Supplementary materials for "Analysis of Optimal Crosslink Density and Platelet Size Insensitivity in Graphene-Based Artificial Nacres"

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Appendix A: A nonlinear shear lag model

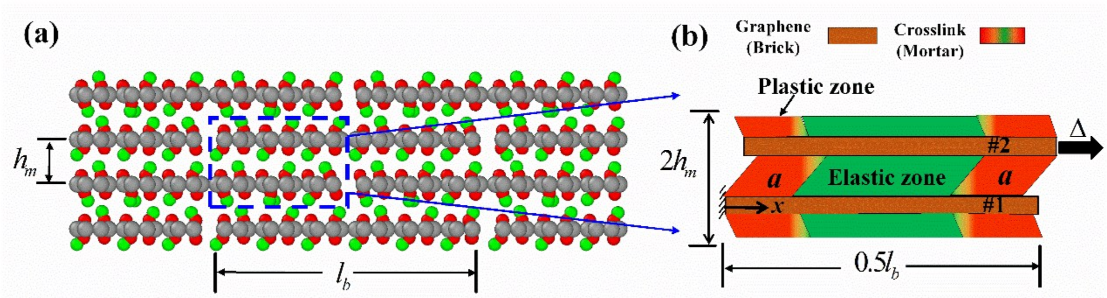

Fig. S1 (a) Schematics of the brick (graphene)-and-motor (crosslinks) structure and representative volume element (RVE, as highlighted as the dash box); (b) Schematics of a nonlinear shear-lag model with elastic-perfectly-plastic interface under tension (plastic zone, as highlighted as the red zone; elastic zone, as highlighted as the green zone).

Fig. S1 shows a continuum model proposed in our previous work.[1] In this model, the tensile stiffness D_g, strength σ_{cr} of graphene sheet and the shear modulus G_m, strength τ^f of the interlayer are expressed as functions of crosslink density d (d is defined as the ratio of the number of functional groups over that of carbon atoms in graphene sheets), respectively, and these functional relationships can be obtained by atomistic simulations. The out-plane deformation is neglected, thus the stiffness of graphene sheet is defined as $D_g = E_b h_b$ (E_b is Young's modulus), where h_b is the graphene sheet thickness. The representative volume element (RVE) under uniaxial tension is simplified as shown in Fig. S1(b), the length of the graphene sheet is l_b and the interlayer crosslinks are considered as a continuum media. We use an elastic perfectly plastic interface with shear modulus G_m, shear strength τ^f, yield strain γ_e^c and failure strain γ_p^f to characterize the interlayer interactions between graphene sheets. And the plastic zone with the length a is marked by red color and the elastic zone is marked by green color. The overall mechanical properties of graphene-based artificial nacre nanocomposites is illustrated through nonlinear shear-lag analysis for RVE.

When the RVE under uniaxial tension, the mechanical equilibrium is governed by

$$\begin{cases} 2\tau(x) = -D_g u_1''(x) & \text{(Graphene \#1)} \\ 2\tau(x) = D_g u_2''(x) & \text{(Graphene \#2)} \end{cases} \tag{A.1}$$

where $u_1(x), u_2(x)$ are the in-plane displacements in the graphene sheet #1 and #2, respectively, $\tau(x)$ is the shear stress in the interface.

The governing equations for the elastic zone ($0 \le x \le a$ and $0.5l_b - a \le x \le 0.5l_b$) and plasticity zone ($a < x < 0.5l_b - a$) of RVE are

$$\tau(x) = \begin{cases} |u_2(x) - u_1(x)| \times G_m / h_m & 0 \le x \le a \text{ and } 0.5l_b - a \le x \le 0.5l_b \\ \tau^f & a < x < 0.5l_b - a \end{cases} \tag{A.2}$$

where h_m is the interlayer distance.

