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Nonstoichiometric wollastonite bioceramic scaffolds with core-shell pore struts and adjustable mechanical and biodegradable properties

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A B S T R A C T

Controllable mechanical strength and biodegradation of bioceramic scaffolds is a great challenge to treat the load-bearing bone defects. Herein a new strategy has been developed to fabricate porous bioceramic scaffolds with adjustable component distributions based on varying the core-shell-structured nozzles in three-dimensional (3D) direct ink writing platform. The porous bioceramic scaffolds composed of different nonstoichiometic calcium silicate (nCSi) with 0%, 4% or 10% of magnesium-substituting-calcium ratio (CSi, CSi-Mg4, CSi-Mg10) was fabricated. Beyond the mechanically mixed composite scaffolds, varying the different nCSi slurries through the coaxially aligned bilayer nozzle makes it easy to create core-shell bilayer bioceramic filaments and better control of the different nCSi distribution in pore strut after sintering. It was evident that the magnesium substitution in CSi contributed to the increase of compressive strength for the single-phasic scaffolds from 11.2 MPa (CSi), to 39.4 MPa (CSi-Mg4) and 80 MPa (CSi-Mg10). The nCSi distribution in pore struts in the series of core-shell-strut scaffolds could significantly adjust the strength [e.g. CSi@CSi-Mg10 (58.9 MPa) *vs* CSi-Mg10@CSi (30.4 MPa)] and biodegradation ratio in Tris buffer for a long time stage (6 weeks). These findings demonstrate that the nCSi components with different distributions in core or shell layer of pore struts lead to tunable strength and biodegradation inside their interconnected macropore architectures of the scaffolds. It is possibly helpful to develop new bioactive scaffolds for time-dependent tailoring mechanical and biological performances to significantly enhance bone regeneration and repair applications, especially in some load-bearing bone defects.

1. Introduction

Bone graft has huge needs in clinic caused by inflammatory, trauma, congenital deformity and bone fracture and so on, while there are many difficulties in reconstructing large bone segments such as lacking of bone sources and low mechanical strength. (Gugala and Gogolewski, 2002; Komaki et al., 2006; Perka et al., 2000). In recent years, material-based approaches are taken into consideration in order to filling great bone vacancy in clinic, and usually associated with normal body movement that requests the graft scaffolds' mechanical properties should match those of the tissues at the site of implantation. At the same time, the challenge in the field of porous scaffolds is developing that bioceramic scaffolds should match the biomechanical properties of autologous bone and also have sufficient bioactivity to stimulate new bone regeneration (Hutmacher, 2000).

In order to satisfy the demands of bone defect repair in situ, the bioactive ceramics with high mechanical strength, good bioactivity and controlled biodegradation are high valuable to fabricate as porous scaffolds for new bone tissue ingrowth. It is well agreed that wollastonite ($CaSiO_3$; CSi) is a promising bone implant material due to its good osteoconductivity and bioresorbability, which has been studied in alloy coating, granules and sintered porous structure with defined shape (Liu and Ding, 2001; Wu and Chang, 2013). However, the degradation rate of CSi is slightly faster than the regeneration rate of new bone tissue (Bratton and Durairaj, 2011; Xu et al., 2008), meanwhile its relatively low mechanical strength fails to meet the specific mechanical

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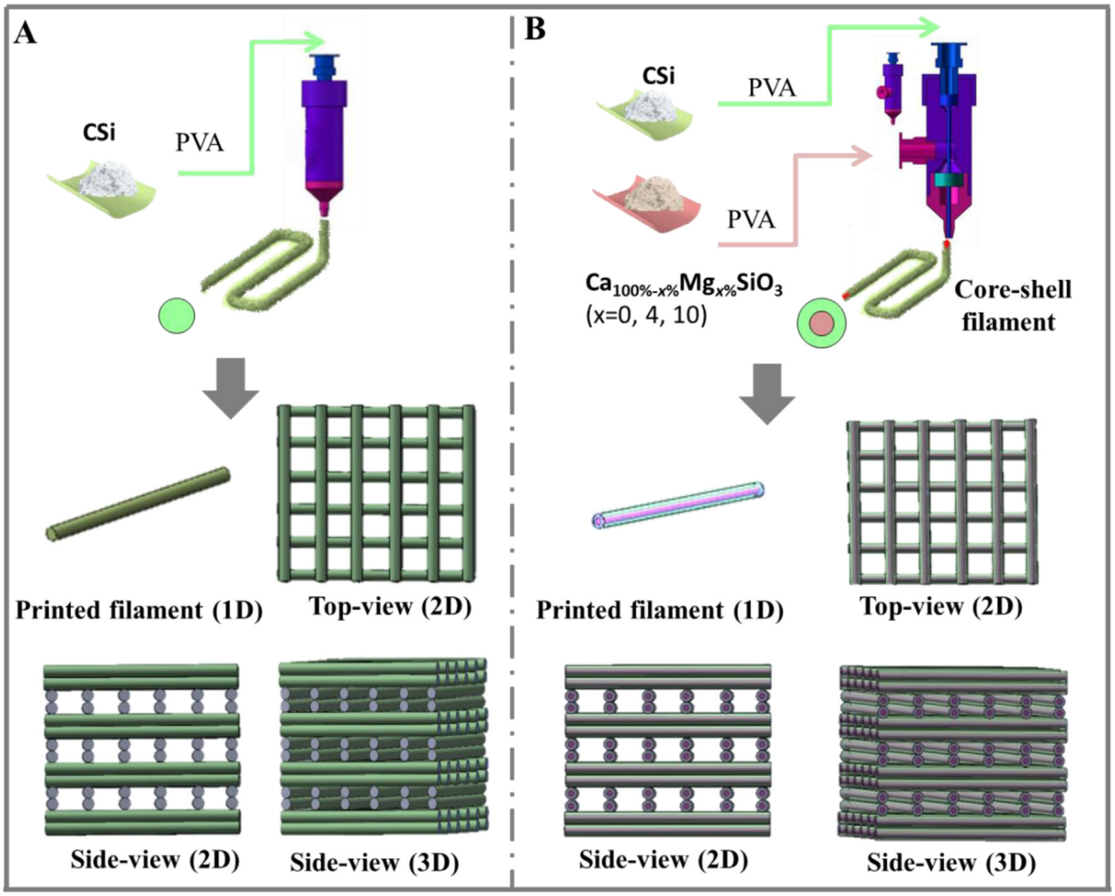

