Biodegradable and Biorecyclable Organic Glass

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Abstract

Glass is ubiquitous in life and widely used in various fields. However, there is an urgent need to develop biodegradable and biorecyclable glasses that have a minimal environmental footprint toward a sustainable society and a circular materials economy. Here, we report a family of eco-friendly organic glasses of biological origin fabricated using biologically-derived amino acids or peptides through the classic heating-quenching procedure. Amino acids and peptides with chemical modification at their ends are found able to form a supercooled liquid before decomposition and eventually glass upon quenching. These developed glasses exhibit excellent glass-forming ability and optical characteristics and are amenable to 3D printed additive manufacturing and mould casting. Crucially, the glasses show biocompatibility, biodegradability and biorecyclability beyond the currently used commercial glasses and plastic materials.

Introduction

The materials and chemicals for tomorrow's earth are highly hoped to be benign rather than toxic, renewable rather than depleting, and degradable rather than persistent. Glass is one of the most important high-performance materials in human civilization. A variety of glass-forming components have been developed as structural building units for the preparation of glasses. For example, the most well-known inorganic glass is usually manufactured from sand, lime and sodium carbonate; poly(methyl methacrylate) (PMMA) glass is a transparent and rigid thermoplastic organic material; metallic glass (or glassy metal) is a noncrystalline material composed of either pure metal or a combination of metal and metalloid components; the recently reported metal-organic framework (MOF) glass is usually composed of metal ions or clusters coordinated by organic ligands arranged in tetrahedral units. However, these glasses are biologically incompatible and not readily degraded in nature, which will cause long-term ecological and environmental burdens for the green life future. Therefore, the development of biodegradable and biorecyclable glasses is expected to have a minimal environmental footprint and to contribute to a lasting improvement among ecological and social impacts.

Amino acids and peptides are abundant biomolecules in living organisms and the materials formed by them are considered completely eco-friendly because they can be reutilized in ecological system. Currently, the predominant approach to making glass is to heat glass formers at a high temperature (above their melting temperature, \(T_m\)) to form a supercooled liquid and then to quench this liquid by cooling at a sufficient fast rate to prevent crystallization. Glass is a nonequilibrium, noncrystalline state of matter that lacks the periodicity of crystals but behaves mechanically like a solid, depending upon the thermal history of the melt. However, native amino acids and peptides have poor thermal stability and easily decompose into amines and carbon dioxide (CO\(_2\)) at high temperatures at or near \(T_m\). As a result, glass cannot be processed and obtained using these native biomolecules. It is reported that amino acids and peptides when subjected to chemical modification at the ends by hydrophobic groups can
significantly improve their thermal stability,\textsuperscript{17} which inspired us that it is possible to use the modified amino acids and peptides to process glass.

In this work, we used chemically modified amino acids and peptides as the glass formers to successfully fabricate organic glasses with biodegradability and biorecyclability (Fig. 1A). We melted them to first form a supercooled liquid upon heating in an inert gas atmosphere before reaching their decomposition temperature ($T_d$). Through the accurate control of the heating and cooling rates, the supercooled liquid was quenched to form glass finally, and crystallization was effectively prevented. We evaluated the glass-forming ability and glass performance of representative organic glasses derived from amino acids or peptides. Kinetic and thermodynamic parameters related to the glass transition were determined, including the glass transition temperature ($T_g$), $T_m$, the reduced glass transition temperature ($T_{rg}=T_g/T_m$), the increase in the glass transition heat capacity ($\Delta C_p$), the enthalpy of fusion ($\Delta H_m$) and the fragility m-index ($m$). Subsequently, we studied the ability of the glasses to transmit light and their adaptability for additive manufacturing (3D printing and mould casting). To determine whether the developed organic glass was eco-friendly, we conducted biodegradation experiments \textit{in vitro} and \textit{in vivo} as well as composting experiments. We found that the organic glasses based on amino acids or peptides possessed a unique combination of functional properties and eco-friendly features, excellent optical characteristics, good mechanical properties and flexible processability, as well as the desired biodegradability and biorecyclability. Whereas these glasses are far from large-scale commercialization, there is an interest in the development of organic glasses with eco-friendly performance, which may be a giant leap towards a sustainable future.

