Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Exploration of Isoelectronic Substitution in Graphene Dioxide for Photocatalytic and Photovoltaic Applications - an *Ab-Initio* Study

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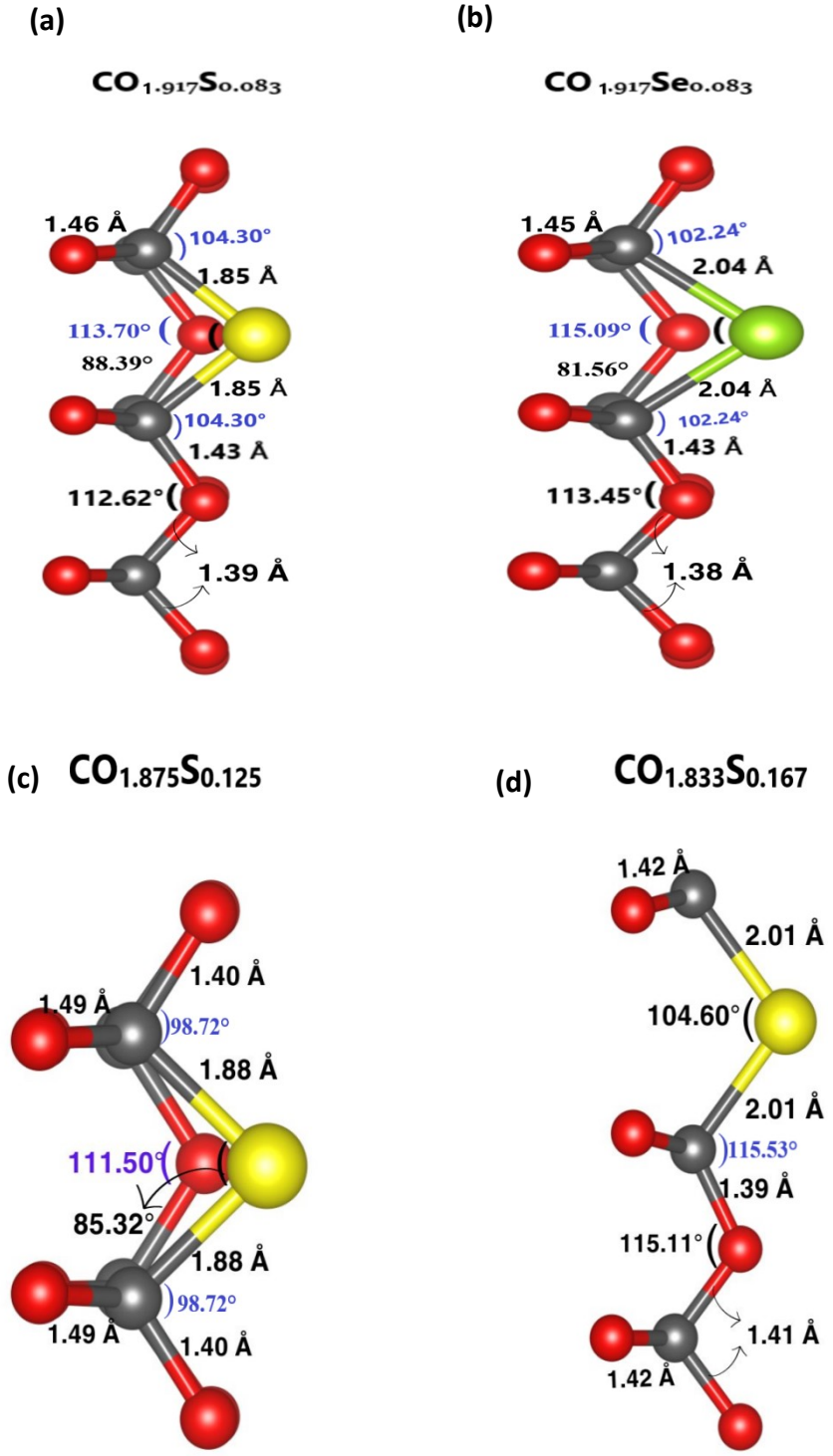

Fig S1. Optimized crystal structure of S/Se substituted GDO side view. The atoms are depicted as C (gray), O (red), S (yellow) and Se (green).