From eqns. (A.1) and (A.2), we have the governing equation for the elastic zone of platelet #1 and platelet #2，which is expressed as

$$\begin{cases} G_m \dfrac{u_2(x)-u_1(x)}{h_m} + \dfrac{1}{2} D_g u_1''(x) = 0 \\ G_m \dfrac{u_2(x)-u_1(x)}{h_m} - \dfrac{1}{2} D_g u_2''(x) = 0 \end{cases}, \quad 0 \le x \le a \text{ and } 0.5 l_b - a \le x \le 0.5 l_b \qquad \text{(A.3a)}$$

And the governing equation for the plasticity zone of platelet #1 and platelet #2 is expressed as

$$\begin{cases} \tau^f + \dfrac{1}{2} D_g u_1''(x) = 0 \\ \tau^f - \dfrac{1}{2} D_g u_2''(x) = 0 \end{cases}, \quad a < x < 0.5 l_b - a \qquad \text{(A.3b)}$$

We define $\bar{a} = a / l_b$ and $\bar{x} = x / l_b$. From eqns. (A.3a) and (A.3b), the normalized equations are given as

$$\begin{cases} \bar{u}_1'' = -2\alpha^2, \ \ 0 \le \bar{x} \le \bar{a} \text{ or } 0.5 - \bar{a} \le \bar{x} \le 0.5 \\ \bar{u}_1'' = 2k_2^2 \left(\bar{u}_1 - \bar{u}_2\right), \ \bar{a} \le \bar{x} \le 0.5\text{-}\bar{a} \\ \bar{u}_2'' = 2\alpha^2, \ \ 0 \le \bar{x} \le \bar{a} \text{ or } 0.5 - \bar{a} \le \bar{x} \le 0.5 \\ \bar{u}_2'' = 2k_2^2 \left(\bar{u}_2 - \bar{u}_1\right), \ \bar{a} \le \bar{x} \le 0.5\text{-}\bar{a} \end{cases} \qquad \text{(A.4)}$$

where $\alpha = \sqrt{\dfrac{\tau^f l_b}{D_g}}$, $k_2 = \sqrt{\dfrac{G_m l_b^2}{D_g h_m}} = \dfrac{l_b}{2 l_c}$, $l_c = \sqrt{\dfrac{D_g h_m}{4 G_m}}$ is defined as a characteristic length below which the shear stress is almost uniform along the interface. The solutions of eqn. (A.4) can be written as

$$\begin{cases} \bar{u}_1 = -\alpha^2 \bar{x}^2 + c_1 \bar{x} + c_2, & 0 \le \bar{x} \le \bar{a} \\ \bar{u}_1 = c_3 + c_4 \bar{x} - c_5 \sinh\left(2k_2 \bar{x}\right) - c_6 \cosh\left(2k_2 \bar{x}\right), & \bar{a} \le \bar{x} \le 0.5 - \bar{a} \\ \bar{u}_1 = -\alpha^2 \bar{x}^2 + c_7 \bar{x} + c_8, & 0.5 - \bar{a} \le \bar{x} \le 0.5 \\ \bar{u}_2 = \alpha^2 \bar{x}^2 + c_9 \bar{x} + c_{10}, & 0 \le \bar{x} \le \bar{a} \\ \bar{u}_2 = c_3 + c_4 \bar{x} + c_5 \sinh\left(2k_2 \bar{x}\right) + c_6 \cosh\left(2k_2 \bar{x}\right), & \bar{a} \le \bar{x} \le 0.5 - \bar{a} \\ \bar{u}_2 = \alpha^2 \bar{x}^2 + c_{11} \bar{x} + c_{12}, & 0.5 - \bar{a} \le \bar{x} \le 0.5 \end{cases} \qquad \text{(A.5)}$$

To get the displacement fields of the RVE, we need to determine thirteen unknown variables, $c_1, c_2, c_3 .... c_{12}, a$ appeared in eqn. (A.5) from the boundary conditions.

Firstly, the stress and displacement in the graphene sheet #1 and #2 are continuous at

$x=\bar{a}$ and $x=0.5-\bar{a}$. They lead to eight equations

$$
\begin{aligned}
&\bar{u}_1'(\bar{x}=\bar{a}_-)=\bar{u}_1'(\bar{x}=\bar{a}_+)\\
&\bar{u}_1(\bar{x}=\bar{a}_-)=\bar{u}_1(\bar{x}=\bar{a}_+)\\
&\bar{u}_1'[\bar{x}=(0.5-\bar{a})_-]=\bar{u}_1'[\bar{x}=(0.5-\bar{a})_+]\\
&\bar{u}_1[\bar{x}=(0.5-\bar{a})_-]=\bar{u}_1[\bar{x}=(0.5-\bar{a})_+]\\
&\bar{u}_2'(\bar{x}=\bar{a}_-)=\bar{u}_2'(\bar{x}=\bar{a}_+)\\
&\bar{u}_2(\bar{x}=\bar{a}_-)=\bar{u}_2(\bar{x}=\bar{a}_+)\\
&\bar{u}_2'[\bar{x}=(0.5-\bar{a})_-]=\bar{u}_2'[\bar{x}=(0.5-\bar{a})_+]\\
&\bar{u}_2[\bar{x}=(0.5-\bar{a})_-]=\bar{u}_2[\bar{x}=(0.5-\bar{a})_+]
\end{aligned}
\tag{A.6}
$$

