



Physicochemical properties of nanocomposite: Hydroxyapatite in reduced graphene oxide



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ABSTRACT

Graphene oxide (GO) based nanocomposites have gained considerable attention in the field of material science due to their excellent physicochemical and biological properties. Incorporation of nanomaterials into GO sheets prevents the formation of π - π stacking bond thereby giving rise to composites that show the improved properties compared to their individual counterparts. In this work, reduced graphene oxide (rGO) - hydroxyapatite (HAP) nanocomposites were synthesized by ultrasonic method. Increasing the *c/a* ratio of HAP in the diffraction pattern of rGO/HAP nanocomposites indicates the *c*-axis oriented grown HAP nanorods interacting with rGO layers. Shift in wavenumber (15 cm^{-1}) and increase of full width at half maximum (45 cm^{-1}) of G band in Raman spectra of the rGO/HAP nanocomposites are observed and attributed to the tensile strain induced due to the intercalated HAP nanorods between the rGO layers. Atomic force microscopy (AFM) and phase imaging studies revealed the intercalation of HAP nanorod with diameter 30 nm and length 110–120 nm in rGO sheets was clearly perceived along with improved elasticity compared to pristine HAP. ^{13}C -NMR results proved the synergistic interaction between both components in rGO/HAP nanocomposite. The novel properties observed and the microscopic mechanism responsible for this are a result of the structural modification in rGO layers brought about by the intercalation of HAP nanorods.

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1. Introduction

A variety of hydroxyapatite (HAP) based composites have widely been used in medical applications as it biologically mimics several mineral components present in human body, particularly in bone, dental enamel and pineal gland of the brain [1] and also its biocompatibility, bioactivity and low solubility in moist medias [2,3]. In addition, crystal lattice flexibility, surface layer instability, finite piezoelectricity and proton conductivity [4] renders HAP suitable for several other prospective applications in various fields such as catalyst [5], as adsorbent in waste removal industry [6] and rare-metal free ferroelectric devices [7]. Polarized HAP enhanced the bone osteobonding and promotes new bone growth due to polarization of OH^- groups confined to the HAP channel formed by the overlapping hexagonal calcium atoms [8]. In order to improve mechanical and biocompatibility of HAP, most research has been implemented to combine it with other materials, e.g. polymers, metals and carbon nanomaterials, for morphological and functional modifications [9–11].

Recently, graphene oxide-hydroxyapatite (GO/HAP) composites have been reported to show higher osseointegration ability with

surrounding tissues, biocompatibility and superior bone cellular proliferation induction [12–16]. The two ends of GO sheets are bonded to the adjacent HAP nanograins inhibiting the crack propagation along grain boundary. This grain bridging effect in GO-HAP composite improves the elastic modulus 40% as compared to pure HAP [12]. Compared to pure HAP coating, GO/HAP coating upon Ti have enhanced adhesion strength, corrosion resistance and promote the cellular proliferation [13]. Nanoscale HAP grain, layered structure of graphene flakes and crack deflection at the HAP-GO interface are the key factors in strengthening the GO-HAP composites [15]. The cell culture and viability test results show that the addition of rGO promote the osteoblast adhesion and proliferation. The cell viability and proliferation of osteoblasts properties are enhanced by combining rGO with the HAP nanoparticles [16]. Reduced graphene oxide (rGO) improves cellular behavior because it is not only biocompatible but also the presence of small number of functional groups such as hydroxyl, epoxy, carboxyl and carbonyl in its basal plane and edges provide a way to design bioactive nanomaterials with tailored microstructure having improved mechanical properties [17–19]. Beside these, ion exchange, adsorption and surface complexation of metal ions through the oxygen-containing groups on the surface of GO and HAP are responsible for the sorption of heavy metal ions in water and soils [20,21]. The *c*-axis oriented HAP is positively charged [22], whereas rGO has both hydrophobic (sp^2

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hybridized carbon plane) and randomly distributed hydrophilic zones (hydroxyl and carboxyl functional group) [23]. When these materials are combined to form a composite, there is a strong electrostatic interaction between them which regulates the integration of HAP with rGO [24]. The interatomic distance mismatch between the two pairs of C atoms in graphene walls and Ca atoms in (300) plane of HAP is ~ 0.04 nm. Similarly, the lattice mismatch between the (002) plane of HAP crystals and graphene walls is 0.01 nm. These values are lower than the incoherence limit of 0.25, suggesting that the (300) plane of HAP crystals forms a coherent interfacial bond with the graphene wall and the cross-section of the graphene sheet make a strong interface with the (002) plane of HAP [14,17].

Graphene oxide and surface layer of nanoHAP undergo a variety of chemical transformations while they are exposed to in the extreme synthesis conditions such as high temperature, pressure and rapid cooling rates [25,26]. In the liquid phase synthesis of HAP, water layer adsorption over the surface is unavoidable, because of its polar nature. Larger surface area at the nanoscale also induce surface layer restructuring [27]. The physicochemical peculiarities of HAP manifests in broad ranges of structural features in presence of rGO are yet to be explored at a molecular level. Thus, the aim of this work is to correlate the surface–property relationships of the nanoscale HAP in the presence of GO under dynamic chemical environment.

2. Experimental

2.1. Samples preparation

Graphite flakes (analytical grade) were oxidized using the previously reported improved Hummers method [28]. In the improved synthesis method of GO, a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and KMnO_4 (18.0 g). This mixed solution was then heated to 50°C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (400 mL) with 30% H_2O_2 (5 mL). The resulting precipitate was then centrifuged and washed with 5% HCl until the supernatant was free from sulfate ions. The GO thus obtained was further washed thoroughly with double distilled water (DDW) and isopropanol. The resulting brownish solution was air dried overnight at 40°C to remove the solvent for obtaining GO nanosheets.

