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Featured Letter

Immobilization of reduced graphene oxide nano-flakes on inert ceramic surfaces using self-assembled monolayer technique

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ABSTRACT

Bioinert ceramic, such as zirconia, provides the mechanical strength required in implants, but its limited bioactivity renders it incapable of osseointegration. Thus, its biomedical application is limited. Graphene and its derivatives possess excellent bioactivity and can enhance osseointegration, hemocompatibility and antibacterial properties. Here, we introduce an innovative technique for functionalizing bioinert ceramic by immobilizing reduced graphene oxide (rGO) onto the surface by tailored self-assembled monolayer (SAM). Three routes have been applied for immobilization: i) spontaneous reaction between —OH groups of zirconia and organic functional groups of rGO, ii) spontaneous reaction between —NH_2 functionalized ZrO_2 attained by silanization and —COOH groups of rGO and iii) reaction between —NH_2 functionalized zirconia and activated —COOH groups of rGO attained by using the catalysts EDC and NHS. The most efficient immobilization was obtained between activated —COOH groups of rGO and —NH_2 functionalized zirconia. Thereby, for the first time rGO was successfully coupled to ZrO_2 using SAM technique. Through this technique, the properties of rGO and zirconia could be merged to create a versatile biomaterial.

1. Introduction

The development of new biomaterials to fulfill ever-challenging clinical demands as well as patients' growing needs has continued to be a prime area of research for the past few decades. Bioinert ceramic such as zirconia has been witnessed as an apt choice in these regards due to its excellent chemical, thermal and mechanical stability [1]. However, its incompetency for osseointegration limits its sectors of application [2].

To improve the bioactivity, various coating strategies were applied [3,4]. However, due to the weak strength of these coatings in the interface between the underlying ceramics these materials were bound to fail [5]. To overcome this problem, SAM, which was initially applied mainly on metal substrates [6], was applied to bioinert ceramics. In a previous study, successful immobilization of biological agents was attained by using SAM on alumina [7]. By comparing various coupling strategies, it could be proven that the most successful coupling could be attained between —COOH and —NH_2 functionalized alumina.

Since its discovery, graphene has been an important research topic due to its exceptional electronic, optical and mechanical properties [8,9]. Likewise, graphene and graphene oxide (GO) have been targeted by biomedical researchers due to their intrinsic biocompatibility and high surface area, great osseointegration, antimicrobial properties and facile chemical/biological functionalization [9]. Relatively, the application of reduced graphene oxide (rGO) in the biomedical field is less explored; however, the structure of rGO profiting the additional advantage of containing organic functional groups (epoxy, —OH, —COOH) on the basal plane with the conjugated network of the graphene lattice is effective in antibacterial applications [10].

The SAM technique has been found to be a viable technique to functionalize bioinert ceramics [7,11]. In previous studies, GO has been successfully immobilized on SiO_2/Si substrate using this technique [12]. The presence of organic functional groups on rGO provides the convenience of its immobilization on precisely functionalized inert surface. We hypothesize that by functionalizing these groups, rGO immobilization could be attained on inert ceramic surfaces.

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2. Materials and methods

2.1. Zirconia surface preparation

Zirconia (TZ-3YS-E, Tosoh, Japan) substrates were manufactured by uniaxial pressing (p = 100 MPa) and subsequent sintering at 1450 °C. The sintered specimens were further polished with1 μm diamond paste.

2.2. rGO preparation

rGO paste was purchased from the Institute of Electronic Materials Technology (ITME) in Warsaw. At first, GO was prepared using modified hummer's method [13] and subsequently reduced using NaH2PO2·H2O and heated until boiling point to obtain rGO suspension. The suspension was drained to achieve rGO paste of 2 wt% concentration (Fig. 1). The manufacturing of rGO was proceeded regarding to our previous study [9].

2.3. Self-assembled monolayer (SAM) formation

SAM of the —NH_2 functional group were introduced on the surface using 3-aminopropyldiisopropylethoxysilane (APDS, Abcr GmbH, Karlsruhe, Germany). In a reflux apparatus containing a solution of APDS and toluol (ratio 1:5) respectively, zirconia and borosilicate glass substrates were added and heated for 3 h at 120 °C, as described in our previous study [8]. Subsequently, the substrates were cleaned, initially with toluene (toluene dried (max. 0.005% H_2O), Merck Millipore, Darmstadt, Germany), deionized water, and dried afterwards.

