Electronic Supplementary Information

Planar Graphitic ZnS, Buckling ZnS Monolayers and Rolled-up Nanotubes as Nonlinear Optical Materials: First-Principles Simulation

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1. Band structure and interlayer distance of wurtzite ZnS

![Figure S1](image)

**Figure S1** (a) band structure calculated with HSE06 functional and (b) interlayer distance of wurtzite ZnS

As can be seen, wurtzite ZnS crystal exhibits a direct bandgap, with the VBM and CBM both
located at the $\Gamma$ (0.0, 0.0, 0.0) point. The band gap of wurtzite ZnS crystal is 3.51 eV, which is close to the experimental value 3.77 eV \(^1\). As shown in Figure 1S(b), similar to planar g-SiC \(^2\), the effective thickness of planar g-ZnS is set as the interlayer distance 3.898 Å of wurtzite ZnS crystal.

2. Band structure of planar g-ZnS

![Figure S2](image)

Figure S2 (a) Band structure of planar g-ZnS monolayer calculated using HSE06 functional, and (b) high symmetry k-point path in the Brillouin zone path $\Gamma$ (0, 0, 0) $\rightarrow$ K (-1/3, 2/3, 0) $\rightarrow$ M (0, 1/2, 0) $\rightarrow$ $\Gamma$ (0, 0, 0).

As suggested by Figure S2, planar g-ZnS monolayer has a direct band gap of 3.80 eV at the $\Gamma$ point.

3. Band structure of buckling R-ZnS monolayer

Figure S3 suggests buckling R-ZnS monolayers have direct bandgaps with the VBM and CMB located at the $\Gamma$ point. The bandgaps of buckling R-ZnS are steady around 3.90 eV with a small variance of $\sim$ 0.10 eV.

![Figure S3](image)

Figure S3 Band structure of buckling R\(_1\)-ZnS, R\(_2\)-ZnS, R\(_3\)-ZnS, R\(_4\)-ZnS and R\(_5\)-ZnS calculated using HSE06 functional. The high symmetry k-point path in the Brillouin Zone, as shown in (c), is chosen as $\Gamma$ (0, 0, 0) $\rightarrow$ K (-1/3, 2/3, 0) $\rightarrow$ M (0, 1/2, 0) $\rightarrow$ $\Gamma$ (0, 0, 0).
4. Band structure and total density of electronic states of a representative (12, 0) ZnS SWNT

Zigzag and chiral ZnS SWNTs show similar electronic structures. As a representative, the band structure and total density of electronic states are given in Figure S4. As can be seen, ZnS (12, 0) SWNT exhibits a direct band gap at the Γ (0.0, 0.0, 0.0) point, and a sharp peak in the top of valence bands.

![Figure S4 Band structure and total density of electronic states of a (12, 0) ZnS SWNT](image)

5. SHG intensity estimation of planar g-ZnS, buckling R-ZnS and ZnS SWNTs

According to the electric dipole theory, the SHG intensity $I_{2\omega}$ is proportional to $\frac{|\chi^{(2)}_{xxxy}|^2 d^2}{n_\omega n_{2\omega}^2}$, where $d$ is the effective thickness of monolayers, $n_\omega$ and $n_{2\omega}$ are respectively the refractive index at frequency $\omega$ of excitation laser and at frequency $2\omega$ of SHG field. Previous experiments demonstrate the nonresonant SHG intensity of monolayer GaSe is stronger than that of monolayer MoS$_2$, WS$_2$, WSe$_2$ and BN. Here, we make a comparison of SHG intensities of monolayer g-ZnS, GaSe and MoS$_2$. The theoretical $n_\omega$, $n_{2\omega}$ at 1600 nm and effective thickness of planar g-ZnS in Table S1, and that of monolayer GaSe and MoS$_2$ is also shown for comparison. The theoretical SHG coefficients $\chi^{(2)}_{xxxy}$ at an excitation wavelength of 1600 nm for monolayer GaSe and planar g-ZnS are 75 pm/V and 42 pm/V, respectively. The estimated ratio of SHG intensities at 1600 nm between monolayer g-ZnS and GaSe is ~0.2. Experiments show the SHG intensity of single-layer MoS$_2$ at 1600 nm is less than 1/10 that of single-layer GaSe. Therefore, the nonresonant SHG
intensity of planar g-ZnS at 1600 nm is stronger than that of single-layer MoS$_2$, which mainly originates from smaller optical refractive indices of planar g-ZnS.

**Table S1.** $n_\omega$, $n_{2\omega}$ at 1600 nm and effective thickness $d$ (Å) of monolayer GaSe, planar g-ZnS, MoS$_2$ and buckling R-ZnS

| Materials | GaSe | g-ZnS | MoS$_2$ | R$_1$-ZnS | R$_2$-ZnS | R$_3$-ZnS | R$_4$-ZnS | R$_5$-ZnS |
|-----------|------|-------|---------|-----------|-----------|-----------|-----------|-----------|
| $d$       | 7.99 | 3.90  | 6.0     | 3.92      | 3.93      | 4.18      | 4.25      | 4.35      |
| $n_\omega$| 2.70 | 2.15  | 4.0     | 2.16      | 2.16      | 2.15      | 2.16      | 2.17      |
| $n_{2\omega}$| 2.77 | 2.18  | 4.5     | 2.19      | 2.19      | 2.17      | 2.18      | 2.20      |

As shown in Figure 2 of the main manuscript, the SHG coefficient of planar g-ZnS nearly keeps constant from zero to 1.0 eV, e.g. 42 pm/V at 1600 nm versus 37.4 pm/V at the static limit, which indicating their nonresonant SHG intensities nearly keep constant. Moreover, the nonresonant SHG regime of planar g-ZnS covers the whole mid-infrared regime (2-8 μm), so planar g-ZnS has a potential application in the mid-infrared regime.

**Table S2.** $n_\omega$ and $n_{2\omega}$ at 1600 nm of ZnS SWNTs

| Materials | (6,0) | (8,0) | (9,0) | (12,0) | (16,0) | (18,0) | (20,0) | (4,2) | (6,3) |
|-----------|-------|-------|-------|--------|--------|--------|--------|-------|-------|
| $n_\omega$| 2.15  | 2.16  | 2.15  | 2.16   | 2.14   | 2.13   | 2.16   | 2.17  |
| $n_{2\omega}$| 2.19  | 2.20  | 2.18  | 2.19   | 2.20   | 2.17   | 2.16   | 2.19  | 2.21  |

Furthermore, the optical refractive indices $n_\omega$ and $n_{2\omega}$ of buckling R-ZnS [cf. Table S1] and ZnS SWNTs [cf. Table S2] are nearly not modified in comparison with that of planar g-ZnS. Resultantly, small refractive indices will also enhance SHG signals of buckling R-ZnS and ZnS SWNTs.

**References**

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