Electronic Supplementary Information

Enhanced Nonlinear Optical Response of Graphene-based Nanoflake van der Waals Heterostructuress

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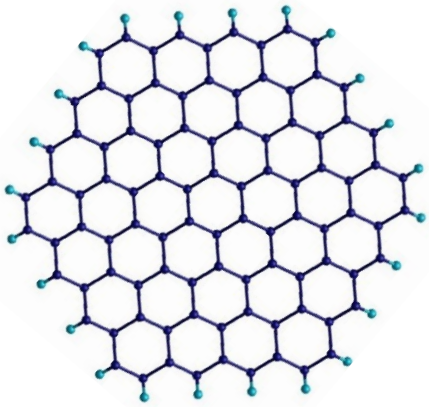
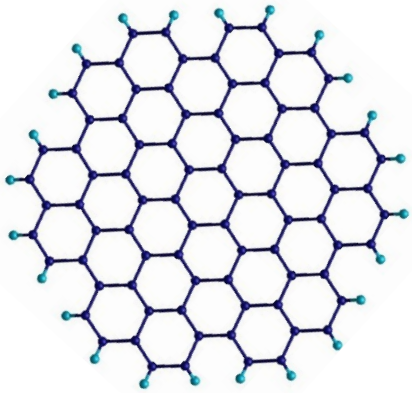
1. Phosphorene nanoflake:



N= 120; width≈24 Å
(a)



N= 108; width≈22 Å
(b)

Fig. S1: Top views of (a) zigzag phosphorene nanoflake (b) armchair phosphorene nanoflake. N is the total number of atoms.

2.0 Polarizability

The average polarizability, $\langle\alpha\rangle\ is\ \frac{1}{3}\left(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}\right)$, and the first hyperpolarizability, β is $\left(\beta_x^2+\beta_y^2+\beta_z^2\right)^{\frac{1}{2}}$. Note that β at (-w; w,0) is related to the Pockels effect, and its value at (-2w; w,w) yields the second harmonic generation (SHG) effect. γ at (-w; w, 0, 0) is related to the optical Kerr effect (OKE) and γ at (2w; w, w, 0) is related to the electric field induced second harmonic generation (EFISHG) effect.

Units:

Length, 1 a. u. =0.529 Å

Electric dipole moment, μ

$1ea_o$ = 1 a.u. = 2.5418 x 10^{-18} statvolt cm^2

Polarizability, α

1 a.u. = 1 $e^2a_o^2E_h^{-1}$ = 1.4817x10^{-25} cm^3 (esu)

First Dipole Hyperpolarizability, β

1 a. u. = 1 $e^3a_o^3E_h^{-2}$ = 8.6392x10^{-33} cm^4 $statvolt^{-1}$ (esu)

1 a. u. = 0.51422 pm/V

Second Dipole Hyperpolarizability, γ

1 a.u. = 1 $e^4a_o^4E_h^{-3}$ = 5.0367x10^{-40} cm^5 $statvolt^{-2}$ (esu)

Second-order Susceptibility, $X^{(2)}$

1 a. u = 0.51422 pm/V

Conversion factor:

1 pm/V = 2.387x10^{-9} esu

2.1 Graphene nanoflake: Basis set dependence of NLO polarizabilities calculated at the DFT (wB97XD) level of theory

The 6-31G basis set is the spilt-valence basis set, whereas the 6-31G+(d,p) basis set is supplemented by a diffuse function together with d and p-type polarization functions on C and H atoms, respectively.

Table S1: Zigzag and armchair graphene nanoflakes. The DFT (wB97XD) polarizabilities calculated using the 6-31G and 6-31+G(d,p) basis sets. α's, β's, and γ's are the polarizability, first hyperpolarizability, and second hyperpolarizability, respectively. The frequency-dependent (hyper) polarizabilities are calculated at λ=1064 nm.

