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Supporting information

Mineral Layer as Effective Binder to Achieve Tough Bonding Between Hydrogel and Solid Titanium Substrate

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Characterization of interfacial regions using inverted optical microscopy

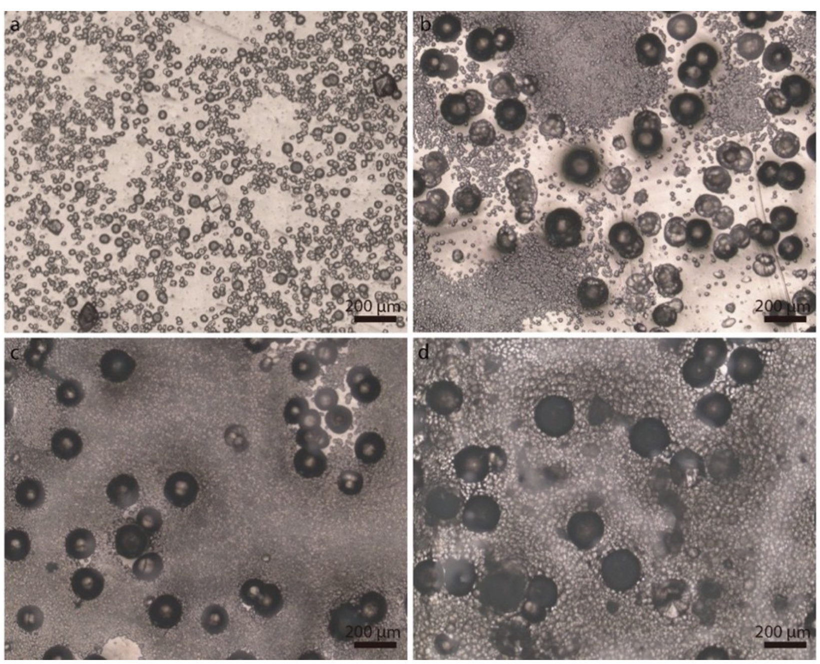

Figure S1. The morphological features of interfacial region at various mineralization time point were observed after shear force-induced failure: (a) mineralized 1 day, (b) mineralized 3 days, (c) mineralized 5 days, (d) mineralized 7 days. The concentration of loaded Ca^{2+} ions is 4 mol L^{-1} and PAMPS-PDMAA hydrogel was employed here.

The optical images shown in **Figure S1** were taken from the residual layer on titanium substrate after shear-induced interfacial failure by inverted optical microscopy. As shown, there was a continuous mineral layer at the interface of hydrogel and titanium substrate when mineralization time increased to 5 days. The obtained minerals crystals were vaterite.

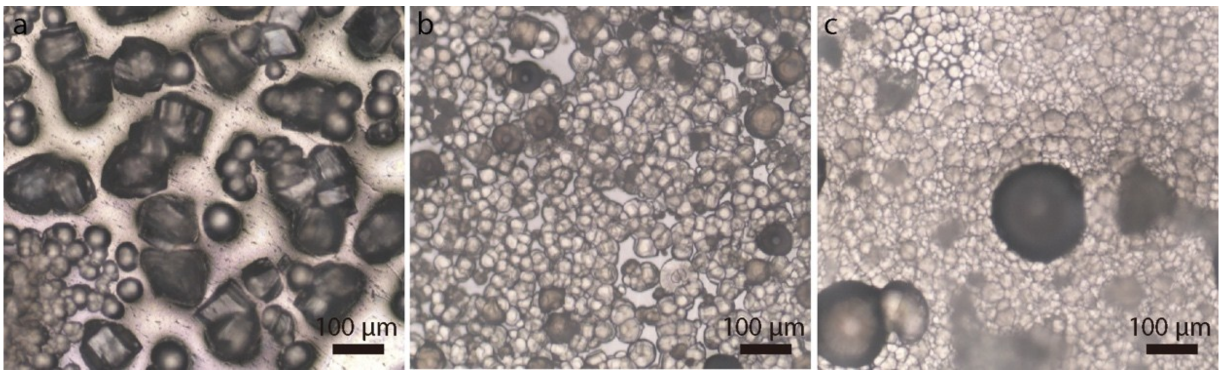

Figure S2. The morphological features of interfacial region for hydrogel samples loaded with Ca^{2+} ions with various concentration were analyzed after shear force-induced failure: (a) 1 mol L^{-1}, (b) 2 mol L^{-1} and (c) 4 mol L^{-1}. PAMPS-PDMAA hydrogel was employed and the samples were prepared after 7 days' mineralization.

