Supplementary file for "Reactive force field Molecular dynamics study on graphene oxide reinforced cement composite: functional groups de-protonation, interfacial bonding and strengthening mechanism"

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# S1. Reaction pathway for water dissociation and functional groups de-protonation

The reaction pathway for water dissociation reaction is shown in Figure S1a. Water molecule firstly moves approximately to interlayer calcium atom, forming Ca- $O_w$  connection. The Ca- $O_w$  association weakens the OH bond. Meanwhile, the water molecule is tightly attracted by the non-bridging oxygen in the silicate tetrahedron by the hydrogen bond. Subsequently, proton dissociates from the water molecule and associates with the neighboring  $O_{nb}$ , producing Si-OH. The left OH group in water forms the coordinate atom of interlayer calcium. Hence, the hydroxyl bond weakening

from calcium atoms and the strong hydrogen bonding from non-bridging oxygen are responsible for the water dissociation reactions. Figure S1b describes the reaction pathway for de-protonation. The proton in C-OH prefers to associate with the non-bridging oxygen in silicate tetrahedron. The proton dissociates from C-OH, producing C=O. The newly formed carbonyl group enhances the polarity of the functional group and connects tightly with the neighboring calcium atoms.



Figure S1 (a) The reaction pathway for the water dissociation near the calcium silicate

sheet (b) The reaction pathway for de-protonation of the C-OH group

#### S2. Reaction pathway for GO/C-S-H composite under tension loading

The water dissociation pathway is shown in Figure S2a. The Ca-O<sub>s</sub> bonds are stretched due to the tensile loading, resulting in distorted local Ca-O octahedron structure. Water molecules move approximate toward Ca ions, forming Ca-O<sub>w</sub> connection. This further weakens the stability of tensioned Ca-O<sub>s</sub> connection. The Ca-Os bond firstly is stretched broken. Subsequently, the proton dissociates from water molecule and reconnects with the non-bridging oxygen atom, producing Si-OH. The left hydroxyl in dissociated water molecule forms Ca-OH bond. The water decomposing into Ca-OH and Si-OH is mainly attributed to that the de-bonding of Ca-O<sub>s</sub> due to tension produces lots of non-bridging oxygen sites with high reactivity. As compared with the oxygen in Ca-O-Si, the de-bonded non-bridging atoms occupy relative higher reactive energy. It can assist the water molecules overcome the energy barrier of the "hydrolytic reaction", contributing to the water dissociation. The chemical reaction is consistent with SCF analysis of Ca-O<sub>s</sub> breakage mentioned above. Figure S2b exhibits the reaction pathway for the proton transferring from Si-OH to C=O. Due to the tensile loading, the calcium atom moves away from the C=O group, increasing the electronegativity of the oxygen in functional group. Hydrogen atom dissociates from Si-OH and connects with the carbonyl oxygen, producing C-OH bond again. This is the reverse reaction of the de-protonation mentioned in Figure 6b.



Figure S2 chemical reaction pathways for (a) water dissociation due to Si-O-Ca breakage (b) Si-OH de-protonation in GO-OH/C-S-H model

#### **S3.** Molecular structural validation

The radial distribution function (RDF) of C-C and C-Oc can be utilized to characterize the molecular structure of the graphene oxide sheet and the functional groups grafted on the GO sheet. In Figure S3, the original graphene model before MD simulation was taken as the reference for the RDF analysis: the first peak is positioned at 1.42 Å, representing the C-C bond length; the second and third peak is located at 2.46 and 2.84 Å, corresponding to the diagonal for the hexagon unit; the peaks in the long range reflect the replicating of the hexagon units. As compared with the original model, the C-C RDF of G and GO model after MD simulation turns broaden and shifts in some extent. In the graphene model, the first peak remains almost unchanged and the second and third one, shifting in longer distance, is pronouncedly broadened. It indicates that the wrinkles at nanometer scale change the ordered two dimensional structures, weakening the spatial order in the long range. As shown in Figure S3, the incorporation of the hydroxyl and epoxy group broadens the first peak and weakens the second and third peak, implying that the functional groups influence the C-C bonding in the substrate. Besides the short range structure change, the long range spatial order in the RDF degrades in great extent after 3 Å for the GO sheets with -COOH and -SO3H. Due to the defections in the substrate, the GO sheets with carboxyl and sulfonic groups are perturbed significantly.