		Zigzag graphene nanoflake (~22 Å)		Armchair graphene nanoflake (~24 Å)	
		6-31G	6-31+G (d,p)	6-31G	6-31+G (d,p)
Symmetry		C_S	C_S	C_S	C_S
$<\alpha>$ (x 10^{-22} esu)	(0)	3.8	3.8	4.2	4.1
	(-ω)	4.2	4.2	4.6	4.5
β (x 10^{-33} esu)	(0)	~0	~0	~0	~0
	(-ω)	~0	~0	~0	~0
	(-2ω)	~0	~0	~0	~0
$\gamma_{xxxx}/\gamma_{yyyy}$ (x 10^{-36} esu)	(0)	1285.0	1190.0	1415.0	1338.3
	(-ω)	2341.7	2195.0	2301.7	2211.7
	(-2ω)	3585.0	42735.0	11665.0	12455.0
γ_{yyxx} (x 10^{-36} esu)	(0)	428.3	400.0	473.3	446.7
	(-ω)	1161.7	1100.0	1013.3	983.3
	(-2ω)	21836.7	26956.7	5490.0	5925.0

Ref 1.1

Ref 2.1

2.2 Armchair graphene nanoflake: NLO polarizabilities calculated using various DFT exchange and correlation functional forms.

Table S2: Armchair graphene nanoflake of width ~24 Å. The polarizabilities calculated using the PBE, PBE+D2, B3LYP, wB97XD, M062X, and , PBE0+GD3 functional forms together with 6-31G basis set; α's, β's, and γ's are the polarizability, first hyperpolarizability, and second hyperpolarizability, respectively. The frequency-dependent (hyper) polarizabilities are calculated at λ=1064 nm.

		Exchange and Correlational functional form					
Armchair graphene nanoflake ($C_{180}H_{72}$)		PBE	PBE+GD2	B3LYP	wB97XD	M062X	PBE0+GD3
Symmetry		C_1	C_1	C_1	C1	C1	C1
$\langle\alpha\rangle$ (x 10^{-22} esu)	(0)	5.2	5.2	4.9	4.2	4.6	4.6
	(-ω)	7.0	7.0	5.9	4.6	5.3	5.3
β (x 10^{-33} esu)	(0)	3.5	3.5	3.1	6.4	6.1	6.1
	(-ω)	4.4	4.5	3.6	7.6	6.2	6.2
	(-2 ω)	17.2	17.6	105.0	7.5	40.2	40.2
$\gamma_{xxxx}/\gamma_{yyyy}$ (x 10^{-36} esu)	(0)	3686	3686	2312	1415	2521.6	2521.6
	(−ω)	25477	25479	8217	2302	6177.5	6177.5
	(−2ω)	319	317	12923	11665	-68678.8	-68678.8
γ_{yyxx} (x 10^{-36} esu)	(0)	1229	1229	903	473	840.2	840.2
	(−ω)	21632	21631	8611	1013	3392.6	3392.6
	(−2ω)	1266	1266	9850	5490	-45023.8	-45023.8

2.3 Zigzag and armchair graphene nanoflakes: Frontier molecular orbitals

The molecular orbitals near Fermi energy are found to be associated with either the edge atoms for zigzag nanoflakes or the atoms of the central region for the armchair nanoflakes.