Composition	C-O (N)	C-O (NN)	C-S/Se
GDO	1.43 Å	-	-
$CO_{1.917}Se_{0.083}$	1.43 Å	1.38 Å	2.04 Å
$CO_{1.917}S_{0.083}$	1.43 Å	1.39 Å	1.85 Å
$CO_{1.875}S_{0.125}$	1.40 Å	1.40 Å	1.88 Å
$CO_{1.833}S_{0.167}$	1.39 Å	1.41 Å	2.01 Å

Table S1: The C-O and C-S/Se bond length of S/Se substituted GDO after structural optimization. C-O (N) corresponds to the most neighboring C-O bond to the S/Se substitution and C-O (NN) stands for the C-O bond length of the next neighboring C-O bond to the S/Se substitution.

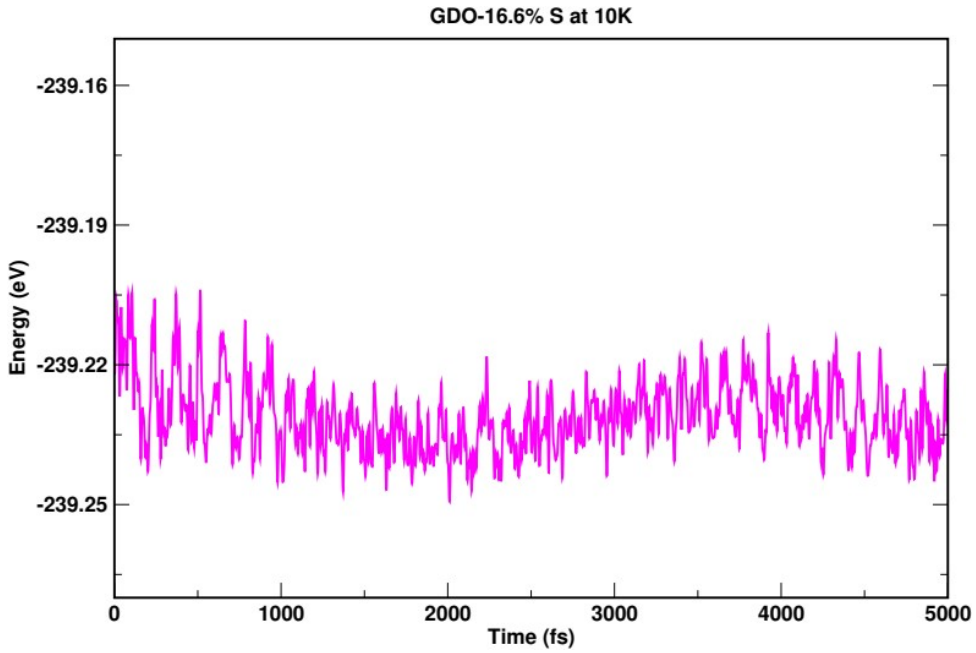

Fig. S2. The AIMD simulation for energy convergence of $CO_{1.833}S_{0.167}$ at 10K for 5000 fs.