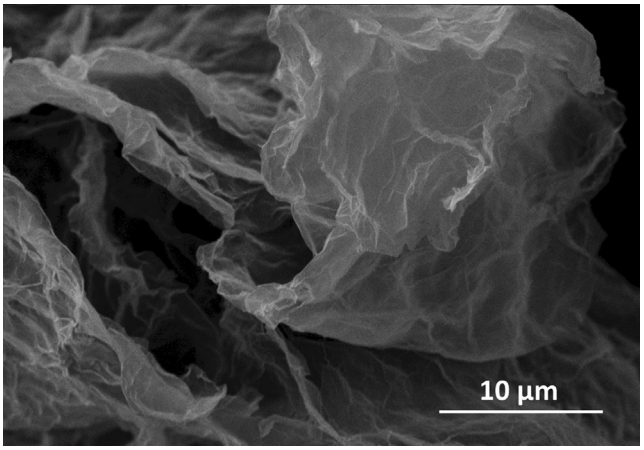

Fig. 1. SEM morphology of rGO nano-flake as received.

2.4. Immobilization of rGO

rGO was immobilized on non-silanized substrates by placing them in a solution containing rGO paste and deionized water (ratio 1:5) respectively (Fig. 2a). Besides zirconia, borosilicate glass (1–6284 Coverglasses, neoLab, Berlin, Germany) samples were taken as control. The same procedure was followed on silanized glass and zirconia substrates to achieve coupling between —NH_2 and —COOH of rGO (Fig. 2b). Furthermore, for the activation of —COOH functional groups a solution containing rGO paste and MES (ratio 1:5) was prepared, and catalysts 1-ethyl-3-[3-dimethylaminopropyl]-carbodiimide hydrochloride (EDC, Thermo Scientific, Dreieich, Germany) and N-hydroxysuccinimide (NHS, Thermo Scientific) were added (20 mg each in 60 ml solution) (Fig. 2c). The immobilization process for every case was carried out for 2 hrs. Every substrate was cleaned thoroughly with deionized water afterwards and dried. To evaluate the mechanical stability, rGO immobilized specimens were put under ultrasonication bath at room temperature and dried afterwards.

3. Results

The successful immobilization of APDS on the substrate surfaces was proven by X-ray photoelectron spectroscopy study (results not shown). rGO was immobilized on all substrates, proven by the SEM (Fig. 3). The flaky morphology was clearly visible in the size range of a few microns. The number of flakes were highest on substrates where coupling between activated —COOH and —NH_2 had taken place (EDC/NHS-activation), which indicate the highest efficiency of this treatment. In activated substrates, considerable amount of immobilized rGO was visualized, even after ultrasonication (Fig. 3d and h).

4. Discussions

Graphene-based materials exhibit multifunctional properties, such as hemocompatibility, osseointegration and antibacterial

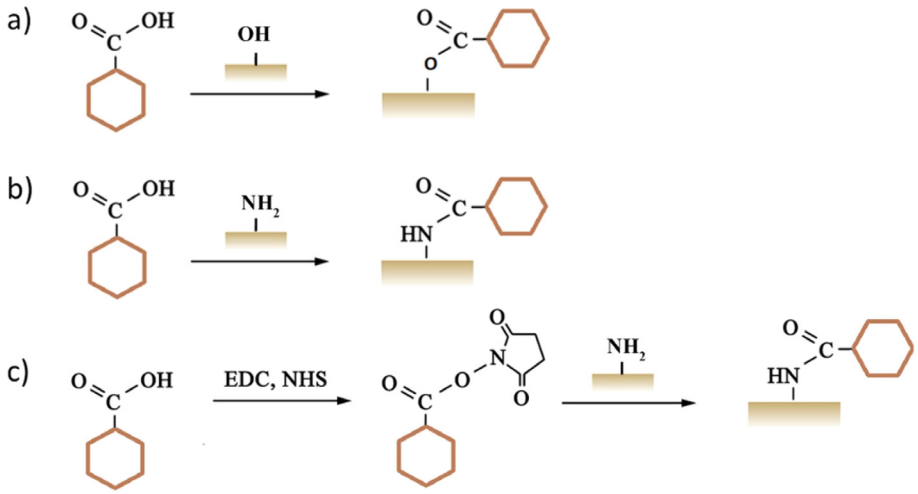

Fig. 2. Pathways for rGO immobilization.