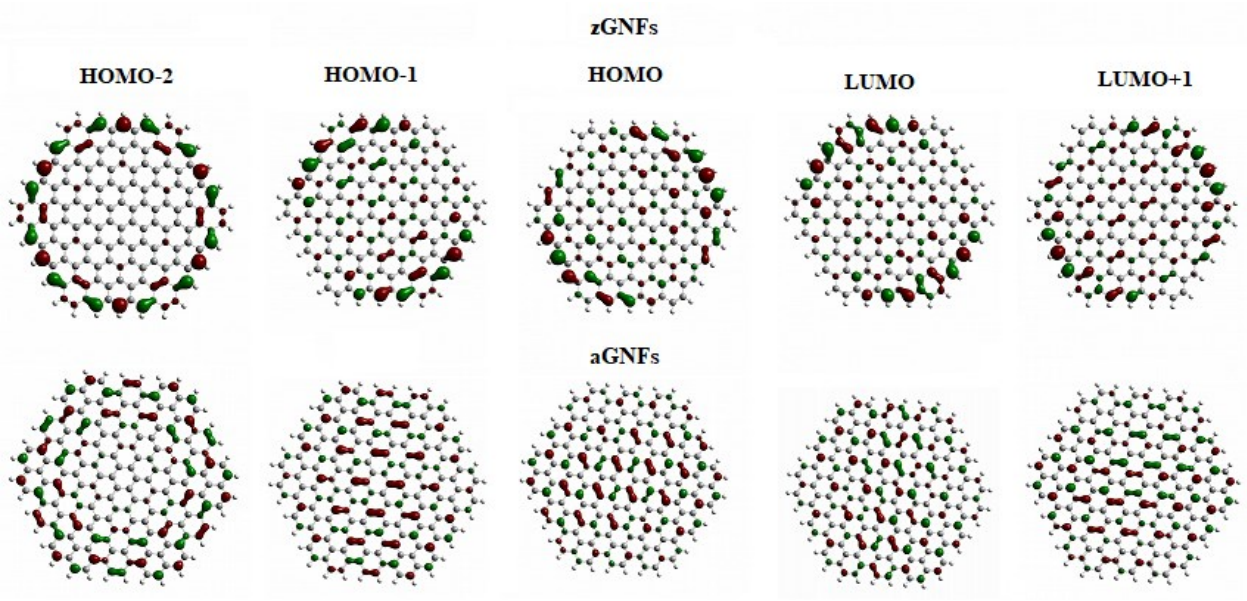


Figure S2: Frontier molecular orbital plots for zigzag and armchair graphene nanoflakes. HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital.

3.0: p-Nitroaniline

p-nitroaniline consists of a benzene ring in which a nitro group is a para to an amino group.

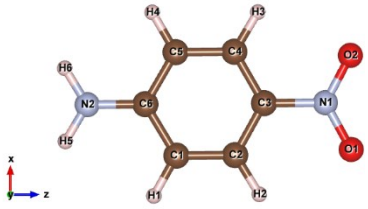


Figure S3: A ball and stick model of p-nitroaniline. Color code: C: grey, O: red, N: blue, H: white.

Table S3: p-nitroaniline: A comparison of the calculated second hyperpolarizability (β) with $\beta_{vec} = \beta_i = 1/3\ \Sigma\ (\beta_{ijj} + \beta_{jij} + \beta_{jii})$ with i=z and j=x and y. λ is 1064 nm.

Referee 1.2

Method	*Reference*	β_{vec} *(0;0,0)* *(10^{-30} esu)*	β_{vec} *(-2w;w,w)* *(10^{-30} esu)*
DFT (wB97XD) (6-31 G basis set)	This work	6.88	10.8
DFT(M062X) (6-31G basis set)	This work	6.97	10.91
DFT(PBE0+GD3) (6-31G basis set)	This work	7.25	12.34
Hartree-Fock (DZV basis set)	Karna 91 (Table V)	4.37	6.20
DFT (LDA) (standard auxiliary basis – ADF program*)	Gisbergen (Erratum-Table I)	7.45	16.99
B3LYP (aug-cc-pVDZ basis)	Salek 02 (Table IV)	6.72	12.33
Experiment (gas phase-EFISH)	Kaatz 98		15.44 ± 0.63

*ADF is the Amsterdam Density Functional package.

