Supporting Information

Enhancement of Charge Transfer between Graphene and Donor-π-Acceptor Molecule for Ultrahigh Sensing Performance

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Table S1. The Raman shift, Peak intensity, Intensity ratio (I_D/I_G) of the ANS-rGO, rGO, GO.

Sample	Raman shift (cm^{-1})		Peak intensity		Intensity ratio
	Peak D	Peak G	Peak D	Peak G	(I_D/I_G)
ANS-rGO	1325	1588	275	202	1.36
rGO	1331	1588	1399	1047	1.34
GO	1331	1593	2021	1814	1.11

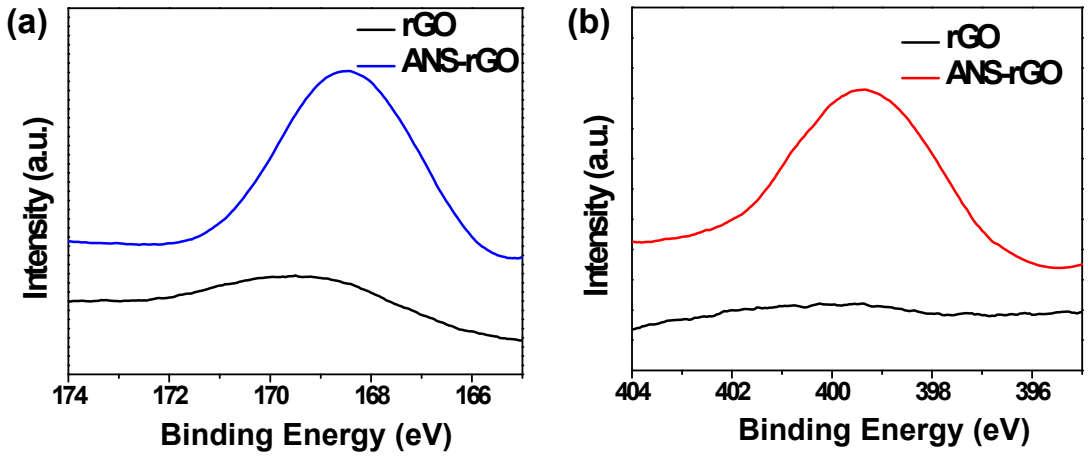

Fig. S1 Typical XPS survey scan spectra (a) of S and (d) N of rGO and ANS-rGO materials.

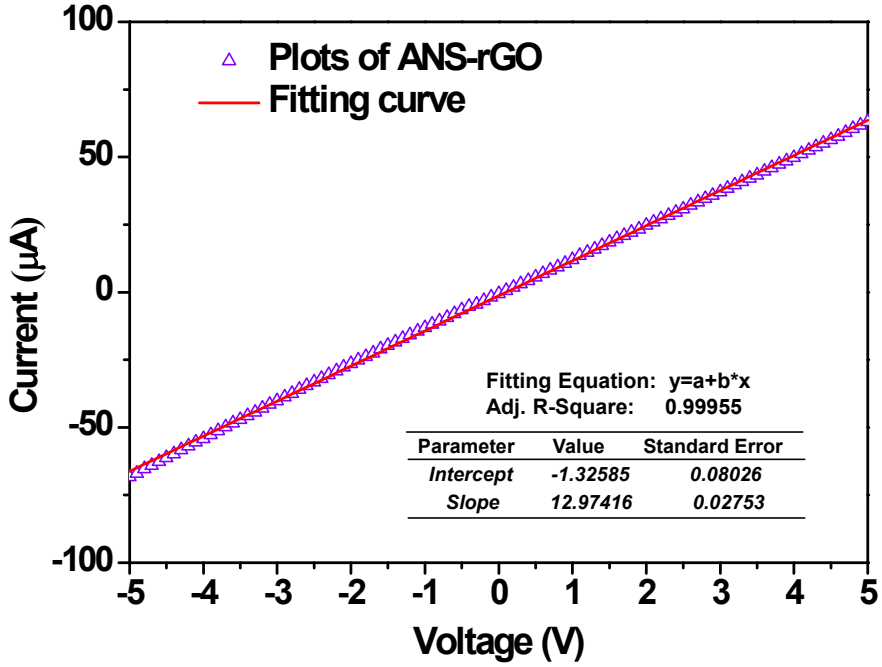

Fig. S2 Current versus voltage curves of ANS-rGO sensor. The results indicated that the Schottky barriers were absent between ANS-rGO and IDEs, which ensures the accuracy of the gas sensing measurement in our work.

