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MWCNT reinforced bone like calcium phosphate—Hydroxyapatite composite coating developed through pulsed electrodeposition with varying amount of apatite phase and crystallinity to promote superior osteoconduction, cytocompatibility and corrosion protection performance compared to bare metallic implant surface

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ABSTRACT

Inconsistent growth of tissues and poor osteoconduction performance on the metallic implant surfaces due to variation of surface energy are major contributing factors for failure of most metallic implant on account of lack of stronger attachment with surrounding bone or tissues. In this study, composite coating of hydroxyapatite, calcium hydrogen phosphate and MWCNT was developed on SS316 surface with varying amount of calcium phosphate-hydroxyapatite phase and crystallinity by pulsed electrodeposition. TEM study revealed that the MWCNTs were bonded strongly with the in situ deposition phases and thus act as reinforcement in the deposited coating similar to the collagen fiber in natural bone structure. Presence of MWCNT reinforcement increased the overall coating modulus of elasticity in the range of 6–10 GPa similar to that of natural bone. Different coating surfaces with varied amount of phase and crystallinity exhibits altogether different phenomena and growth geometry of apatite formation during osteoconduction period under contact with SBF. Coatings with highest amount of hydroxyapatite phase exhibit formation of porous spherical (~1 μm) and rod like (~600 nm) scaffold structure along with presence of nanopores (~100 nm) all along the contact surfaces. Cell proliferation study indicated uniform and fast spreading of cells over the coating surfaces as compared to bare metallic implant. EIS study illustrated five times high corrosion resistance capability along with formation of passivation layer under contact with SBF for coating comes with 66% of hydroxyapatite phase.

1. Introduction

Over past few decades, researchers were successfully able to develop different biomaterials and technologies related to joint replacement in human body. These materials are selected mostly based on their bulk mechanical properties nearly matching with human bone properties and inertness towards the body tissues or fluid [1–2]. However, human body fluid acts as relatively corrosive environment for metallic implants over the period of implant age [3]. Even at any point of time, releasing metallic ions may lead to an allergic reaction and thus can cause infection in surrounding tissues, which occasionally lead to failure of overall implant joint [4]. It is now a well-established fact that almost all the metallic implant surfaces used as on date are bio-inert in nature with the surrounding tissues over the human joints and thus biologically isolated from the bone surfaces or tissues [5–6]. On the other hand, bioactive material can react and form different compound phases similar to or close to bone materials under direct contact with body fluid and blood plasma proteins over a period of time. Those compound phases over the bio active materials are generally inert in nature towards corrosion by body fluid. Also the body tissues are able to grow faster on that bio active material surfaces. But, those bio active materials are mostly ceramic in nature and they are not very much suitable as implant material in view of their poor bulk mechanical properties like strength, toughness etc. [7]. Keeping in view of this, it is therefore essential to coat the metallic implant surface with bioactive and corrosive resistance material in order to have a better bonding with the surrounding bone/tissues along with longer self-life. Also the bioactive material would be

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able to bond with the surrounding bone/tissues through formation of hydroxyapatite similar to natural bone structure on its surface under contact with body fluid or blood plasma [8]. Thus bio active materials on the implant surface trend to exhibit faster cell growth and better bonding with surrounding tissues as compared to bio-inert metallic implant surfaces. Furthermore, any polycrystalline metal surface/coating consists of multi-oriented grain structure with different surface energy. This difference in surface energy creates anisotropic bonding of tissues over the implant surface which may lead to partial detachment. Furthermore, in metallic alloys, segregation takes place at the grain boundaries, which also creates a variation in surface energy vis-à-vis bonding energy [9].

In order to overcome this problem of surface energy variation, a bio active material coating is envisaged over the implant metal surface. Researchers found that the best bio active coating is hydroxyapatite, which is one of the major elements in our natural bone [10–11]. Over the last decade several techniques were tried to develop coating of bio active hydroxyapatite over the implant material [12–13]. A few successful coating techniques are sol-gel technique, pulsed laser deposition, laser cladding etc. [14]. Amongst these methods, only plasma spray method is clinically accepted till now. However, plasma spray method suffers from some drawbacks such as extremely high application temperature which affects homogeneity of the coatings and structure of metallic implants, because of unpredictable phase changes of calcium-phosphorous ceramic during coating, particle release and delamination [15]. Author's earlier work on this area also indicates the enhanced biocompatibility of implant surfaces with hydroxyapatite and its group compound composite coating synthesized through pulsed electro deposition [16]. It was revealed that the relative amount of hydroxyapatite phase along with its degree of crystallinity play an important role for faster cell growth and bonding with surrounding tissues.