\section*{Results And Discussion}

\subsection*{Glass preparation and characterization}

To enable the formation and subsequent quenching of supercooled liquids without molecular decomposition, we chemically modified a series of amino acids and peptides using acetyl (Ac-), 9-fluorenylmethyloxycarbonyl (Fmoc-) and benzyloxycarbonyl (Cbz-) groups. Upon heating, randomly selected native amino acids, including glutamine (Q), histidine (H), phenylalanine (F) and tyrosine (Y), were found to undergo a total weight loss greater than 15%, whereas valine (V) and leucine (L) burned completely, with a total weight loss greater than 90% at $T_m$ (Fig.S1). It was found that the $T_m$ values of these modified molecules were far below their decomposition temperatures (Tab.S1). Next, organic glasses were successfully prepared from these modified amino acids and peptides by following programmed heating and quenching procedures at heating and cooling rates of 10 K min\textsuperscript{-1} in an inert atmosphere (Fig.S2, Tab.S2). The successful melting of the biomolecular compounds prior to decomposition is undoubtedly a breakthrough for the preparation of novel glasses.

The formation of organic glass from amino acids or peptides can be monitored by changes in enthalpy or volume as a function of temperature. Here, an Ac-modified amino acid (Ac-F) and a Cbz-modified
tripeptide (Cbz-(D)-FF-glycine, Cbz-FFG) were selected as representative samples. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under nitrogen (Fig. 1B) according to a preset temperature program (Fig. 1C). In the TGA curve and enthalpic response of Ac-F obtained in the *Upscan* 1 region, we observed a sharp endothermic peak at $T_m = 442.30$ K followed by a broad decomposition peak centred at $T_d = 534.50$ K (Fig. 1D). The DSC-TGA results showed no evidence of qualitative decomposition or volatilization during the formation of the glass. Upon reheating the amorphous product, a typical glass transition was observed. $T_g$ was measured as the onset temperature of the glass transition peak, as the temperature at the intercept between an extrapolated straight line of the enthalpy curve and a tangent line at the inflection point of the sharply rising enthalpy curve.$^{18}$ In the enthalpic responses of Ac-F obtained in the *Upscan* 2 region, we observed the glass transition at $T_g = 312.50$ K. The $\Delta C_p$ for the transition from a glass to a supercooled liquid at $T_g$ was calculated to be $0.70 \text{ J K}^{-1} \text{ g}^{-1}$. Next, similar experiments were performed for the tripeptide derivative Cbz-FFG. In the TGA curve for this sample, peaks were observed at 374.60 K, 428.20 K, 438.60 K and 453.30 K, corresponding to water release, solvent loss, exothermic thermal amorphization and melting, respectively (Fig. 1E). During this process, a weight loss of 3.86% was observed before peptide decomposition. $T_g$ was determined to be 332.70 K, and $\Delta C_p$ was calculated to be $0.67 \text{ J K}^{-1} \text{ g}^{-1}$. These results clearly put in evidence that temperature-driven glass transitions can be achieved by modified amino acids or peptides.

The X-ray diffraction (XRD) patterns of the Ac-F and Cbz-FFG powders showed sharp diffraction peaks, which indicated that the raw powders had a crystalline nature, suggesting that long-range order occurred within the powder samples (Fig. 1F, Fig.S3). In contrast, broad bands without well-defined diffraction peaks were observed in the XRD patterns of their glassy counterparts, reflecting an amorphous nature of the glass samples.$^{19}$ Polarized optical microscopy (POM) was then performed to determine the phases of the crystalline and glassy states (Fig. 1H). For the Ac-F and Cbz-FFG powder samples, strong optical anisotropy was observed, indicating the orientational organization within the crystalline powders. In sharp contrast, no detectable anisotropic birefringence was observed for either the Ac-F or Cbz-FFG glasses, indicating that these samples had an isotropic and amorphous feature. Notably, the $^{1}H$ solution nuclear magnetic resonance (NMR) spectra (Fig. 1G) confirmed that there were no changes in the chemical structures of these glass samples during the melting and quenching procedures. These results indicated that the modified amino acids and peptides are robust for formation of organic glass through the melting and quenching approach.