To investigate the effect of concentration of Ca^{2+} ions on interfacial bonding strength between hydrogel and titanium substrates, PAMPS-PDMAA hydrogel was pre-loaded with Ca^{2+} ions with different concentration from 1 to 4 mol L^{-1}. After 7 days' mineralization, non-continuous mineral layer was obtained at the interface of hydrogel-titanium at lower concentration of Ca^{2+} (1 mol L^{-1}). The formed minerals were calcite as the crystals were rhombohedral (**Figure S2a**). When the concentration increased to 4 mol L^{-1}, the continuous $CaCO_3$ mineral layer with spherical morphology was obtained, suggesting an enlarged bonded area between minerals and hydrogel/titanium.

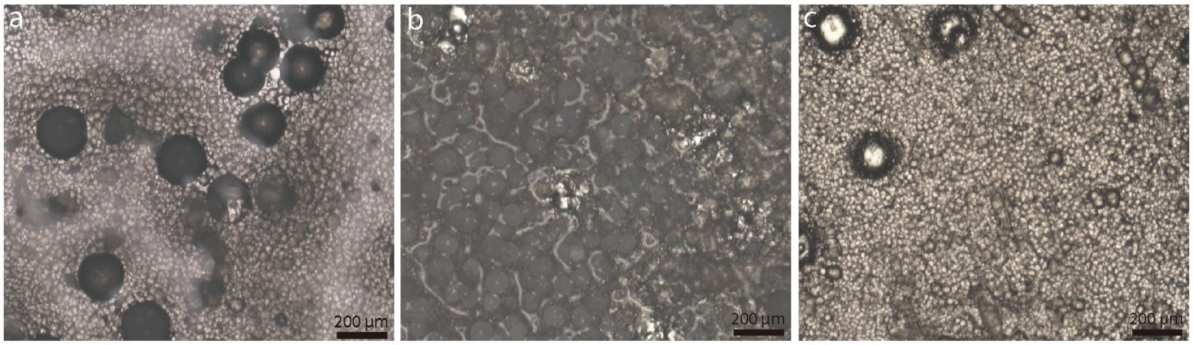

Figure S3. The morphological features of interfacial region for titanium samples with various surface chemical groups were observed: (a) NaOH-treated titanium with Ti-OH groups (b) APS-modified titanium with $-NH_2$ groups, (c) SAA-modified titanium with -COOH groups. PAMPS-PDMAA hydrogel loading with 4 mol L^{-1} Ca^{2+} ions was employed and the samples were prepared after 7 days' mineralization.

In this study, titanium substrate was chemically modified by $-NH_2$ and -COOH groups based on silanization method. After shear force-induced failure, there were residual layers on titanium substrate composed of $CaCO_3$ crystals and polymeric hydrogels for all samples except for the control sample as shown in **Figure S3**. The morphology of $CaCO_3$ crystals was not changed by various chemical groups which was still spherical. These results suggested that this binding strategy could avoid complex surface chemical modification such as silanization since only NaOH treatment already provide robust bonding between mineralized hydrogel and titanium substrate. The bonding strength was achieved by electrostatic force between Ca^{2+} ions of minerals and negatively surface charged groups including -OH, $-NH_2$ and –COOH.

For all hydrogels that were introduced, there were residual layers on titanium surface after shear force induced failure as shown in **Figure S4**. These layers composed of calcium carbonate and polymeric hydrogels, suggesting that the interfacial failure mainly occurred in bulk of hydrogels.