Table S2. The adsorption energy of the NA molecules or ANS molecules adsorbed on graphene via AA or AB stacking.

Stacking	NA-graphene	ANS-graphene
EAA	-686.1246 eV	-695.5830 eV
EAB	-686.1823 eV	-696.6350 eV
EAB-AA	-0.057.7eV	-1.052eV

Table S2 shows that the adsorption energy of NA molecules and ANS molecules on graphene with AB stacking are 0.057.7eV and 1.052eV lower than AA stacking respectively.

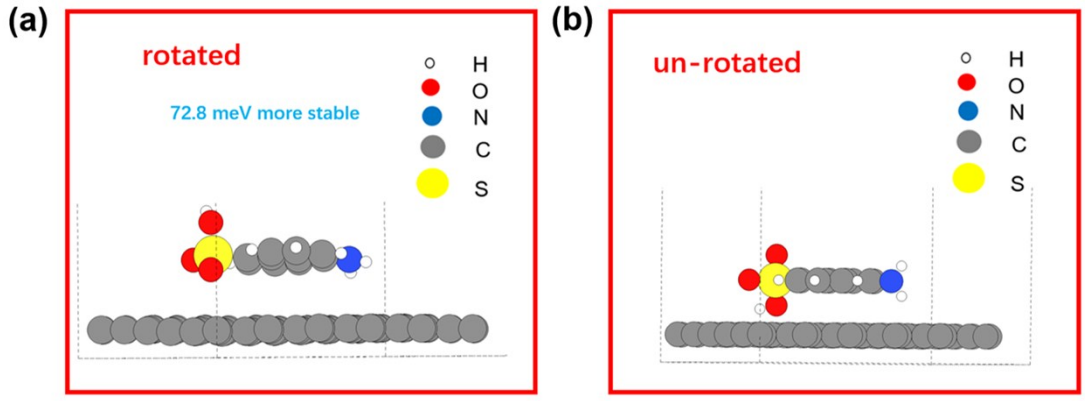

Fig. S3 The rotated ANS and un-rotated ANS molecules absorbed on graphene in (a) and (b), respectively. White, red, blue, gray, and yellow spheres donate the H, O, N, C, S atoms, respectively.

The charge density difference plot is defined as the difference between the charge density before and after bonding. From the calculation and analysis of the charge density difference plot, it is clear that the charge transfer and charge density redistribution happen during the bonding process.

As shown in Fig. S3, the adsorption energy of the rotated ANS molecules on the graphene surface is 72.8 meV stronger than the un-rotated one, thus, the rotated configuration with AB stacking has higher stability.

In order to confirm the electrons migration from the $-NH_2$ to $-SO_3H$ in the ANS molecule, we calculate the charge density difference based on the following formula

(Fig. S4).

$$\Delta\rho = (\rho_A + \rho_B) - (\rho_C + \rho_D + \rho_E)$$

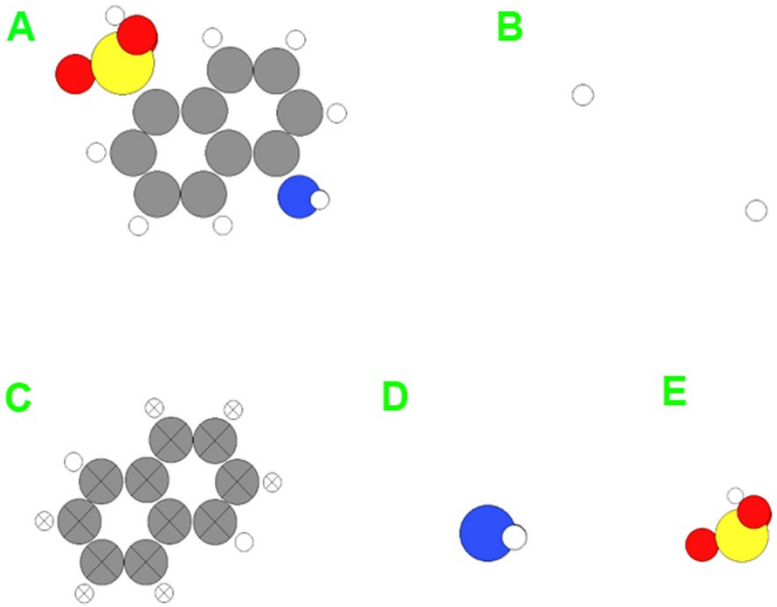

Fig. S4 Molecular structures of -NH_2, -SO_3H and ANS. The charge density difference is calculated by the formula shown above, where A is the ANS molecule. B, C, D and E are isolated hydrogen atoms, naphthalene molecule, isolated NH_2, isolated SO_3H group, respectively. Gray, white, yellow, red and blue spheres denote carbon, hydrogen, oxygen, sulfur and nitrogen atoms, respectively.