Karna 91: S. P. Karna and P. N. Prasad, Nonlinear optical properties of *p*-nitroaniline: An *ab initio* time-dependent coupled perturbed Hartree–Fock study, J. Chem. Phys., 94, 1177 (1991)
Gisbergen 99: S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory, J. Chem. Phys. 109, 10644 (1998) – **Erratum**: J. Chem. Phys. 111, 6652 (1999).
Salek 02: P. Sałek, O. Vahtras, T. Helgaker, and H. Ågren, Density-functional theory of linear and nonlinear time-dependent molecular properties, J. Chem. Phys. 117, 9630 (2002).
Kaatz 98: P. Kaatz, E. A. Donley, and D. P. Shelton, A comparison of molecular hyperpolarizabilities from gas and liquid phase measurements, J. Chem. Phys. 108, 849 (1998).

3.0 Nanoflake heterostructure:

3.1 Bonding

Ref 1.4

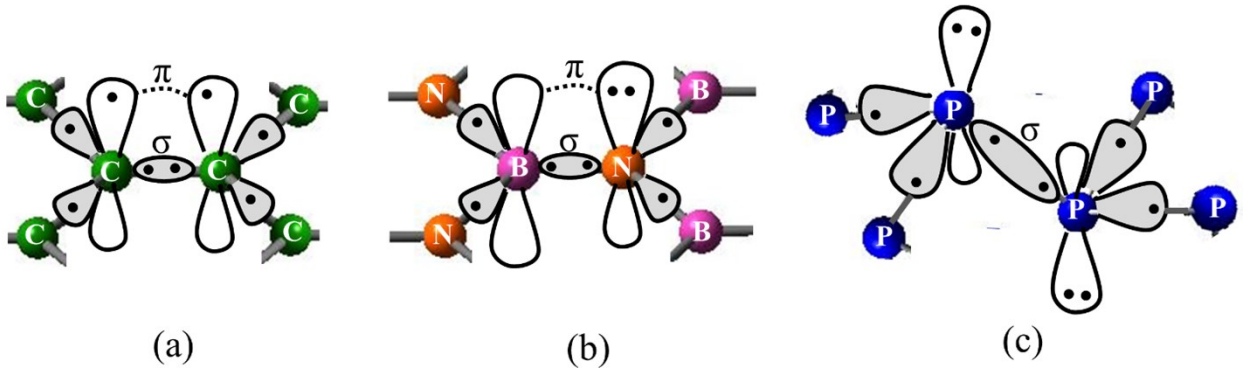


Fig S4. Bonding in pristine (a) graphene, (b) h-BN monolayer, and (c) phosphorene displaying sp^2, and sp^3 hybridization. The calculated bond lengths are 1.43 Å ($R_{(C-C)}$), 1.45 Å ($R_{(B-N)}$), and 2.37 Å ($R_{(P-P)}$) in the pristine graphene, h-BN monolayer and phosphorene, respectively.