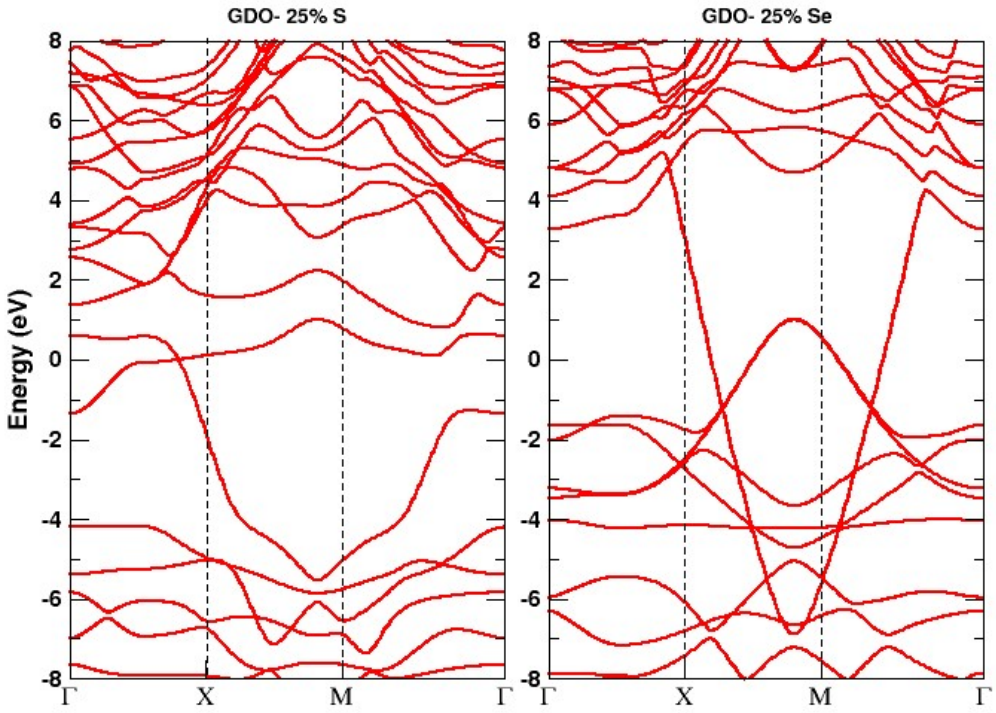

Fig. S3: The electronic band structure of 25% S and Se substituted GDO using PBE functional.

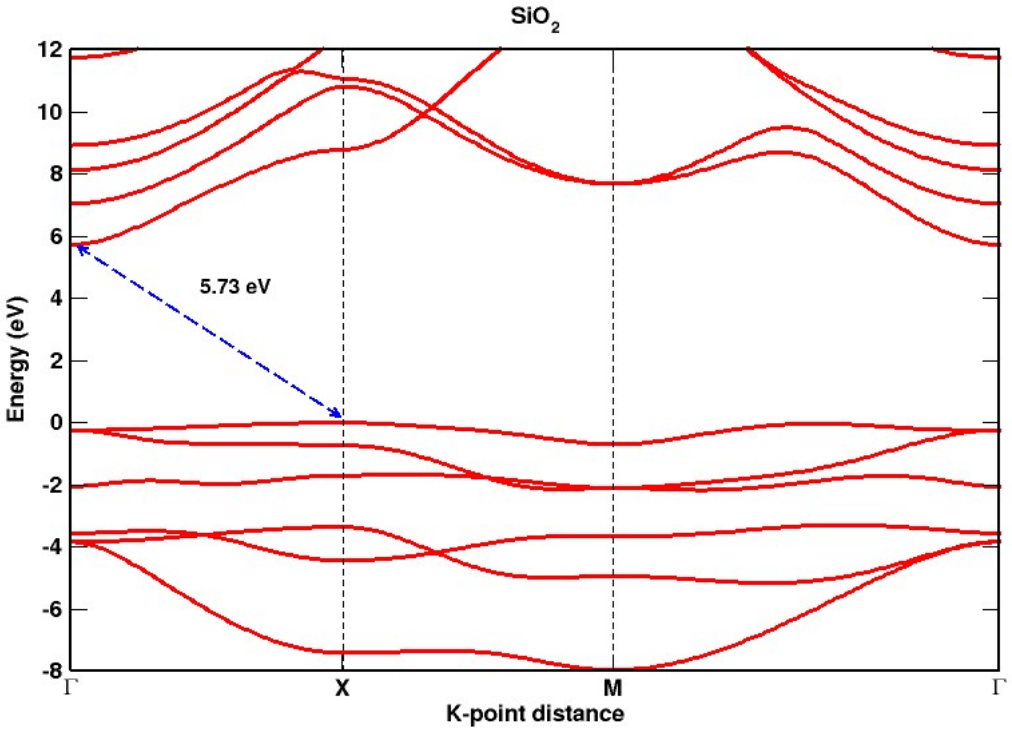

Fig S4. The electronic band structure of Si substituted GDO using PBE functional. The Fermi level is set to 0 eV.