There are four boundary conditions for RVE

$$
\begin{aligned}
&\bar{u}_1(0)=0, \quad u_2'(0)=0\\
&\bar{u}_1'(\bar{a})=\bar{u}_2'(0.5-a), \quad \bar{u}_2(0.5)=\bar{\Delta}
\end{aligned}
\tag{A.7}
$$

Substituting eqns. (A.6), (A.7) into eqn. (A.5), c_1 to c_{12} can be determined by $\bar{\Delta}=\Delta/l_b$, k_2 and α

$$
\begin{aligned}
c_1&=\frac{4\bar{a}\alpha^2\cosh\left[(-0.5+2\bar{a})k_2\right]-2k_2\left(2\bar{a}^2\alpha^2+\bar{\Delta}\right)\sinh\left[(-0.5+2\bar{a})k_2\right]}{\cosh\left[(-0.5+2\bar{a})k_2\right]-(0.5+2\bar{a})k_2\sinh\left[(-0.5+2\bar{a})k_2\right]}\\
c_2&=0\\
c_3&=\frac{\left(-0.5\bar{a}\alpha^2+0.5\bar{\Delta}\right)\cosh\left[2(-0.25+\bar{a})k_2\right]+\bar{a}k_2\left(0.5\bar{a}\alpha^2-\bar{\Delta}\right)\sinh\left[2(-0.25+\bar{a})k_2\right]}{\cosh\left[2(-0.25+\bar{a})k_2\right]+(-0.5-2\bar{a})k_2\sinh\left[2(-0.25+\bar{a})k_2\right]}\\
c_4&=-\frac{-2\bar{a}\alpha^2\cosh\left[2(-0.25+\bar{a})k_2\right]+k_2\left(2\bar{a}^2\alpha^2+\bar{\Delta}\right)\sinh\left[2(-0.25+\bar{a})k_2\right]}{\cosh\left[2(-0.25+\bar{a})k_2\right]-2(0.25+\bar{a})k_2\sinh\left[2(-0.25+\bar{a})k_2\right]}\\
c_5&=-\frac{\left(2\bar{a}(0.5+\bar{a})\alpha^2-\bar{\Delta}\right)Sech\left[2(-0.25+\bar{a})k_2\right]^2\left(\sinh\left[2(0.5-\bar{a})k_2\right]+\sinh\left[2\bar{a}k_2\right]\right)}{-4+8(0.25+\bar{a})k_2\tanh\left[2(-0.25+\bar{a})k_2\right]}\\
c_6&=\frac{\left(2\bar{a}(0.5+\bar{a})\alpha^2-\bar{\Delta}\right)\left(\cosh\left[2(-0.5+\bar{a})k_2\right]+\cosh\left[2\bar{a}k_2\right]\right)Sech\left[2(-0.25+\bar{a})k_2\right]^2}{-4+8(0.25+\bar{a})k_2\tanh\left[2(-0.25+\bar{a})k_2\right]}\\
c_7&=\alpha^2\\
c_8&=\frac{(-0.25+\bar{a})\alpha^2\cosh\left[2(-0.25+\bar{a})k_2\right]+k_2\left(\left(0.125+(0.5-\bar{a})\bar{a}\right)\alpha^2-0.5\bar{\Delta}\right)\sinh\left[2(-0.25+\bar{a})k_2\right]}{\cosh\left[2(-0.25+\bar{a})k_2\right]+(-0.5-2\bar{a})k_2\sinh\left[2(-0.25+\bar{a})k_2\right]}\\
c_9&=0\\
c_{10}&=\frac{\left(-\bar{a}\alpha^2+\bar{\Delta}\right)\cosh\left[2(-0.25+\bar{a})k_2\right]+ak_2\left(\bar{a}\alpha^2-2\bar{\Delta}\right)\sinh\left[2(-0.25+\bar{a})k_2\right]}{\cosh\left[2(-0.25+\bar{a})k_2\right]-2(0.25+\bar{a})k_2\sinh\left[2(-0.25+\bar{a})k_2\right]}\\
c_{11}&=\frac{4(-0.25+\bar{a})\alpha^2\cosh\left[2(-0.25+\bar{a})k_2\right]-2k_2\left(2\left(-0.125+(-0.5+\bar{a})\bar{a}\right)\alpha^2+\bar{\Delta}\right)\sinh\left[2(-0.25+\bar{a})k_2\right]}{\cosh\left[2(-0.25+\bar{a})k_2\right]-2(0.25+\bar{a})k_2\sinh\left[2(-0.25+\bar{a})k_2\right]}\\
c_{12}&=-2(-0.125+\bar{a})\alpha^2+\bar{\Delta}-\frac{0.5k_2\left(2\bar{a}(0.5+\bar{a})\alpha^2-\bar{\Delta}\right)Sech\left[2(-0.25+\bar{a})k_2\right]^2\sinh\left[k_2-4\bar{a}k_2\right]}{-1+2(0.25+\bar{a})k_2\tanh\left[2(-0.25+\bar{a})k_2\right]}
\end{aligned}
\tag{A.8}
$$

