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1 **Fabrication of patterned calcium cross-linked alginate hydrogel films and coatings through**
2 **reductive cation exchange**

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11 **Abstract:** Calcium cross-linked alginate hydrogels are widely used in targeted drug delivery, tissue
12 engineering, wound treatment, and other biomedical applications. We developed a method for preparing
13 homogeneous alginate hydrogels cross-linked with Ca^{2+} cations using reductive cation exchange in
14 homogeneous iron(III) cross-linked alginate hydrogels. Treatment of iron(III) cross-linked alginate
15 hydrogels with calcium salts and sodium ascorbate results in reduction of iron(III) cations to iron(II) that
16 are instantaneously replaced with Ca^{2+} cations, producing homogeneous ionically cross-linking hydrogels.
17 Alternatively, the cation exchange can be performed by photochemical reduction in the presence of
18 calcium chloride using a sacrificial photoreductant. This approach allows fabrication of patterned calcium
19 alginate hydrogels through photochemical patterning of iron(III) cross-linked alginate hydrogel followed
20 by the photochemical reductive exchange of iron cations to calcium.

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