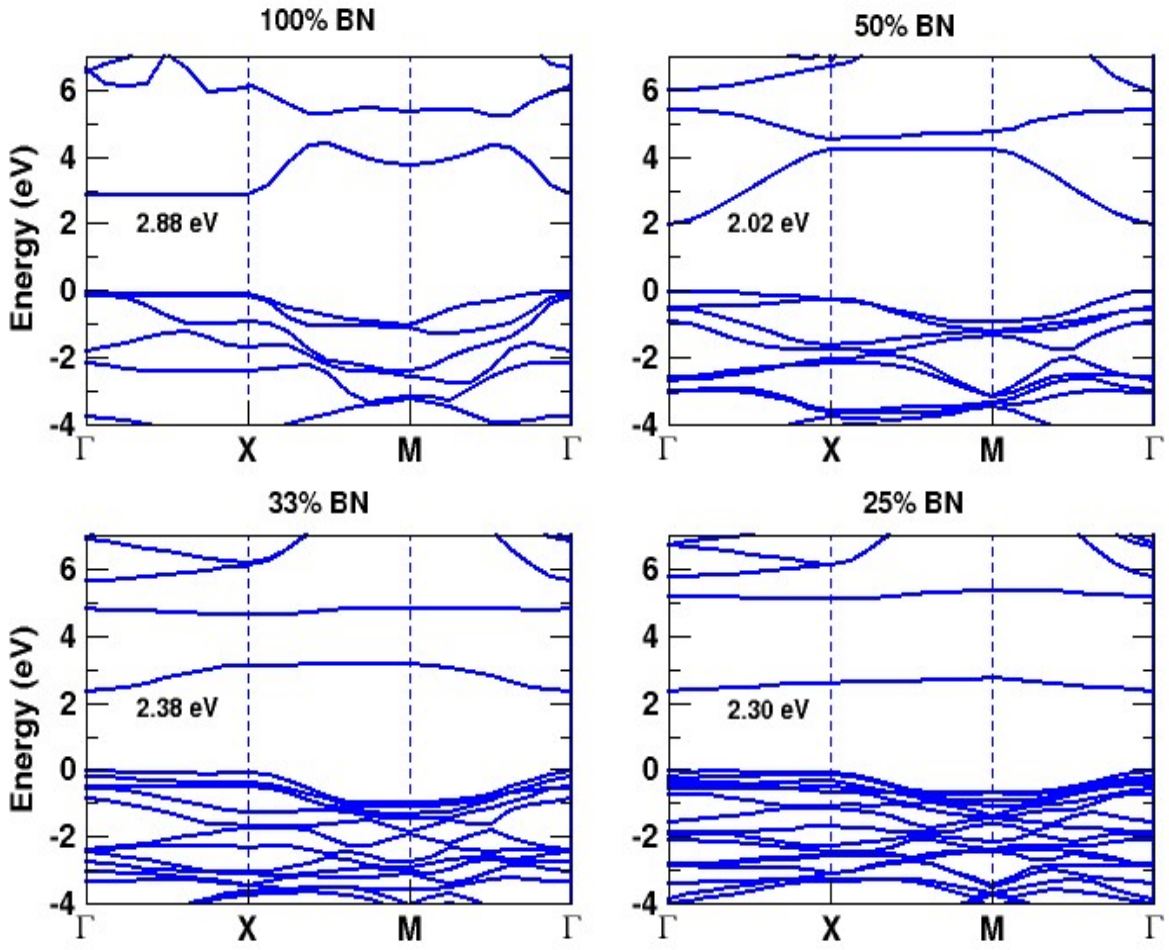

Fig. S5. The electronic band structure of (B,N) co-substituted GDO for various concentrations, using HSE06 functional. The Fermi level is set to 0 eV.