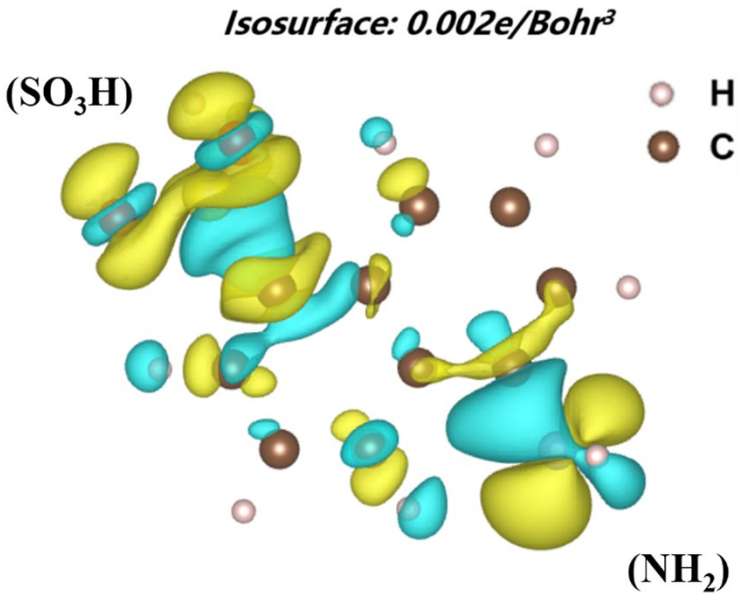

Fig. S5 The charge density difference plot of ANS at charge density isosurface 0.002e/Bohr^3. Brown sphere denotes carbon atom and white sphere denotes hydrogen atom. Yellow region indicates electron accumulation, and light blue region stand for electron deficiency.

In addition, From Fig. S5, it is intuitively demonstrated that the -NH_2 group donates a small amount of electron to the conjugated benzene rings, and the conjugated benzene rings donate a small amount of electron to the -SO_3H group. The π-bridge facilitates the electron migration from the -NH_2 to -SO_3H, significantly.

$$\Delta\rho=(\rho_A+\rho_B)-(\rho_C+\rho_D)$$

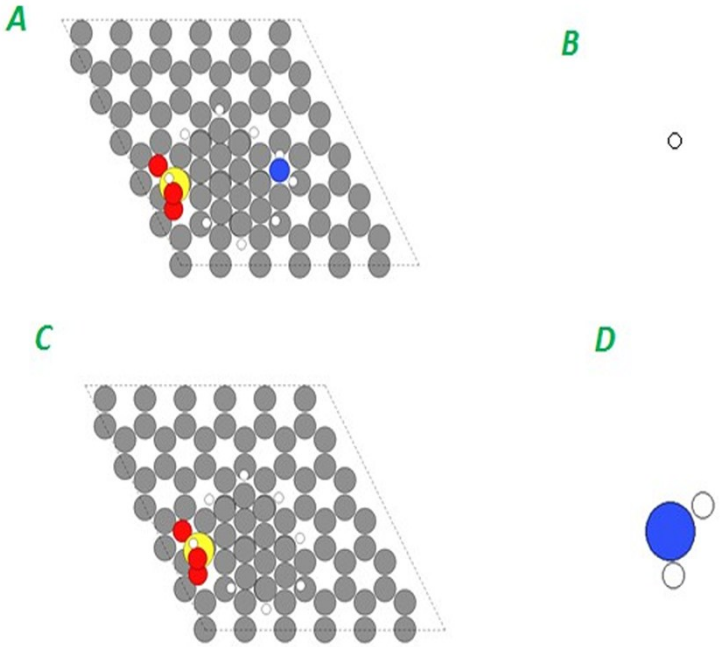

Fig. S6 Molecular structures of ANS on graphene. The charge density difference is calculated by the formula shown in the figure, where A is the ANS molecule on graphene. B, C and D are isolated hydrogen atoms, naphthalene sulfonic acid on graphene and isolated NH_2, respectively. Gray, white, yellow, red and blue spheres denote carbon, hydrogen, oxygen, sulfur and nitrogen atoms, respectively.

