Journal of the European Ceramic Society 36 (2016) 319–332

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Electrophoretic deposition of calcium silicate–reduced graphene oxide composites on titanium substrate

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ARTICLE INFO

Article history:
Received 28 February 2015
Received in revised form 4 August 2015
Accepted 20 August 2015
Available online 2 September 2015

Keywords:
Calcium silicate
Reduced graphene oxide
Electrophoretic deposition
Coating
Biocompatibility

ABSTRACT

Calcium silicate (CS)/graphene coatings have been used to improve the biological and mechanical fixation of metallic prosthesis. Among the extraordinary features of graphene is its very high mechanical strength, which makes it an attractive nanoreinforcement material for composites. Calcium silicate–reduced graphene oxide (CS–rGO) composites were synthesized, using an in situ hydrothermal method. CS nanowires were uniformly decorated on the rGO, with an appropriate interfacial bonding. The CS–rGO composites behaved like hybrid composites when deposited on a titanium substrate by cathodic electrophoretic deposition (EPD). Compared to a pure CS coating on Ti, the CS–1 wt% rGO coating has improved adhesion by 70%, hardness by 150% and the elastic modulus by 240%. The CS–rGO composite coatings exhibit good apatite-forming ability in simulated body fluid (SBF). Moreover, the effect of addition of rGO on morphology, adhesion and proliferation of human osteoblast cells (hFOB) was investigated in vitro.

1. Introduction

Metals still account for a substantial percentage of clinically used materials for orthopedic implants [1]. Among those, titanium (Ti) and its alloys are the most commonly used metallic materials for medical implants subjected to heavy loads, thanks to their high strength-to-weight ratio, relatively low elastic modulus, good fracture toughness, biocompatibility and excellent corrosion resistance [1,2]. Nevertheless, implant failures still occur due to weak bone bonding or insufficient osseointegration [3]. Hence, there is a growing interest in shortening the process toward osseointegration, and thereby reducing the healing time for patients with load bearing Ti-implants. In the past three decades, various bioactive materials have been developed and applied for coating of titanium implants [4–6]. Among the bioactive ceramics, calcium silicate ($CaSiO_3$, CS) has been investigated as a bioactive biomaterial for bone regeneration due to its excellent properties including: (1) osteoconductivity (promotes bonding to bone), (2) osteoinductivity (induces osteogenic differentiation of cells and generates new bone) and (3) better bioactivity than stoichiometric hydroxyapatite (HA) [7–9]. Previous studies have shown that CS coatings on Ti-implants possess excellent bioactivity and biocompatibility, and have the potential to quickly induce the formation of a bone-like apatite layer on their surface after immersing in simulated body fluid (SBF), in cell culture and after implantation in-vivo [10–12]. Moreover, the thermal expansion coefficient of CS is close to that of Ti and its alloys, which allows for good interface bonding between the coating and the substrates compared with traditional HA coatings [10,13]. However, the inferior mechanical features of the CS ceramics have prevented the development of CS coatings on metallic implants for orthopedic and dental applications [9]. Improving the mechanical properties of the coating by the formation of composite coatings through the addition of a second phase is a possible way to overcome this problem [4,14,15].

Graphene consists of a two-dimensional (2D) monolayer structure of hexagonally arranged sp^2-bonded carbon atoms, and has attracted intensive attention because of its unique and excellent mechanical, chemical, thermal and electrical properties [16–19]. In recent years, there has been a considerable advance in the use of graphene-based nanofillers, such as graphene oxide (GO), graphene microsheets, multi-layer graphene (MLG), and reduced graphene oxide (rGO), to improve the mechanical performance of ceramics and bioceramics such as silicon nitride [20], alumina [21], silicon carbide [22], hydroxyapatite [23], zirconia [24] and biphasic calcium phosphate [25,26]. The advantage of graphene as a reinforcing

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.08.025
0955-2219/

material is that exhibit improved mechanical properties such as hardness, elastic modulus, fracture toughness, wear resistance and flexural strength when used in composite materials [27,28]. It is notable that the dispersion and structure of the graphene are the dominating factors for the mechanical improvement of graphene reinforced ceramic composites [28]. In recent years, the cytotoxicity and biocompatibility of graphene has also been widely studied. It was found to be compatible with various cells such as human fetal osteoblast (hFOB), human oligodendroglia (HOG), rat pheochromocytoma (neuroendocrine cell, PC12) primary osteoblasts and human mesenchymal stem cells (hMSCs) [29].

Many processing methods, such as plasma spraying and electrodeposition have been developed to coat CS on metal substrates in order to enable the CS composite to have suitable mechanical properties and good biocompatibility [9,14]. However, Liu et al., [30] reported that the purity of CS was not retained after plasma spraying and that the presence of other phases such as tridymite (SiO_2) and calcium oxide (CaO) was detected along with the CS phase. Electrophoretic deposition (EPD) is considered to be one of the most promising techniques due to its simplicity, low cost, easy control of the coating thickness and feasible design of complex shapes [31–33]. Previous research studies have shown the feasibility of EPD of calcium silicate and its composite coating to modify the surface of metal implants [9,14,34,35]. Moreover, EPD can be used to fabricate advanced nanostructured graphene coatings for various applications [36]. In the EPD method, the deposition of two or more components simultaneously from the same suspension is far more complex than that of single component as a number of factors must be considered such as ionic charge, density of powder and deposition rate of the different components. However, a homogeneous mix between the different components is essential to obtain uniform coatings. In order to overcome these disadvantages, a possible way is to preassemble two components to form a complex, and then disperse this in a single suspension [37].