Figure S4 demonstrates the spatial correlation between carbon atoms and the oxygen atoms in the functional groups. Correspondingly, the molecular structures of the functional groups are shown in Figure S5. As shown in Figure S4a, the peaks of C-Oc RDF in GO/OH model have two peaks located at 1.33 Å and 1.44 Å, which represents carbonyl and hydroxyl groups in the GO sheet. It should be noted that the C=O, initially not arranged in GO sheet, was produced after the reaction with C-S-H surface. In the GO-OH system, nearly 40.2% of C-OH transforms to C=O groups, which results in the binomial distribution of the C-Oc bond. In Figure S4b, the RDF of C-Oc

in epoxy groups shows predominated peak with high intensity located at 1.48 Å and a small shoulder at 1.33 Å, implying the coexistence of C=O and epoxide bond in the GO-Oo model. As shown in Figure S4c and Figure S4d, binomial distribution for the C-O RDF has also been observed. In the carboxyl and sulfonic groups, there are two types of oxygen atoms associated with proton and without proton, as exhibited in Figure S5d and Figure S5e. Similar de-protonation reactions also happen in GO-COOH and GO-SO3H system, where 73.6 % and 68.1 % proton dissociation from the COOH and SO3H strengthen the first intensity in the C-O RDF distribution. The structural information of different chemical bonds has been listed in Table S1. Previous experimental results and first principal computational results are also listed for comparison. The bond length of chemical bonds in C-S-H and GO structures calculated by this study is consistent with previous results, which confirms the accuracy of our molecular dynamics model.



Figure S3 Radial distribution function for C-C of G/GO and C-S-H models



(a)





(c)



Figure S4 RDF for C(S)-Oc in (a) GO-OH (b) GO-Oo (c) GO-COOH (d) GO-SO3H



(a)



(b)



(c)





(e)

Figure S5 local structure of (a) C-OH (b) C=O (c) C-Oo (d) C-COOH (e) C-SO3H

As shown in Figure S6, there are six types of hydrogen bonds formed in interlayer region between C-S-H and GO/G sheet. Figure S6a and Figure S6c exhibit that the Si-OH in the silicate chains donates and accepts hydrogen bond from the neighboring functional groups on the GO sheet. These hydrogen bonds, directly connecting the C-S-H and GO/G sheet, are the most important component in H-bond network in determining the interfacial cohesion strength. On the other hand, interlayer water molecule plays as intermedia to indirectly bridge the GO sheet and C-S-H layer in the other four types of hydrogen bond.



(a)



(b)





(d)





(f)

Figure S6 The local structure of the H-bonds network (a) Os-Hs donate to Oc (b) Os-Hs donate to Ow (c) Oc-Hc donate to Os (d) Oc-Hc donate to Ow (e) Ow-Hw donate to Oc (f) Ow-Hw donate to Os

Table S1. Chemical bond length in GO sheet and C-S-H gel from this study and previous experimental results, first principle calculation and other molecular modeling.

	other model (Å)	first principle (Å)	experiment (Å)	This study (Å)
C-C	1.42ª	1.42ª	1.42 <sup>g</sup>	1.42
C=O	1.32ª	1.24ª		1.34
С-ОН	1.42ª	1.36ª		1.42
C-O <sub>o</sub>	1.45-1.48ª	1.47ª		1.45
Si-O <sub>s</sub>	1.61 <sup>b</sup>		1.62°	1.59
Ca-O <sub>s</sub>	2.4 <sup>f</sup>		2.44°	2.38
O <sub>w</sub> -H <sub>w</sub>	1 <sup>d</sup>		0.984 <sup>e</sup>	0.968

a. ref [1]

b. ref [2]

c. ref [3]

d. ref [4]

e. ref [5]

f. ref [6]

g.ref [7]

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