The detailed charge density difference calculation of the supramolecular assembled ANS-rGO was performed in Fig. S6, highlighting the charge density redistribution caused by -NH_2 group in ANS molecule and in between ANS and graphene.

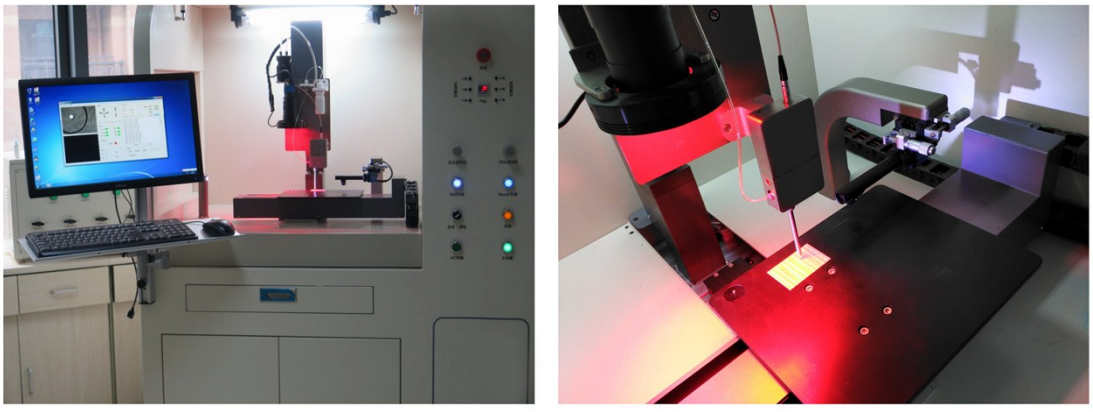

Fig. S7 The metal-jetting system and process of jetting Ag-Pd paste on ceramic plates.

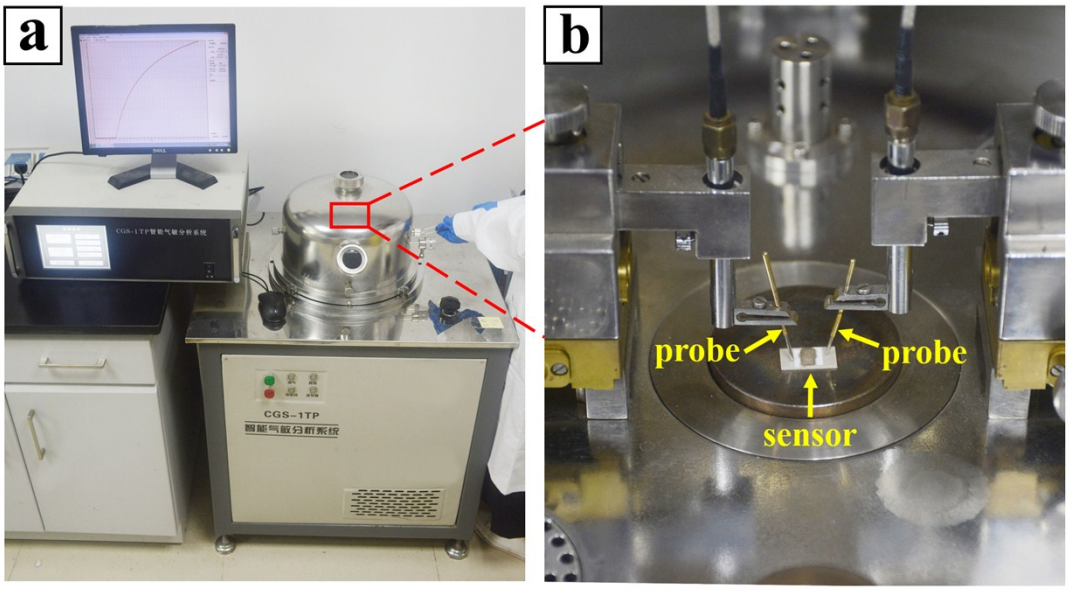

Fig. S8 (a) Experimental set up for gas sensing measurement and an ideal NO_2 gas was injected to gas chamber exhibiting sensor signals. (b)The image of test platform of inside gas chamber.