HAP was synthesized by wet chemical method. To prevent any residual impurity during the chemical reaction, calcium hydroxide ($\text{Ca}(\text{OH})_2$) and orthophosphoric acid (H_3PO_4) were used as a precursor. In this method, 100 mL of $\text{Ca}(\text{OH})_2$ (Fisher Scientific) (38.08 mmol) and H_3PO_4 (Merck)(23.8 mmol) were independently dissolved in isopropanol at room temperature. The phosphate containing solution and ammonium hydroxide (NH_4OH) were simultaneously added drop by drop to the calcium solution. pH of final solution was adjusted to 11 and the resulting mixture was stirred for 2 h at 40°C . Finally, the mixture was cooled to room temperature and aged overnight without stirring. The obtained precipitate was filtered, washed repeatedly with DDW till neutrality and air-dried at 100°C overnight. The dried sample was calcined at 650°C for 90 min yielding HAP in powder form. For the rGO/HAP composite preparation, already synthesized GO nanosheets were sonicated in a mixture of isopropyl alcohol and water (1:1 volume ratio) for 90 min. The calcined HAP was added to the GO suspended solution. The resulting black solution was subjected to ultrasonication for 90 min using a bath sonicator operated (PCi Analytics) at 50 KHz and the solvent was allowed to air-dry slowly overnight at a temperature of 40°C . The ultrasonic reaction was performed without cooling and the solution temperature attained nearly 80°C . Similarly, three kinds of rGO/HAP composites were prepared at 1:1, 1:1.5 and 1:3 GO and HAP weight ratios (hereafter referred to as 1:1, 1:1.5 and 1:3 samples, respectively). To understand the effect of ultrasonication, the as prepared GO sample was subjected to sonicated for 90 min and labeled as reduced GO (rGO).

2.2. Characterizations

The X-ray diffraction measurements was carried out for these samples using a STOE X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) over the 2θ range of $8\text{--}60^\circ$, using a step size of 0.05° and step time of 4 s. The UNITCELL program was used to calculate the lattice parameters of indexed diffraction lines as obtained from XRD analysis for HAP and rGO-HAP nanocomposites [29]. The vibrational characterization was performed using Raman spectroscopy (in Via, Renishaw) with 514.5 nm excitation of an Ar^+ laser. A 50X objective lens was used to focus on the laser beam (about 1 mm spot size) and to collect the Raman spectral signal in the back-scattering configuration. Instrument calibration was carried out by checking the Si band at 520.7 cm^{-1} . A grating with 2400 lines/mm was used for monochromatization of the scattered waves. Morphological studies were carried out by a scanning probe microscope NTEGRA, NT-MDT. Imaging of rGO/HAP composites using atomic force microscopy (AFM) was performed with special emphasis on sheet thickness, morphological features, lateral dimensions and compositional differences. Topographic images were obtained in semicontact mode using a stiff Si cantilever having a force constant of 12 N/m and radius of curvature 5 nm. Local variation of elasticity, adhesion and friction were investigated using phase detection microscopy (PDM) in semicontact mode by means of phase shift in the free vibration of the cantilever. During these studies, extensive experiments and analysis on each sample along with Si (100) substrate as a local standard for all samples was executed to evaluate the relative mechanical properties. For this experiments, samples of the isopropanol dispersion were placed on Si (100) substrate and spin-coated at 2000 rpm and evaporated at 40°C . ^{13}C Nuclear magnetic resonance (NMR) experiments were performed at room temperature using a Bruker 9.4 T magnet with resonance frequency at 100.64 MHz and magic angle spinning (MAS) rate of 5 kHz. ^{13}C NMR spectra were recorded with high power proton decoupling pulse sequence and $\pi/2$ pulse lengths were kept at $4 \mu\text{s}$ with recycle delay of 5 s. Typically 8192 scans were obtained.

3. Results and discussion

3.1. Structural characterization

The crystallographic phase purity of HAP and HAP intercalated rGO nanosheets were analyzed by XRD. XRD patterns of pure HAP, 1:1, 1:1.5, 1:3, rGO and GO samples are presented in Fig. 1. The (001) peak at 9.79° of GO indicates an interlayer distance of 0.9 nm, which is in good agreement with previously reported results [30]. Ultrasonic irradiated GO diffraction pattern exhibits a (001) reflection at 11.50° ,

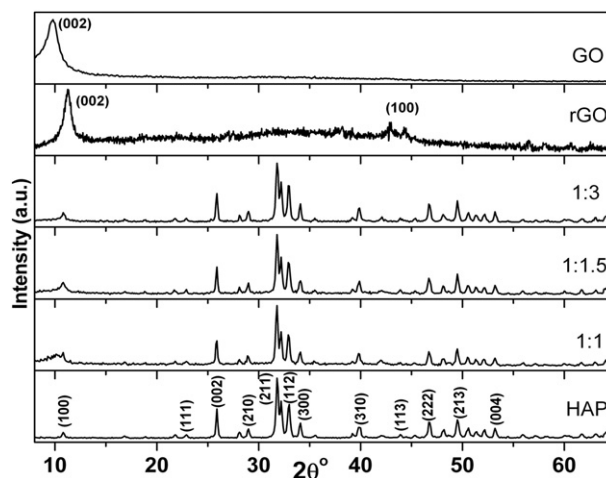


Fig. 1. XRD patterns of pure HAP, 1:1, 1:1.5, 1:3, rGO and GO samples.

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