Supporting Information for

Oysters Produce an Organic-Inorganic Adhesive for Intertidal Reef Construction

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Methods

Sample collection and preparation:
Clusters of oysters were collected from the North Inlet estuary at the Baruch Marine Field Laboratory, near Georgetown, South Carolina, USA. North Inlet is in the National Estuarine Research Reserve system and has large, intact intertidal oyster reefs throughout. A tile saw was used to cut apart oyster clusters to reveal cross sections. In order to separate cement from shell, cross sections were cut and then individual shells were separated by running a punch into the cement region. Cement could then be scraped off the shells. For comparison, samples of outer shell (without any cement) were also scraped and collected to yield powders. Likewise, smooth pseudonacre from the shell insides was scraped and collected. Each powder can be seen in Figure S1.

Instrumentation:
Electron paramagnetic resonance (EPR) spectra were recorded on isolated powders at 150 K with a Bruker (Billerica, MA) 300E. A Jasco (Tokyo, Japan) FTIR 6300 fitted with a ZnSe attenuated total reflectance crystal was used to collect the infrared (IR) spectra. For thermogravimetric analyses, a TA Instruments (New Castle, DE) TA-TGA 2050 was used from room temperature up to 1050 °C, increased by 30 °C per minute. Regions of water (~25 - ~200 °C), organic (~200 - ~550 °C), and inorganic (~550+ °C) mass loss in temperature-versus-mass graphs were determined using derivative plots.

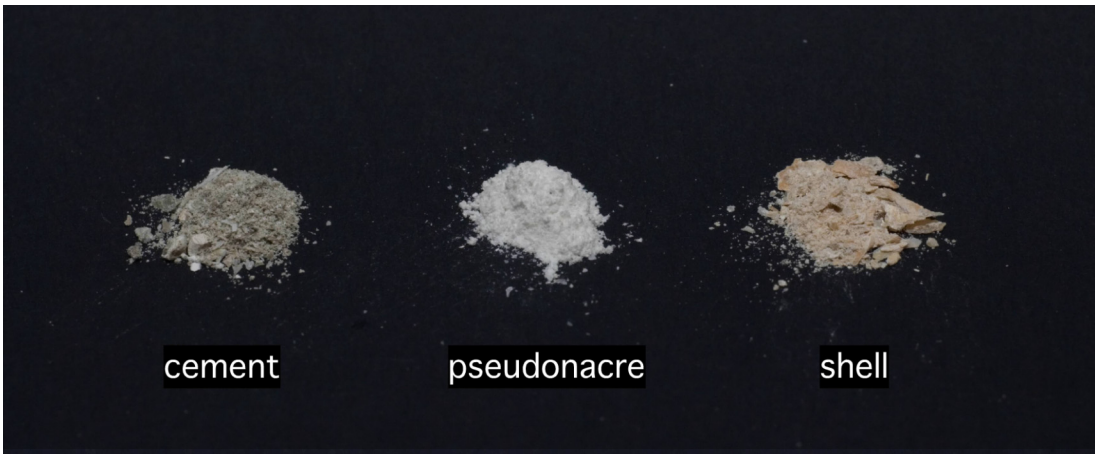

Figure S1. Isolated samples of cement, pseudonacre, and outer shell.