**Glass transition mechanism and computational simulations**

To probe the mechanism of glass transition, variable-temperature in situ XRD (Fig.S4) and Raman spectroscopy (Fig. 2A) were conducted over the entire phase transition process (from crystals to glass) of Ac-F. When the temperature was increased from 298.15 K to 397.15 K, no obvious changes in the XRD patterns were observed (Fig.S4), suggesting a stable ordered molecular organization in the starting crystals. This stability was confirmed by the Raman spectra, evidencing by no signal change over the
range from 298.15 K to 423.15 K (Fig. 2A). When the temperature was further increased above $T_m = 442.30$ K, the sharp Bragg peaks in the XRD pattern disappeared, implying the collapse of the long-range order in the crystalline structures. This can be attributed to the disruption of the regular molecular arrangement, which was confirmed by the disappearance of the fine peaks in the Raman spectra, especially the C = O stretching band of the carboxyl group at 1730 cm$^{-1}$, the O-H stretching band near about 3400 cm$^{-1}$, the N-H stretching band in the range from at 3324 cm$^{-1}$ to 3200 cm$^{-1}$, and the C-H stretching band occurring at 3100 - 2800 cm$^{-1}$. During the quenching process, no sharp Bragg peaks were observed, suggesting that quenching prevented the Ac-F supercooled liquid from following the thermodynamically favourable path towards crystalline formation and trapped the system in a metastable amorphous state. In addition, small increases in the intensity of the N-H and O-H stretching bands in the Raman spectra were observed, suggesting that molecular rearrangement occurred during the quenching process. The Raman bands corresponding to the C = O stretching, the N-H stretching and the C-H stretching vibrations and the $^{13}$C signals in the solid-state NMR spectra (ssNMR) (Fig.S5) were significantly broadened, demonstrating the coexistence of multiple types of hydrogen bonding interactions in the glass. Similar evidence of molecular rearrangements was observed during the formation of melt-quenched Cbz-FFG glass (Fig.S6).

Furthermore, to investigate the molecular mechanism underlying the vitrification of amino acids and peptides, a combination of ssNMR, in situ Raman spectroscopy and all-atom molecular dynamics (AAMD) simulations were performed (Fig. 2). Ac-F was selected as a simple typical model to elucidate the evolution of molecular packing patterns from single crystal to glass. Theoretical simulation results showed that two kinds of predominant hydrogen bonds, $-\text{N–H}\cdots\text{O} = \text{C}$ (N–H···O3) and $-\text{O–H}\cdots\text{O} = \text{C}$ (O2–H···O1), were found to stabilize the single-crystal structure of Ac-F (Fig. 2A inset, 2D, and Fig.S7A), which was consistent with the sharp peaks in the Raman spectra (Fig. 2A) and ssNMR spectra (Fig.S5). Upon heating (Fig. 2B), the abundance of these two types of hydrogen bonds decreased, indicating loss of the single-crystal structure (Fig. 2C). After the subsequent melting-cooling treatment, multiple types of hydrogen bonds, especially O2–H···O3 and N–H···O1, appeared and became more abundant (Fig. 2E, Fig.S7B), consistent with the emergence of broadened bands in the Raman and ssNMR spectra and implying the formation of an amorphous glass (Fig.S7). Therefore, it was concluded that the glass transition was a kinetic freezing process and that the cooperation of multiple weak intermolecular interactions facilitated the stabilization of the Ac-F glass with disordered molecular packing.

Since the glass transition is considered a kinetic phenomenon, the final enthalpy and $T_g$ of the glass depend on the cooling rate. To confirm the above conclusion, the $T_g$ values of glasses obtained at different cooling rates were investigated due to the dependence of $T_g$ on the chemical structure and mobility of the glass formers. Fig.S8 shows the enthalpy change curves of Ac-F as a function of temperature at different cooling rates (termed $q_c$). The heating rate (termed $q_h$) equalled $q_c$ for all the DSC tests. These results showed that $T_g$ decreased with increasing cooling rate and reached a plateau above
10 K min$^{-1}$. At a higher cooling rate, lower $T_g$ values were observed, suggesting that the system had less time for molecular rearrangement and resulted in looser molecular packing patterns.

**Glass-forming ability (GFA) and the fragility index ($m$)**

GFA refers to the ability of a liquid to avoid crystallization during quenching and is usually measured by $T_{rg}$ (which is defined as $T_g/T_m$). Systems with higher $T_{rg}$ values (> 2/3) have greater thermal stability and glass-forming ability.$^{27}$ The $T_{rg}$ values were calculated to be 0.71 for Ac-F and 0.73 for Cbz-FFG (Tab.S1), which satisfy the requirement of Kauzmann's 2/3 Law,$^4$ indicating that Ac-F melts have good resistance to crystallization in their supercooled state. However, not all molecules conformed to this empirical rule. For example, although Ac-G and Ac-Q exhibited lower $T_{rg}$ values of 0.61 and 0.64, respectively, they still formed transparent glasses (Fig.S9, Tab.S1). The GFA is often influenced by competing effects that suppress local order, leading to crystal formation.$^{28}$ Molecules with lower $T_{rg}$ values usually show a strong crystallization tendency, and these components are not desired in glass manufacturing. Notably, Kauzmann's 2/3 Law originates from data on routine melt-quenched (MQ) glasses based on traditional ionic and covalent bonds,$^29$ so the observation that the glasses developed in this study do not all obey this law suggests that these glasses based on amino acids and peptides represent a novel glass type.