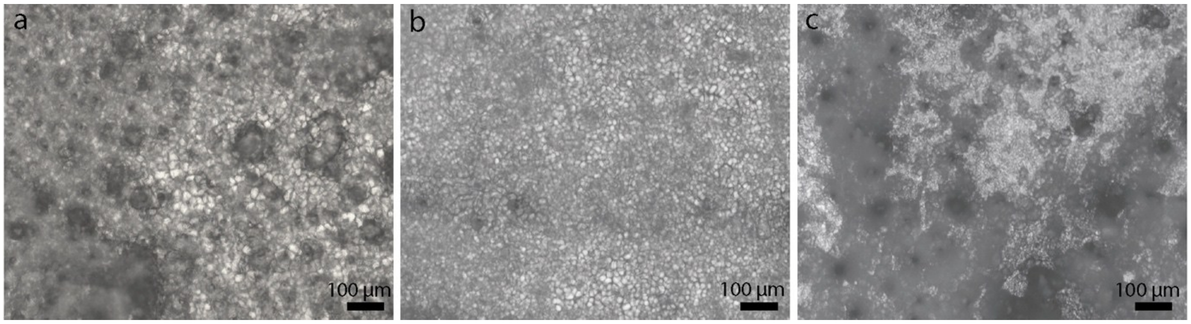

Figure S4. The morphological features of interfacial region for various hydrogels were observed by inverted optical microscopy after shear force-induced failure (a) PDMAA hydrogel (b) PAMPS-PAAm hydrogel, (c) PVA hydrogel. The samples were prepared after 7 days' mineralization with 4 mol L^{-1} Ca^{2+} ions.

Characterization of interfacial region using Energy Dispersive X- ray (EDX)

To estimate the atomic compositions of residual layer on titanium substrate after shear force induced interfacial failure, EDX analysis was performed. As shown in **Figure S5c**, EDX results only revealed the presence of C, S, N and O elements related to PAMPS-PDMAA hydrogel on top side of residual layer (only little amount of $CaCl_2$ showing up), suggesting that there was a polymeric hydrogel layer covering on $CaCO_3$ minerals after shear force induced failure. EDX analysis on the attached-side of residual layer on titanium did not show any atomic components related to polymeric hydrogel only $CaCO_3$ minerals (Figure S5d).

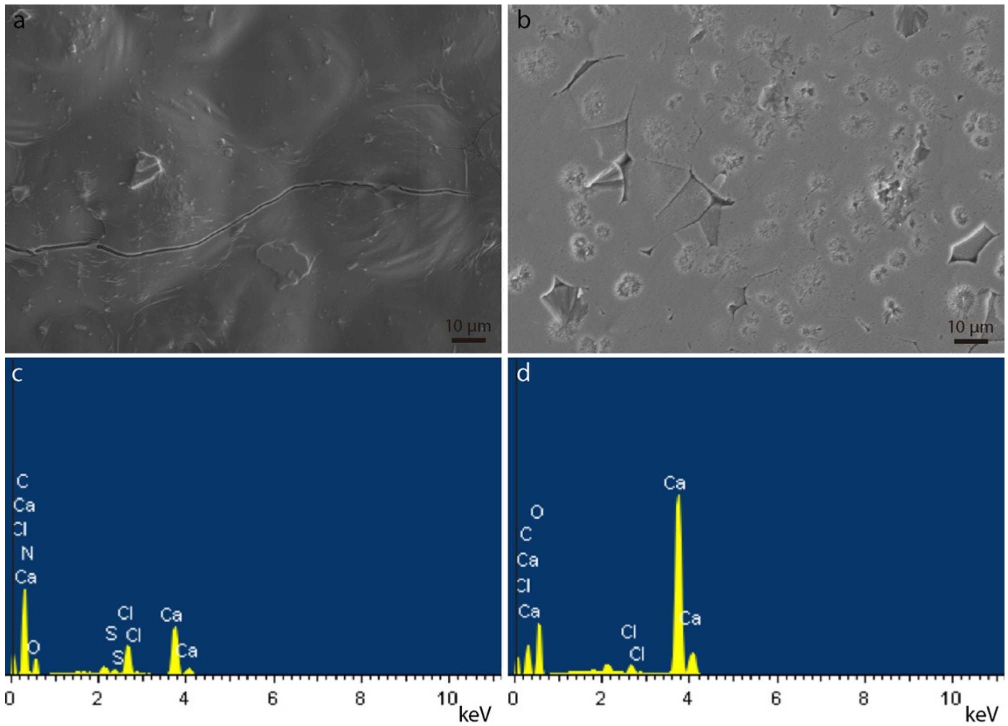

Figure S5. Energy dispersive X- ray (EDX) spectroscopy analysis (c and d) were carried out on the same samples as SEM analysis (a and b), respectively. The samples were prepared after 7 days' mineralization with 4 mol L^{-1} Ca^{2+} ions, and PAMPS-PDMAA hydrogel was used.