The value of $\bar{a}$ can be determined by continuity of the shear stress

$\bar{\tau} = \tau / \tau^f = -\bar{u}_1'' / (2\alpha^2)$ at the point $\bar{x} = \bar{a}$. From eqn. (A.3), the shear stress of interface between graphene sheet #1 and #2 is

$$\bar{\tau} = \begin{cases} 1 & 0 \le \bar{x} \le \bar{a} \\ \dfrac{2k_2^2}{\alpha^2}[c_5 \sinh(2k_2\bar{x}) + c_6 \cosh(2k_2\bar{x})], & \bar{a} \le \bar{x} \le 0.5 - \bar{a} \\ 1 & 0.5 - \bar{a} \le \bar{x} \le 0.5 \end{cases} \tag{A.9}$$

The shear stress is $\tau = \tau^f$ at the point $x = \bar{a}$, so

$$\frac{2k_2^2}{\alpha^2}[c_5 \sinh(2k_2\bar{a}) + c_6 \cosh(2k_2\bar{a})] = 1 \tag{A.10}$$

Substituting the forms of c_5 and c_6 in eqn. (A.8) into eqn. (A.10), we get the functional relationship between the applied dimensionless displacement $\bar{\Delta}$ and the plastic zone size $\bar{a}$

$$\bar{\Delta} = \frac{\left\{(1 + 2\bar{a}^2 k_2^2 + \bar{a}k_2^2 - k_2(2\bar{a} + 0.5) \times \tanh\left[k_2(2\bar{a} - 0.5)\right]\right\}}{k_2} \times \frac{2\tau^f l_c}{D_g} \tag{A.11}$$

In the regular structure, the average strain of the RVE is

$$\varepsilon_c = 2\bar{\Delta} \tag{A.12}$$

The apply stress is satisfied with $\sigma_c = 2\int_0^{0.5} \sigma d\bar{x}$, where σ is the tensile stress in graphene sheet, so it is expressed as

$$\sigma_c = \left\{2k_2\bar{a} - \tanh\left[k_2(2\bar{a} - 0.5)\right]\right\} \times 2\tau^f l_c / h_b \tag{A.13}$$

where $\bar{a} = a / l_b$ is the dimensionless length of the plastic zone.

Further, the tensile strength of the RVE depends on the failure mode. There are two failure modes of graphene-derived materials,[2] when the maximum shear strain of interface reaches the failure strain $\gamma(x = 0) = \gamma_p^f$, the strength σ_s of the RVE is the max applied stress, which is predicted as (Mode I)

$$\sigma_s = \left\{2k_2\bar{a}_m - \tanh\left[k_2(2\bar{a}_m - 0.5)\right]\right\} \times 2\tau^f l_c / h_b \tag{A.14}$$

where $\overline{a}_m = a_m / l_b$ is the maximum dimensionless size of the plastic zone, it can be calculated as follow:

When the shear strain is the yield strain γ_e^c at the point of $\overline{x} = \overline{a}_m$ and the shear strain is the failure strain γ_p^f at the point of $\overline{x} = 0$, the maximum size $\overline{a}_m$ of the plastic zone is predicted as

$$\frac{\gamma_p^f}{\gamma_e^c} = \frac{u_2(0) - u_1(0)}{u_2(\overline{a}_m) - u_1(\overline{a}_m)} = 1 + 2\overline{a}_m^2 k_2^2 \tanh\left[k_2(2\overline{a}_m - 0.5)\right] \tag{A.15}$$

Further, if graphene failure occurs firstly, the strength of the RVE is predicted as (Mode G)

$$\sigma_s = \frac{\sigma_{cr} h_b}{2h_m} \tag{A.16}$$

where σ_{cr} is the tensile strength of graphene sheet, h_m is the interlayer distance. So the strength of the RVE is

$$\sigma_s = \begin{cases} \dfrac{\sigma_{cr} h_b}{2h_m} & \text{Mode G} \\ \left\{2k_2\overline{a}_m - \tanh\left[k_2(2\overline{a}_m - 0.5)\right]\right\} \times 2\tau^f l_c / h_b & \text{Mode I} \end{cases} \tag{A.17}$$

Appendix B: The toughness of graphene-based artificial nacres with brittle interface

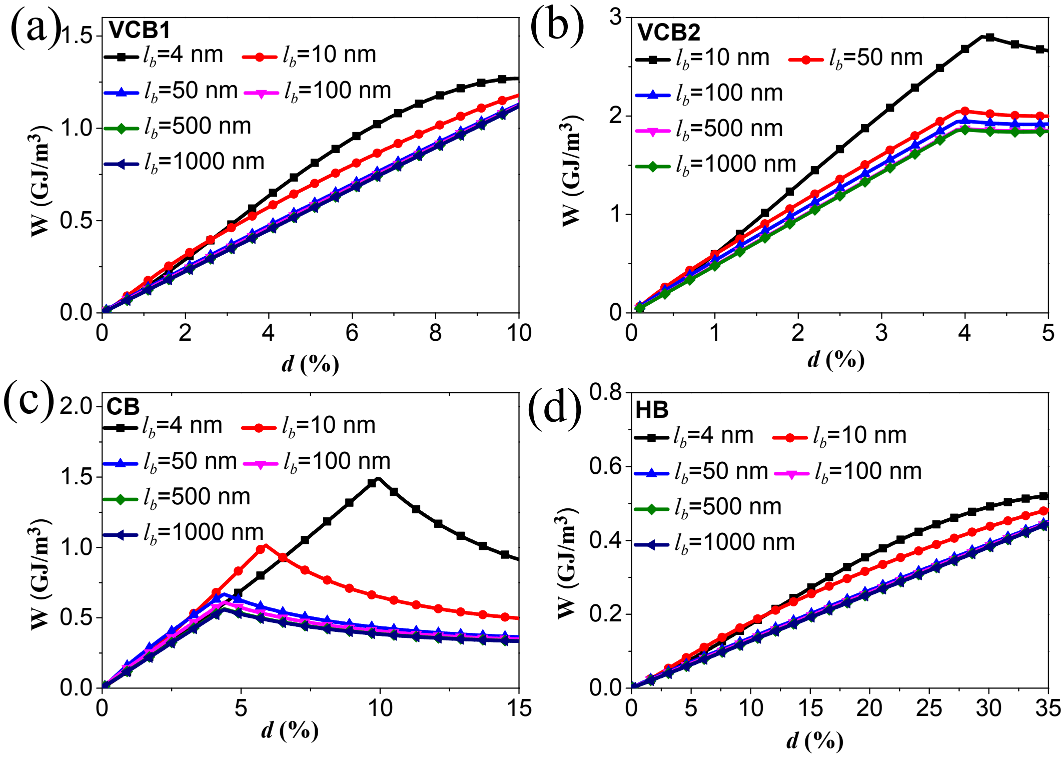

Fig. S2 Plots of the calculated effective toughness of graphene-based artificial nacres with brittle interface as a function of the crosslink density under different sizes of the graphene sheets for (a) VCB1, (b) VCB2, (c) CB and (d) HB crosslinks.

References

1. Y. Ni, Z. Song, H. Jiang, S.-H. Yu and L. He, *Journal of the Mechanics and Physics of Solids*, 2015, **81**, 41-57.
2. Y. Liu and Z. Xu, *Journal of the Mechanics and Physics of Solids*, 2014, **70**, 30-41.