_3$N$_4$ nanosheets sonication at various time intervals: 3, 6, 12 and 18 h, (c) XPS core level survey scan spectra of the g-C$_3$N$_4$ nanosheets films based sonication time intervals: 3, 6, 12 and 18 h.

The molecular structural analysis of the exfoliated g-C$_3$N$_4$ nanosheets based on the sonication time: 3, 6, 12 and 18 h were investigated using Fourier transform infrared spectroscopy (FTIR) in the range of 600-4000 cm^{-1}, BET and X-ray photoelectron spectroscopy (XPS) as shown in the Fig S4 (a, b & c).[1, 2] As shown in the Fig. S4(a) the absorption peaks of FTIR spectra appears in the region of 800 to 880 cm^{-1} were ascribed to the characteristics breathing modes of s-triazine ring units of the g-C$_3$N$_4$, which corresponding to the condensed C-N heterocycles. [1, 3, 4] In which the absorption band located in between 1200 and 1700 cm^{-1} were attributed to the band stretching vibrational modes of the C-N heterocycles. [1, 4] The bands observed between 2900 and 3700 were assigned to the N-H functional groups which was found as increased with increasing in the edge boundaries in exfoliated nanosheets (increases with sonication time). [1] In addition, the band pronounced at 1232 related to the C-H bond, and it can be observed that the intensity of the absorption peak enhanced with increase in sonication time, that could be attributed to the breaking of nanosheets from the bridging N atoms. [1, 3] Further, the absorption peak located at 1634 indicating the C-C/C-N bonds which increases with sonication time, indicating the nanosheets were highly exfoliated. It is to be noted that the interplanar distance between the carbon and nitrogen bonds were cleaved with increase in sonication that leads to form the nanosheets as layer by layer with a strong molecular coagulation bridging bonds which was in accordance with our SEM and TEM analysis. [2, 4]

Further, if the sonication time increase the interplanar bridging distance between the C and N would increases more, causes to the separation sheets and sometimes provokes to break the linking bonds, which further effects the active surface area and the conductivity of the g-C_3N_4 nanosheets. [1, 2] Thus, the sample sonicated for 18 h exhibited a low intense peak. Moreover, as compared to all the as prepared samples, 12 h sonicated g-C_3N_4 nanosheets showed an intense absorption peak that further expected to show better gas sensing performances. [1, 4] Furthermore, to support the FTIR analysis the BET absorption desorption experiment was performed and explored the surface area of all samples as displayed in Fig. S4(b). [2] Based on the BET surface analysis, the estimated surface area of the samples were found to be 3 h g-C_3N_4 (19.25 m²/g), 6 h g-C_3N_4 (37.54 m²/g), 12h g-C_3N_4 (58.37 m²/g) and 12h g-C_3N_4 (55.98 m²/g). Further, XPS analysis were used to estimate the chemical constituent composition ratio of the exfoliated g-C_3N_4 nanosheets based on the sonication time. Fig S4(c) displays the survey scan spectrum of g-C_3N_4 nanosheets based on the sonication time.

Fig S5(a-d) represents the deconvoluted XPS core level N 1s spectra of the g-C_3N_4 nanosheets sonicated at different time intervals (3-18 h). The N 1s spectra of each sample was resolved into the four major peaks at their respective positions which were assigned to the C-N-C, N-$(C)_3$, C-N-H and π-excitations as displayed in Fig. S4. [1] The N 1s spectra of the g-C_3N_4 nanosheets were considered as a benchmark, to further explore the excellent bridging nature between the self-doping of C and N atoms, which would be the key aspect for the better sensing performances. [1] It was well established that the healthy arrangement of C-N bonding can be estimated from the low intensity ratio of N-$(C)_3$/C-N-C of N 1s spectra, that clearly signifies the self-doping of C atoms to tertiary N. [1] The lowest intensity ratio of N-$(C)_3$/C-N-C peaks indicates the well-arranged bridging connectivity between the C and N atoms, that further helps