The fragility index $m$, which corresponds to the activation energy of viscosity ($\eta$) at $T_g$,$^{27}$ was calculated to be 48 for Ac-F glass and 63 for Cbz-FFG glass (Tab.S1). These results are comparable to those for As$_2$Se$_3$ ($m = 47$) and B$_2$O$_3$ ($m = 50$)$^{30}$ and superior to those for PMMA ($m = 145$)$^{31}$ Strong supercooled liquids typically have low values of $m$, while fragile supercooled liquids have high values of $m$. $^{32}$ The $m$ values of phenylalanine derivatives showed distinct differences. For example, the Cbz-F glass exhibited a low fragility ($m = 13$), and the Fmoc-F glass exhibited a high fragility ($m = 58$). Likewise, the $m$ value of Fmoc-G glass ($m = 51$) was significantly greater than that of Ac-G glass ($m = 15$). These differences can be attributed to the structural rigidity of the Fmoc group. Another possible explanation could be related to the enhanced hydrophobic effects due to the presence of Fmoc groups. All of these suggest that modified amino acids or peptides possess a good glass-forming ability and have potential to be processed into glass.

**Additive 3D manufacturing and mould casting**

Precision glass processing opens up an enormous variety of possible glass types and geometries.$^{33}$ The glass transition process of Ac-F sample is schematically demonstrated in Fig. 3A. An obvious phase transition was observed during the heating and cooling treatment, with the structure changing from a crystalline state (raw material powder) to an intermediate state (transparent viscous liquid) and finally to a glassy state (transparent solid). To investigate the optical performance of these transparent glasses, transmittance spectra in the UV-visible (200–800 nm) and NIR (800–3000 nm) regions were obtained (Fig. 3B). These developed glasses exhibited good optical performance (up to ~ 90% transmittance), which was superior to that of the glass used in ordinary commercial lighting applications (80% on average).$^{34}$ In addition, carbon quantum dots (CQDs) and dyes were mixed with transparent viscous
liquids of the amino acids and peptides, and a series of coloured glasses with diverse fluorescence were prepared (Fig. 3C). Above results indicated that these organic glasses possessed high optical transmittance and flexible processability.

Encouraged by the optical properties and processability of these organic glasses, herein, we prepared 3D-printed Ac-F glass samples showing the clear and stereoscopic logo of “CAS” (the abbreviation for the Chinese Academy of Sciences) using a commercial biological 3D printer with a temperature-controlled barrel (Fig. 3D). As a further test, we poured uniform and bubble-free supercooled liquid into specific moulds and obtained a series of bionic marine shells without distortion (Fig. 3E). Normally, fused glasses are notoriously difficult to shape, glasses characterized by a high softening point usually show a strong crystallization tendency during processing. These drawbacks have made traditional glasses inaccessible to modern manufacturing technologies. Using glasses derived from amino acids or peptides, here we created a variety of glass components by both 3D manufacturing and mould casting. Finally, cyclic viscosity temperature curves were plotted to show the changes in the $\eta$ of the Ac-F system (Fig.S10). The broad linear viscoelastic region of the Ac-F supercooled liquid provided accurate time windows for 3D-printed additive manufacturing and mould casting, which may explain the flexible processability of these organic glasses.

Degradation of biomolecular organic glasses in vitro and in vivo

To verify the biodegradability and biorecyclability of the developed organic glasses, we first investigated their degradation behaviours when exposed to proteinase K solution, simulated gastric fluid (SGF$_{[sp]}$) containing pepsin and simulated intestinal fluid (SIF$_{[sp]}$) containing pancreatin (Fig.S11). We observed that Ac-F and Cbz-FFG glass beads with 0.3 cm diameters were completely degraded after incubation in proteinase K solution for one week and five months, respectively. The Ac-F glass rapidly degraded upon immersion in the simulated enzymatic hydrolysates. After 4 h of incubation, the size of the glass beads decreased significantly, and after two days of incubation, the glass beads were no longer visible. By comparison, the complete degradation of Cbz-FFG glass required more time (approximately 5 months).