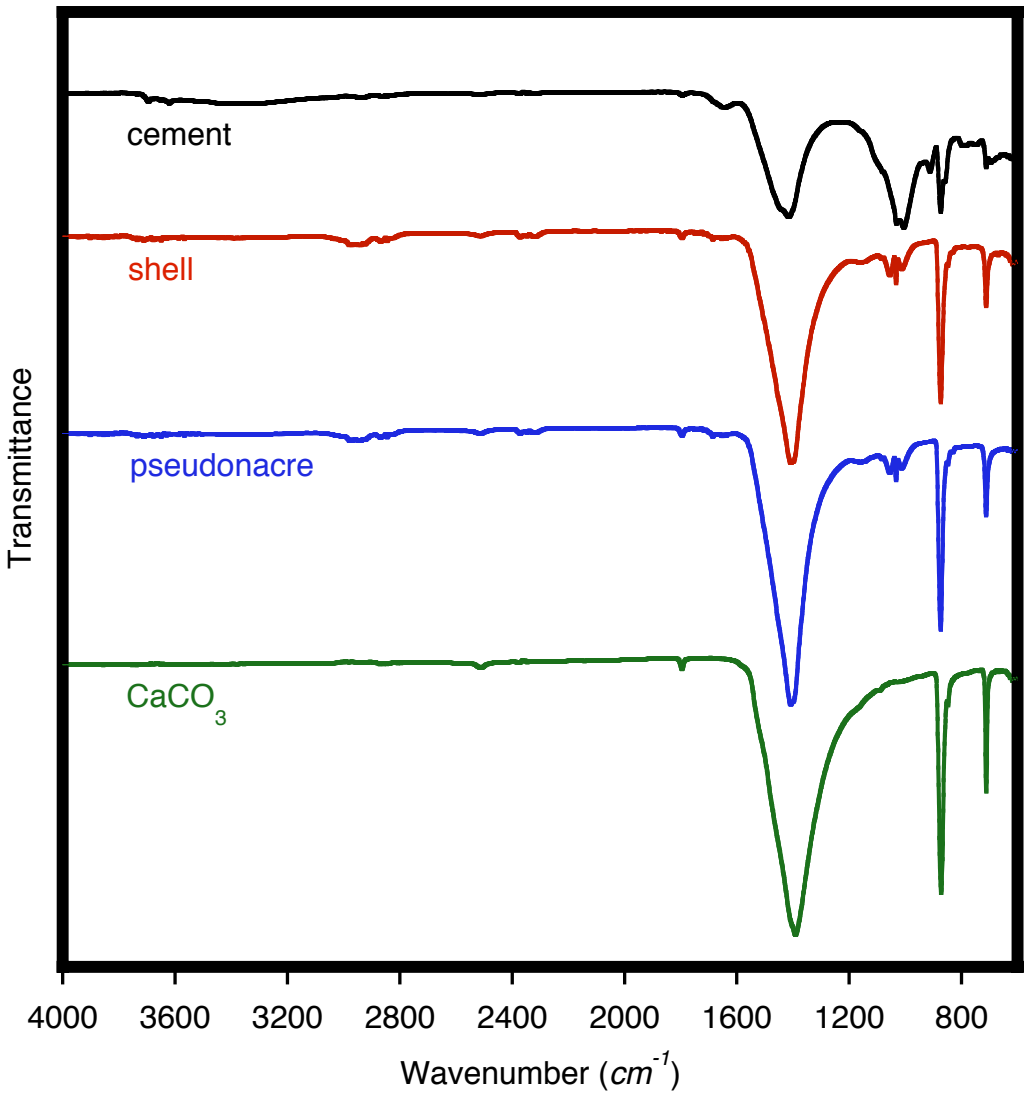

Figure S2. Full width infrared spectra of oyster cement, shell, pseudonacre, and calcium carbonate.

Table S1. Thermogravimetric analysis of oyster cement, shell, pseudonacre, and calcium carbonate. Mass losses are shown for water, organic, and inorganic components upon heating up to 1050 °C.

	Water	Organic	Inorganic	Estimate of residual CaO[a]	Estimate of total mass loss + residual CaO[b]
Cement	3.1%	11.2%	20.0%	28.9%	63.2%
Outer shell	0.5%	2.0%	30.7%	44.4%	77.6%
Pseudonacre	0.5%	1.3%	32.0%	46.3%	80.1%
$CaCO_3$	0%	0%	38.7%	56.0%[c]	94.7%

[a] Made by attributing the inorganic mass loss to CO_2 produced upon heating $CaCO_3$. Values for cement, outer shell, and pseudonacre were determined by scaling the observed inorganic mass loss to that of the $CaCO_3$ sample.

[b] Summation of water, organic, and inorganic mass loss plus estimated, residual CaO.

[c] Theoretical maximum CaO from pure $CaCO_3$.