to maintain excellent electronic conductivity, improving the functional groups and effectively enhances the active surface area in nanosheets, which were in accordance with FTIR and BET analysis. [1, 2] In which we estimated the intensity ratio of each sample as displayed in the Table S0, and it was found that the g-C_3N_4 nanosheets sonicated at 12 h exhibited the lowest value (0.75) as compared to the other samples. Henceforth, we have concluded that 12 h sonicated g-C_3N_4 nanosheets would be the better sample among the others, that clearly reflects in the gas sensing measurements as well as displayed in Fig. S2.
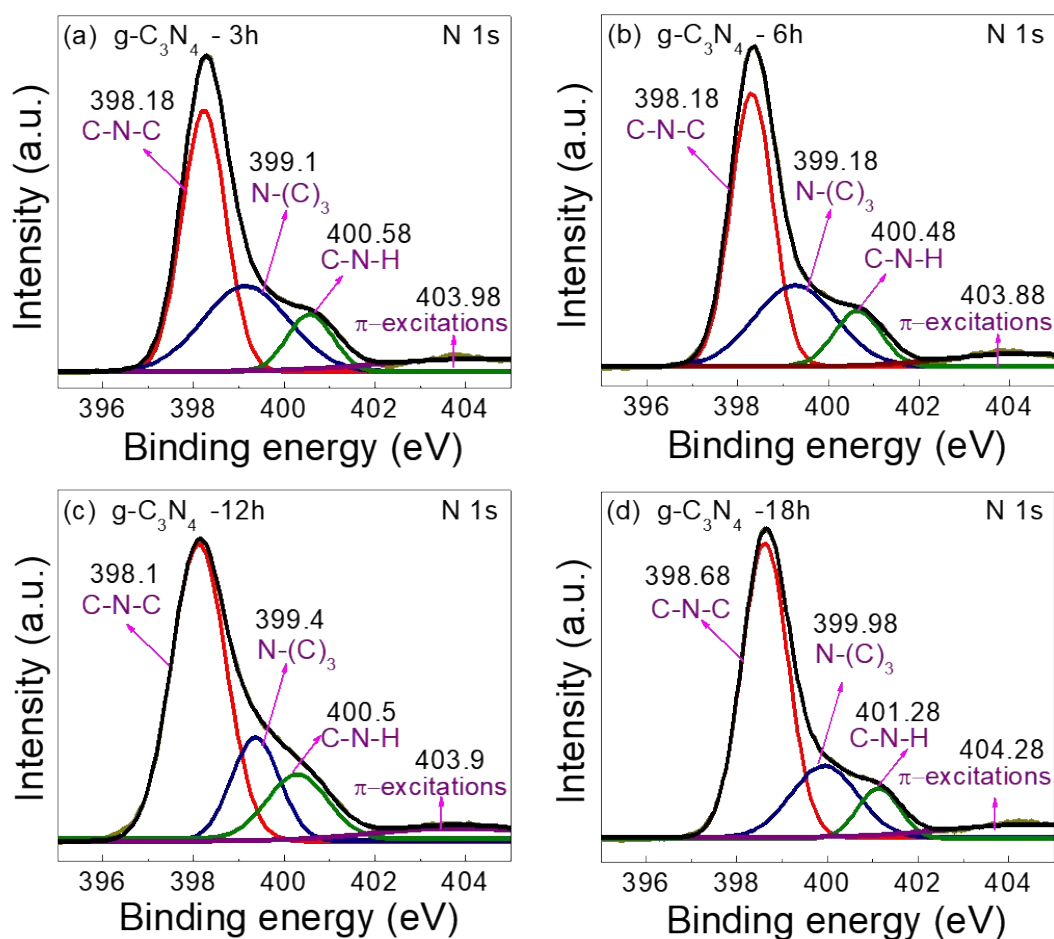

Fig. S5 XPS core level deconvoluted N 1s spectra of g-C_3N_4 nanosheets based on the sonication time intervals: (a) 3, (b) 6, (c) 12 and (d) 18 h.

Table S0: XPS deconvoluted peak composition of N 1s spectra of each of g-C_3N_4 nanosheets sample sonicate at different time intervals: 3, 6, 12 and 18 h.

	N 1S			
S. NO:	C-N-C	N-(C)$_3$	Π-excitations	Peak intensity ratio
g-C_3N_4 NS-3 h	46.5	42.2	11.1	0.91
g-C_3N_4 NS-6 h	48.8	43.3	7.6	0.88
g-C_3N_4 NS-12 h	**53.2**	**40.1**	**6.5**	**0.75**
g-C_3N_4 NS-18 h	53.8	42.6	3.4	0.79

Table S1: Comparison of sensing parameters of the various thickness of g-C_3N_4 nanosheets towards the 100 ppm of NO_2 gas at RT

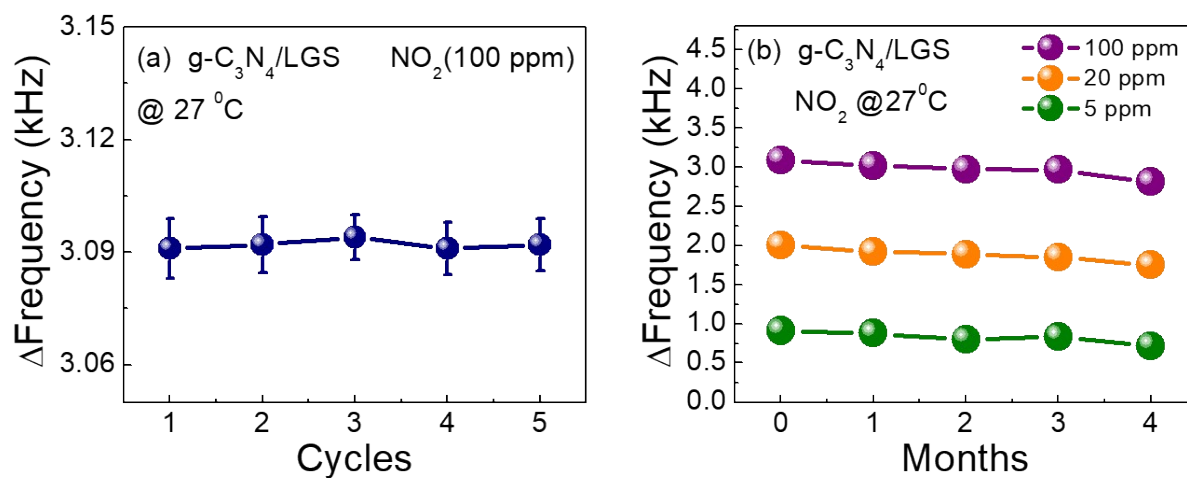| g-C_3N_4 nanosheets thickness	Sensitivity (kHz)	Response/recovery time (sec)	Noise level (Hz)
90 nm	0.320	48/36 s	~120±10
160 nm	1.42	46/34 s	~227±15
220 nm	**3.16**	**42/22 s**	**~231±15**
300 nm	3.72	50/141 s	~413±25
380 nm	2.12	69/43 s	~393±20

Fig. S6 (a) Stable frequency response plots of g-C$_3$N$_4$/LGS SAW sensor per each cycle under 100 ppm of NO$_2$ gas at RT, (b) long term stability and ageing effect of g-C$_3$N$_4$/LGS SAW sensor for every consecutive month from staring day to 4 month to the 5, 20 and 100 ppm of NO$_2$ gas at RT.

References:

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