We next sought to probe the degradation of the Cbz-FFG glass in more detail by employing electrospray ionization mass spectrometry (ESI-MS) (Fig. 4A, Fig.S12). The results suggested that the Cbz-FFG backbone degraded into several substructure units. Upon cleavage of amide links, Cbz-F and Cbz-FF were obtained, as verified by the emergence of peaks at 298.2 and 449.4, respectively. Concurrently, cleavage of the Cbz-modifier group yielded F, FF and FG, as verified by the emergence of peaks at 167.9, 314.1 and 224.4, respectively. Amino acids and peptides are endogenous biomolecules and have long been recognized as eco-friendly and degradable. In this regard, these glasses that can be degraded back into their original monomers or other small harmless molecules are highly desirable.

Composting is one of the cost-optimal techniques for treating waste. To verify the compostable and biorecyclable theses glasses, a composting device consistent with ASTM standards was developed for evaluating organic glasses derived from amino acids or peptides for use in landfills. Ac-F glass and
Cbz-FFG glass both underwent degradation in soil composts (Fig. 4B). Ac-F glass significantly decomposed in 3 weeks within the compost facilities. Cbz-FFG glass clearly disintegrated after being buried for 7.5 months. These developed glasses found in landfills have the potential to be utilized as sources of green energy. If properly planned and engineered landfills are built in appropriate locations, these glasses can be used as a sustainable energy source.

Encouraged by the promising results of in vitro degradation, we next explored the degradation of the developed glasses in vivo. Cbz-FFG glass bead and Cbz-FFG-CA glass bead encapsulating the immunosuppressive cyclic peptide cyclosporin A (CA) were implanted subcutaneously in mice (Fig. 4C). The survival status and body weight of the mice were monitored in real time. Throughout the experimental period, no mice exhibited any pain-related behaviour that may have been induced by the glass implantation, and none of them experienced significant weight loss (Fig. 4D). In addition, no symptoms of implant rejection, such as oedema or exudation, occurred during the in vivo experiment. The degradation and inflammatory responses to Cbz-FFG glass and Cbz-FFG-CA glass were studied as follows. The skin surfaces and incisions were photographed on the 2nd, 12th and 30th days after implantation to record the changes in the glasses (Fig. 4E, Fig. 4F). The photographs showed that at 2 days post-implantation, the Cbz-FFG glass had obviously softened, while at 12 days post-implantation, it was completely degraded and absorbed in vivo (Fig. 4F). The introduction of CA significantly prolonged the degradation time of the glass in vivo, which was attributed to the immunosuppressive effect of CA. Specifically, locally released CA is known to inhibit the proliferation and function of immune-related cells (e.g., T cells, B cells and macrophages) to reduce the immune response. These glass implants were completely degraded one month after they were embedded. The skin of the mice recovered completely, and the hair around the embedding site grew effectively.

In addition, the tissues in contact with the glass implants, including the skin and muscle layers (Fig. 4C), were harvested and stained with haematoxylin and eosin (H&E) (Fig.S13). Inflammatory cell infiltration (ICI) and cuticle thickening were observed in the mice in the blank group (skin incisions and wound closure) and the glass groups on the 2nd day, which can be attributed to the initial tissue damage caused by surgery. H&E staining showed that the inward migration of muscle fibre cell nuclei and the distance between muscle cells significantly increased, and these changes were accompanied by nonuniform cell sizes and shapes in the mice in the blank group and the Cbz-FFG group, suggesting that muscle fibre atrophy had occurred. However, these phenomena were not severe in the mice in the Cbz-FFG-CA glass group. ICI was greatly alleviated in mice on the 12th day, especially in mice in the Cbz-FFG-CA glass group, demonstrating the immunomodulatory effect and anti-inflammatory function of CA that was released upon glass degradation. On the 30th day, the structure of the muscle tissue appeared normal, the muscle fibres were arranged in an ordered manner, and no obvious ICI was observed. The above results revealed that the developed organic glasses display excellent biocompatibility and biosafety in vivo. Thus, these materials have potential to be the most attractive candidates used to fabricate biodegradable and biorecyclable devices that are conducive to life.
Conclusions

We report the first prototype of biodegradable and biorecyclable organic glasses composed of naturally-derived amino acids and peptides. This represents a critical step towards the development of eco-friendly glasses of biological origin beyond the currently used commercial glasses and plastic materials. These novel organic glasses have excellent glass-forming ability and optical characteristics, and they are amenable to additive manufacturing. Our \textit{in vitro} and \textit{in vivo} experimental results reveal that these glasses are biocompatible, compostable, biodegradable and biorecyclable. Originating from naturally occurring amino acids or peptides, these organic glasses with notable properties show advantage and promise for interfacing the biological and material worlds. This concept of organic glass derived from amino acids or peptides with biodegradability and biorecyclability represents an advanced demonstration of harmonious coexistence between humans and nature, and it is critical for tomorrow's earth.