Hence, our aim was to explore the potential of graphene into CS as reinforcement to improve the mechanical properties of CS coating on titanium substrate. Therefore, firstly we prepared CS–rGO composites by a hydrothermal method before the EPD process. The CS nanowires were grown on the reduced graphene oxide sheets, and then the CS–rGO composite, acting as a hybrid composite particle was homogeneously dispersed in a suspension. EPD was used to coat the CS–rGO composite on a pure titanium substrate with the aim of improving the mechanical properties of the coating and the adhesion to the substrate as compared to pure CS coatings. In addition, we also investigated the kinetics of the electrophoretic deposition, apatite-forming ability and in-vitro osteoblast cellular responses to the coatings.

2. Materials and methods

2.1. Raw materials

The graphite flakes used in this project were purchased from Ashbury Inc. The sulfuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 98%), potassium permanganate ($KMnO_4$, 99.9%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%) and isopropyl alcohol were purchased from Merck (Malaysia). Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and sodium metasilicate nonahydrate ($Na_2SiO_3{\cdot}9H_2O$) were purchased from Sigma–Aldrich Company.

Titanium plates (commercially pure, grade 2) were cut into the desired size (25 × 10 × 1 mm), polished by grit SiC papers (from 240 to 1200 grit), and ultrasonically cleaned in distilled water ethanol and acetone.

2.2. Synthesis of powders

The GO was prepared from the graphite flakes using a simplified Hummers' method [23]. After the synthesis of GO, 208.14 mg of GO was ultrasonically dispersed in 40 mL of distilled water for 2 h. In the first step, the GO solution was added dropwise to 20 mL of 0.2 M calcium nitrate tetrahydrate ($Ca\,(NO_3)_2{\cdot}4H_2O$) under stirring for 30 min, and the pH was adjusted to 11.5 with NaOH. Then, 20 mL of 0.2 M sodium metasilicate nonahydrate ($Na_2SiO_3{\cdot}9H_2O$) solution was added dropwise into the first solution, and the suspension was mechanically stirred for 1 h at room temperature to obtain a homogeneous suspension. In the final step, the suspension was transferred into a 60 mL Teflon-lined stainless-steel autoclave, heated to 200 °C for 24 h, and then naturally cooled to room temperature. Both the reduction of GO–rGO and the in situ synthesis of CS–rGO nanocomposites were expected to occur during the hydrothermal process. CS–rGO composite powders with different rGO contents (0, 0.5 and 1 wt%) were produced. Finally, the synthesized powders were filtered, washed, and dried at 100 °C for 24 h.

2.3. CS–rGO suspension preparation and EPD

In order to prepare a stable suspension of CS–rGO powders for the EPD process, zeta potential, electrophoretic mobility and suspension conductivity were measured using a Nano-Zetasizer (Malvern Instruments, Worcestershire, UK). The suspensions of CS–rGO powders (0, 0.5 and 1 wt% rGO) with concentration of 1 mg/mL were prepared in isopropanol. The suspensions were dispersed in an ultrasonic bath for 30 min, and then the suspensions were used for EPD without further aging. In all the experiments, the pH was not adjusted for any of the suspensions.

The pure CS and CS–rGO composites powders were positively charged in the isopropanol alcohol, moving towards the cathode under DC voltage and were deposited there. To deposit powders on titanium substrates, an electrophoretic cell was made with commercially pure titanium as cathode and a stainless steel electrode as anode. The suspensions used for EPD were prepared by suspending 40 mg powder in 40 mL isopropanol alcohol. The distance between the two electrodes was 5 mm and all the coatings were deposited at voltage of 60 V with a deposition time of 5 min. The coated specimens were carefully removed from the EPD cell to minimize any drag between the wet coating and the remaining suspension. The samples were dried in air at room temperature for 12 h and then kept in an oven at 100 °C for 24 h. The coated samples were sintered at 900 °C for 1 h to improve coating adhesion. This heat treatment was carried out in a vacuum furnace with argon backfilling. Heating and cooling rates were less than 5 °C/min to prevent the appearance of cracks due to differences in the thermal expansion coefficients of the phases that could form during sintering.

2.4. Characterization methods

The microstructures of the synthesized powders and coated samples were observed using a high-resolution FEI Quanta 200F field emission scanning electron microscope (FESEM). Energy dispersive X-ray spectroscopy (EDS) with an EDS system attached to the FESEM instrument was used to investigate the elemental composition of the samples. Fourier-transform infrared spectroscopy (FTIR) was performed using a PerkinElmer System series 2000 spectrophotometer (USA) with a frequency range of 400–4000 cm^{-1}. The X-ray diffraction (XRD) patterns of the powders and composites were obtained using an automated X-ray powder diffractometer (XRD, PANalytical's Empyrean) with monochromated CuKα radiation (λ = 1.54056 Å), operated at 45 kV and 40 mA with a step size of 0.026° and a scanning rate of 0.1 $^{\circ}s^{-1}$ in the 2θ range of 20–60°.