3.2 Charge Density

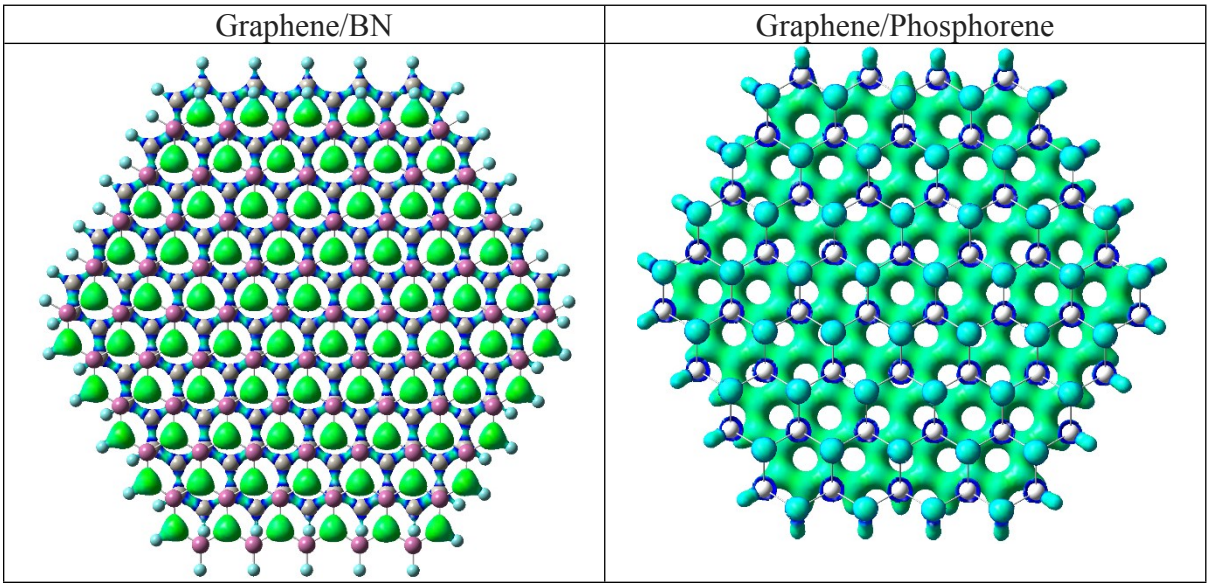


Figure S5: Total charge density of zigzag AB-stacked Graphene/BN and Graphene/Phosphorene. The isovalue of the charge density contour is ~0.3 $e^-/a.u^3$ for both graphene/BN and graphene/phosphorene heterostructures.

3.3 Graphene/BN nanoflake heterostructure: β vs. interlayer dependence

Table S4: Graphene/BN heterostructure nanoflakes: Calculated DFT (wB97XD) results of zigzag AA-stacked configuration showing the relationship between the interlayer distance and NLO polarizability; μ is dipole moment. α's, β's, and γ's are the polarizability, first hyperpolarizability, and second hyperpolarizability values, respectively. λ is 1064 nm.

		AA-stacked	
		Case A	Case B
Symmetry		C_1	C_1
Interlayer distance, Å		3.4 (equilibrium separation)	3.0
$E_{(HOMO-LUMO\ gap)}$, eV		3.4	3.4
μ (D)		3.3	3.9
$<\alpha>$ ($\times 10^{-22}$ esu)	(0)	5.4	5.4
	(- ω)	6.1	6.2
β ($\times 10^{-33}$ esu)	β(0)	5620.8	18677.0
	β(- ω)	7116.5	52712.0
	β(-2 ω)	78504.8	122449.0
$\gamma_{xxxx}/\gamma_{yyyy}$ ($\times 10^{-36}$ esu)	(0)	1630.0	1741.7
	(−ω)	4160.0	4985.7
	(−2ω)	-695.0	-20347.3
γ_{yyxx} ($\times 10^{-36}$ esu)	(0)	542.6	581.2
	(−ω)	2543.7	3192.5
	(−2ω)	10659.5	-5612.7