Declarations

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Competing interests

The authors declare no competing interests.

References


**Figures**
Figure 1

Glass transitions and glass-forming ability of amino acids and peptides. (A) Schematic diagram of the formation of glass. The structural units are derivatives of molecular amino acids or peptides used to prepare a supercooled liquid through a high-temperature melting process and then processed into a glass by a quenching procedure. These organic glasses are biodegradable and biorecyclable and can be degraded by microbes, enzymes and other substances in the environment. (B) Schematic diagram of the DSC-TGA equipment. “R” indicates the reference crucible, and “S” indicates the sample crucible. (C) Procedure for the DSC-TGA measurements. For the Upscan 1 stage, the powder sample was heated from room temperature ($T_0$) to a temperature ($T_1$) greater than $T_m$ but less than $T_d$. Quenching treatment followed an isothermal procedure at $T_1$ for 15 min. For the Upscan 2 stage, the product was reheated...
from $T_2$ to $T_3$, and the glass transition was observed. Thermogravimetric analysis and enthalpic responses of the Ac-F glass (D) and Cbz-FFG glass (E). $T_m$, $T_d$, water release, desolvation and thermal amorphization are indicated in the "Upscan 1" curves. $T_g$ is indicated in the "Upscan 2" curves. The heating and cooling rates were $\pm 10$ K min$^{-1}$. The XRD patterns (F), $^1$H solution NMR spectra (G) and POM images (H) of Ac-F glass (i) and Cbz-FFG glass (ii) show the obvious crystalline state of the raw material powders and the amorphous state of the glasses; the chemical structure of the molecules did not change obviously during the formation of the glass.

Figure 2

Molecular mechanism of the formation of a glass starting from a single crystal. (A) In situ Raman spectra of Ac-F as a function of temperature. The Ac-F single crystal was heated, melted and then quenched to form a glass. The inset shows the chemical structure of Ac-F with the atom types labelled.
The temperature change curve during the simulated annealing process. (C) The evolution of the number and types of hydrogen bonds during the simulated annealing process. Molecular dynamics simulations of the Ac-F single crystal (D) and glass (E), indicating regularly arranged hydrogen bond networks in the crystalline state and a chaotic molecular arrangement in the glassy state.

Figure 3

Light transmittance and additive manufacturing of glasses. (A) Photographs of the glass transition of Ac-F from the crystalline state to the glassy state during heating-cooling treatment. The red arrow indicates the tweezer. (B) Transmittance spectra of glasses in the UV–visible region (left) and NIR region (right). (C) Photographs of an Ac-F glass doped with CQDs or dyes that emitted diverse fluorescence upon excitation with ultraviolet light at a wavelength of 365 nm. The middle image shows the pure glass without doping by fluorescent species. (D) Additive manufacturing of Ac-F fluorescent glass using a 3D printer via a well-designed program. i: Schematic diagram of the 3D printer with a temperature-controlled barrel; ii: photographs of the printed glass architecture (upper: bright field; bottom: fluorescence field). Note: the fluorescence results for the encapsulated CQDs. “CAS” is the abbreviation for the Chinese Academy of Sciences. (E) Photographs of dark field (upper) and fluorescent (bottom) glasses cast with commercial moulds. Note: The mass ratio of CQDs or dyes to biomolecules was 1:10^5, and the powders were evenly mixed before melting.
Figure 4

**In vitro and in vivo degradation of glasses.** (A) The enzymatic degradation products of Cbz-FFG glass identified by ESI-MS. Before the ESI-MS experiment, glass beads 0.3 cm in diameter were dipped in solutions (proteinase K solution, SGF$_{sp}$ and SIF$_{sp}$) and incubated at 37 °C for 72 h. (B) Degradation of glass beads with 0.5 cm diameter in composting soil consistent with ASTM standards. (C) Schematic diagram of glass subcutaneous implantation. Glass beads with a diameter of 0.35 mm were implanted
between the skin and muscle layers. (D) The body weight vs. time curve showing negligible weight loss after implantation of glass beads. (E) Photographs of glass degradation \textit{in vivo} over time. (F) Anatomical data for mouse skin. The arrows indicate the position of glass.

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