It was also found that due to its ceramic nature, hydroxyapatite alone is unable to provide better bonding and modulus of elasticity as compared to natural bone surface. Natural bone consists of collagen fiber (30 to 40 nm in diameter) reinforcement along with crystallite hydroxyapatite [17]. The reinforcement provides strength vis-à-vis better bonding of the ceramic hydroxyapatite crystal in the natural bone. Keeping in view of improving the long term stability of the hydroxyapatite coating over the implant surfaces, it is necessary to improve the cohesive strength of the hydroxyapatite phases present in the synthesized coating. One of the most suitable solution is to introduce reinforcement in the coating same as of natural bone. Considering the biocompatibility of the overall composite coatings, multi walled carbon nanotube (MWCNT) stands as a potential candidate as reinforcement on account of their high specific surface area similar to collagen fiber in natural bone and extraordinary mechanical properties [18–20]. Also the biocompatibility of the CNTs was found suitable to promote bone growth, increase proliferation and enhance different osteoblast in vitro activity [21–22]. Studies related to synthesis of plasma sprayed CNT reinforced hydroxyapatite coating have been tried out by many researchers [23]. But, they all started with a mixture of hydroxyapatite and CNT and no significant work was reported in field of in situ formation of hydroxyapatite along with co-deposition of the same with CNT. Thus in situ formation may be able to provide a better adhesion and bonding of hydroxyapatite with the wall of CNT as compared to the other manufacturing routes like electrophoretic deposition or plasma spraying.

Keeping in view of the above, this study aims at developing a composite coating of hydroxyapatite and its phases (with optimum degree of crystallinity suitable for enhanced bio compatibility) along with internal reinforcement of multi walled carbon nanotube to provide enhanced corrosion resistivity and sustainability under contact with body fluid. The development of the coatings is focused through a simple process of pulsed electro deposition along with in situ formation of phases over MWCNT and metallic implant surfaces.

Table 1
EDS quantification of substrate material composition (weight %).

	P	S	Si	Mn	Mo	Ni	Cr	Fe
SS316	trace	trace	0.8	2.0	2.1	9.7	17.5	67.9

2. Materials and methods

2.1. Materials

Commercial grade stainless steel (SS316) sheet of 180 μm thickness, composed of elements as shown in Table 1, was used as substrates for electro-deposition. Substrate surface was polished with SiC emery papers (600 and 800 grit) followed by ultrasonic cleansing in distilled water and acetone for several times. Epoxy resin was used to mask the surface so that it leaves an exact exposed area of 5 cm^2 on one side of the substrate for deposition.

2.2. Functionalization of MWCNT

Multi walled carbon nanotube (MWCNTs cylindrical tubes, outer diameter 13 to 20 nm, length – 2.5–20 μm, make-Sigma-Aldrich-USA) was used in these experiments. The MWCNT were functionalized with COOH group in order have a better suspension in the aqueous electrolyte medium during deposition period along with creation of defect sites for nucleation during deposition. MWCNTs were functionalized with the help of the following steps as described in figure below [24–25] [Fig. 1].

The dispersion properties of functionalized MWCNT in the aqueous medium were assessed with the help of particle analyser system (Microtrac Zetatrac USA). Neutral surfactant Triton X 100 (Sigma Aldrich USA) was added to the solution in critical micelle concentration in order to enhance the dispensability of MWCNT in aqueous solution for longer time. The particle analyser results (Fig. 2) clearly indicate the well dispersion of functionalized MWCNT in the presence of neutral surfactant as compared to water.

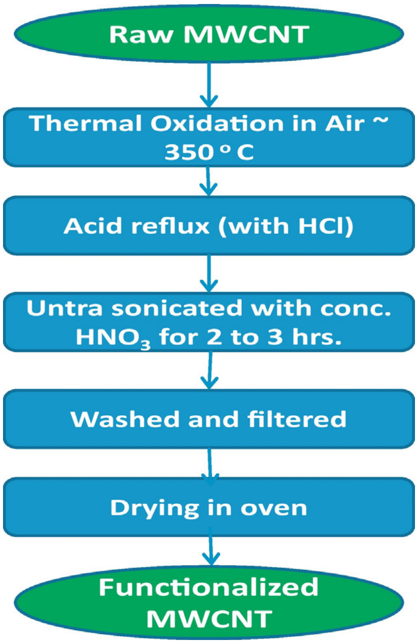

Fig. 1. Flow chart for MWCNT functionalization process adopted.