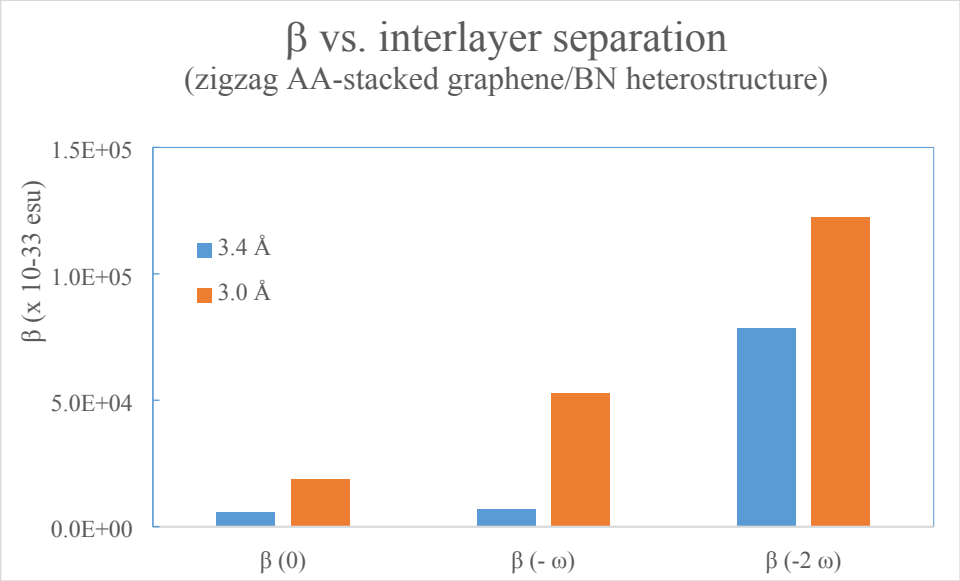


Fig S6. β vs interlayer separation for the zigzag AA-stacked graphene/BN heterostructure.

4.0 Estimation of second-harmonic generation (SHG):

SHG or frequency doubling is estimated [1, 2] as

$$SHG = X^{(2)}/2 = (\beta * 2\pi / V)/2 \quad (1)$$

Here, β is the (microscopic) first hyperpolarizability and $X^{(2)}$ is the (macroscopic) second-order susceptibility. V is volume approximated as (t_{layer} x $R_{interlayer}$) where t is the thickness and $R_{interlayer}$ is the interlayer separation. The thickness of a heterostructure, t is the sum of the thickness of the first layer, interlayer separation, and the thickness of the second layer. We have taken the thickness of graphene and h-BN monolayer to be 0.335 nm [2] and that of phosphorene is taken to be 0.85 nm [3].

Table S5: The estimated SHG values of pristine nanoflakes and their heterostructures. Atomic units are used (volume: $Bohr^3$)

Zigzag		**Graphene**	**BN**	**Phosphorene**	**C/BN-AA stacked**	**C/BN-AB stacked**	**C/P**
Atomic Unit	Area	1315.7	1315.7	1315.7	1315.7	1315.7	1315.7
	thickness	6.3	6.3	12.3	19.1	18.7	38.94
	Volume	8288.91	8288.91	16183.11	25129.87	24603.59	51233.36
	2 PI/V	0.0008	0.0008	0.0004	0.0002	0.0003	0.0001
	β (-2ω)	0.14	19.71	1.68	9087.10	69088.00	419586.40
	$X^{(2)}$	0.0001	0.0149	0.0007	2.2709	17.6345	51.4314
pm/V	$X^{(2)}$	0.0002	0.0290	0.0013	4.4162	34.2937	100.0183
pm/V	SHG	0.0001	0.0145	0.0006	2.2081	17.1469	50.0091
Armchair							
Atomic Unit	Area	1615.80	1615.80	1615.80	1615.80	1615.80	1615.80
	thickness	6.3	6.3	12.3	19.1	18.7	38.94
	Volume	10179.54	10179.54	19874.34	30861.78	30215.46	62919.25
	2 PI/V	0.0006	0.0006	0.0003	0.0002	0.0002	0.0001
	β (-2ω)	0.14	25.96	1.90	1465.10	11956.90	15294.70
	$X^{(2)}$	0.0001	0.0160	0.0006	0.2981	2.4851	1.5266
pm/V	$X^{(2)}$	0.0002	0.0311	0.0012	0.5798	4.8328	2.9687
pm/V	SHG	0.0001	0.0156	0.0006	0.2899	2.4164	1.4844

References:

1. https://www.crystal.unito.it/Manuals/crystal17.pdf
2. R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rerat, S. Casassa, J. Baima, S. Salustro, B. Kirtman, WIREs Comput Mol Sci. 8, e1360 (2018).
3. Ni et al., "Graphene Thickness Determination Using Reflection and Contrast Spectroscopy", Nano Lett. 7, 2758-2763 (2007).
4. Lu et al., "Plasma-assisted fabrication of monolayer phosphorene and its Raman characterization", Nano Res. 7, 853–859 (2014).