Fig. 1. Schematic illustration for 3D printing nonstoichiometric wollastonite (CSi-Mg*x*) bioceramic scaffolds with single nozzle (A) and core-shell-structured nozzle (B), respectively.

requirement in thin-wall load-bearing bone defects which constrains its applications (Bratton and Durairaj, 2011). To reinforce the mechanical strength as well as decreases the rate of degradation, we have developed the new dilute Mg doping wollastonite (CSi-Mg) compact bioceramics (Xie et al., 2016) and porous scaffolds (Xie et al., 2015). Our studies have demonstrated that the doped Mg plays a critical role in assisted sintering and densification of CSi ceramics and its pore struts, whose mechanical strength is significantly higher than that of pure CSi. Meanwhile, when the CSi-Mg was acted as substitute phase or sintering agent, the mechanically mixed biphasic bioceramic porous scaffolds in the presence of tricalcium phosphate or diopside still maintained appreciable compressive resistance (Shao et al., 2016; He et al., 2016). Furthermore, it has been confirmed that the biodegradation rate of the CSi-Mg in vivo and in vitro could be tailored by Mg dopant (Shao et al., 2017; Zhuang et al., 2017). In fact, Mg is an important mineral element in bone metabolism, and is closely related to cell differentiation and mineralization of calcined tissue and has an indirect effect on mineral metabolism (Castiglioni et al., 2013). Therefore, it can be concluded that adjustment of Mg distribution in bioceramic scaffolds would has significant effects on the mechanical and biological performance in vivo.

On the other hand, the special custom scaffolds for patients are a tendency of anatomically correct surgical models. Additive manufacture (AM) is known as a versatile material processing technology to create porous constructs or prototypes layer-by-layer directly by a computer-aided design (CAD) file (Warner et al., 2017). Direct ink writing (DIW) is one of the additive manufacture technologies and it works guiding consolidating ceramic inks into a 3D porous architecture in a designed shape in pre-mixing organic agent (Lewis, 2006). This technology offers unparalleled flexibility in achieving controlled composition, geometric shape, function and complexity in comparison with other conventional sacrificial template (porogen) sintering methods (Gratson et al., 2004). Most recently, the 3D printing has been employed as new valuable tool for quantifying the effect of structural deterioration on the mechanical properties of trabecular bone, and this approach this technology is thought to help us attain better individual bone replicas from patients suffering excessive bone resorption (Barak and Black, 2018). However, the bioceramic powders are generally designed as concentrated ink in polymer solution that exhibit significant shear thinning to allow extrusion through micro-nozzles. Although this technology is intriguing, this method is either confined to pressureless compacting or pressureless sintering, which impairs the densification and strength of bioceramic struts (Lewis, 2006). There are some attempts that add the secondary phase to assist the sintering or create mechanically strong porous bioceramic architectures. Moreover, the hollow-strut bioceramic Ca-silicate scaffolds have also been developed by Wu et al. in the past several years (Feng et al., 2017; Zhang et al., 2017). The hollow struts are thought to be extremely favorable for neovascularization and new bone tissue ingrowth (Rnjak-Kovacina et al., 2014; Wray et al., 2012). Ideally, the macropores of scaffolds are fully interconnected with the evolution of pore structures, and which matches tissue regeneration beyond the limits of passive diffusion (Bose et al., 2013). In general, the macroporous structures and mechanical strength of the porous scaffolds are particularly important both at early stages of neovascularization and the later stages of new bone turnover when most of the young bony tissue has grown and filled the porous network (Otsuki et al., 2006; Zadpoor, 2015). Accordingly, the bioceramic porous scaffolds with precisely controlled pore-structure and mechanical stability with time are a valuable pursuit for enhancing bone tissue regeneration and remodeling. In this regard, although the