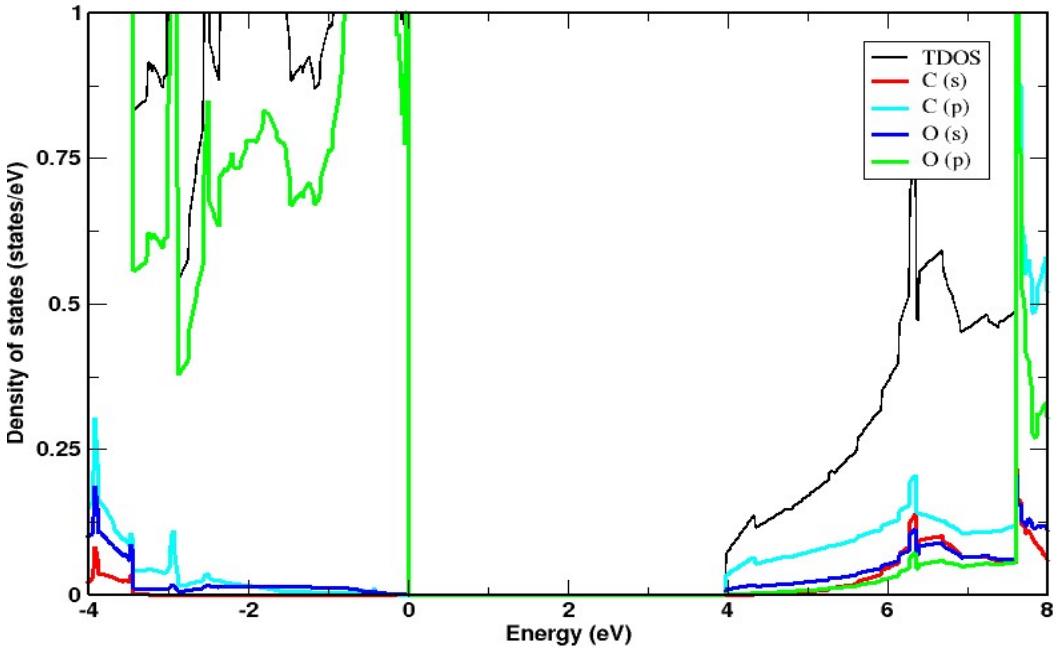

Fig.

Fig. S6. The total (in states eV^{-1}) and site projected density of states (in states eV^{-1} $atom^{-1}$) for GDO. The Fermi level is set to 0 eV.

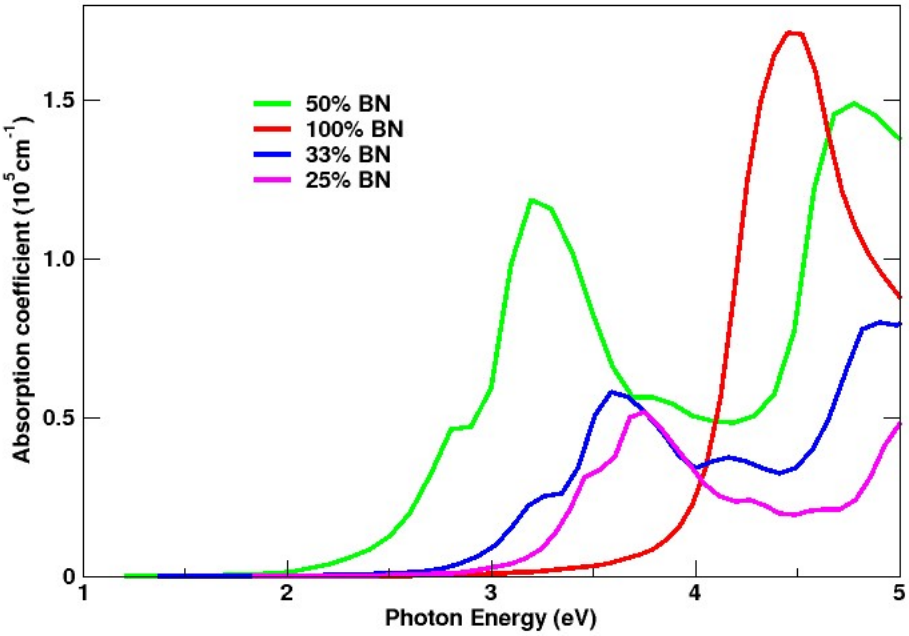

Fig. S7. Optical absorption spectra of GDO with varying concentrations of (B,N) co-substitution.

Composition	**E_g (PBE) (eV)**	**E_g (HSE06) (eV)**	**m_e* (m_o)**	**m_h* (m_o)**
100% BN	1.56	2.88	0.691	1.181 (Γ->M)
50% BN	0.80	2.02	0.267 0.654	1.525 (X->Γ) 1.294 (Γ->M)
33% BN	1.26	2.38	0.475 0.863	2.145 (Γ->X) 2.429 (Γ->M)
25% BN	1.03	2.30	1.534	1.291 (Γ->M)

Table S2: Calculated band gap value (in eV) using PBE and HSE06 functionals, effective mass of electrons (m_e*) and holes (m_h*) (in m_0), and for (B,N)-Co-substituted GDO.