Reduced graphene oxide-mediated electron-hole separation in titanium dioxide for boosting photocatalytic antibacterial activity of bone scaffold

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Abstract

Fast electron-hole recombination in the photocatalysis process of titanium dioxide (TiO_2) limits its application in preventing bacterial infection for bone defect repair. In this study, TiO_2@reduced graphene oxide (rGO) composites were synthesized through a hydrothermal method, in which rGO with superior electrical conductivity promoted the separation of photoelectron-hole pairs of TiO_2, thus improving the efficiency of photocatalytic production of reactive oxygen species (ROS). Subsequently, the TiO_2@rGO composites were introduced into poly-l-lactic acid (PLLA) to prepare bone scaffold with photocatalytic antibacterial function via selective laser sintering. It showed that TiO_2 grew on the surface of rGO and formed a covalent bond connection (Ti-O-C) with rGO. The electrochemical impedance of TiO_2@rGO composites was decreased, and the transient photocurrent intensity was increased from 0.05 $\mu A/cm^2$ to 0.5 $\mu A/cm^2$. The electron spin resonance resulted that the photocatalytic products of TiO_2 were $\bullet OH$ and $\bullet O_2^-$, which were two kinds of ROS that could kill bacteria via destroying the bacterial membrane structure *in vitro* antibacterial experiment. The antibacterial rates of PLLA/TiO_2@rGO scaffold against *E. coli* and *S. aureus* were 60% and 71%, respectively. Additionally, the scaffold exhibited enhanced mechanical properties due to the addition of TiO_2@rGO as reinforcement phase and good biocompatibility for cell activity and proliferation.

Keywords reduced graphene oxide, photocatalysis, reactive oxygen species, antibacterial properties, bone scaffold

Introduction

Bacterial infection is one of the most common complications in bone defect repair after the implantation of artificial bone scaffold[1, 2]. The formation of bacterial biofilms on scaffold will release acid and enzymes, interfere with bone metabolism, destroy bone matrix, inhibit cell proliferation, delay bone healing[3-5]. Metal oxide nanoparticles, such as ZnO, CuO and TiO_2, and so on, have been widely studied in the field of antibacterial due to their photocatalytic production of reactive oxygen species (ROS)[6-8], which can kill bacteria or inhibiting their growth and reproduction[9-11]. TiO_2 is a kind of metal oxide semiconductor material with wide band gap, making its photoelectron-hole pairs have high redox activity to reacts with water (H_2O) and oxygen (O_2) in the environment to produce ROS [12-14]. However, the rapid recombination of photoelectron-hole pairs leads to the low photocatalytic efficiency, which limits the application of TiO_2.

To enhance the antibacterial efficiency of TiO_2, various methods were used to increase the lifetime and separation efficiency of photocarriers, such as changing the crystal structure and surface properties of TiO_2, etc., in order to enhance the photocatalytic reaction rate and increase ROS production, thereby improving antibacterial ability[15, 16]. Alotaibi[17] et al. synthesized Cu-doped TiO_2 films by means of aerosol-assisted chemical vapor deposition. The results indicated that Cu ions in TiO_2 created defects and introduced oxygen vacancies, which acted as traps to capture photogenerated electrons, thereby boosting the separation of electrons and holes and providing redox active sites for oxidation-reduction reactions. Compared with pure anatase, the film exhibited strong photocatalytic activity and good antibacterial ability against Staphylococcus aureus and Escherichia coli. Thukkaram[18] et al. used plasma electrolytic oxidation technique to deposit Ag on TiO_2. The results indicated that the excellent conductivity of Ag can transfer photogenerated electrons from the surface of TiO_2 to Ag, effectively separating electrons and holes, thereby improving the photocatalytic antibacterial ability. However, previous studies have shown that metal ions have certain cytotoxicity, which can inhibit cell growth and differentiation in the defect area, and even kill surrounding healthy cells, thus affecting the repair of bone defect[19].

Reduced graphene oxide (rGO) is a derivative of graphene, which can be obtained by reducing graphene oxide (GO)[20, 21]. Each carbon atom in the honeycomb lattice structure of rGO forms a covalent bond with three surrounding carbon atoms, forming a conjugated structure with π electrons that can move freely, giving rGO excellent conductivity[22, 23]. Zhao[24] et al. used a simple solvothermal calcination method to anchor Fe_2VO_4 onto rGO. The results indicated the highly conductive rGO accelerated the transport of electrons/ions, solving the problem of rapid decay of capacity caused by the low conductivity of Fe_2VO_4, which the prepared Fe_2VO_4/rGO has a large and stable capacity. At the same time, rGO retains some structural defects from graphene oxide, containing oxygen functional groups, and has stronger hydrophilicity than graphene leading to less biotoxic. As a compromise between graphene and GO, rGO has good biocompatibility and conductivity[25]. Based on the above analysis, it is reasonable conjecture that the excellent conductivity of rGO may promote the separation of photogenerated carriers when rGO combined with TiO_2, thereby increasing its photocatalytic antibacterial properties.

In this study, using titanium tetra-butyl titanate as a precursor, TiO_2 was successfully grown in situ on the surface of rGO via a hydrothermal method. During the process, the GO was reduced to rGO, and TiO_2@rGO composites were prepared, where the superior electrical conductivity of rGO was used to promote the separation of photogenerated electron-hole pairs of TiO_2. The chemical composition and morphology of the TiO_2@rGO composites were evaluated, and the photocatalytic mechanism and activity were studied and evaluated. Subsequently, TiO_2@rGO composites were incorporated into poly-l-lactic acid (PLLA) powders for the fabricating of personalized scaffold with photocatalytic antibacterial function using selective laser sintering (SLS) method[26-28]. The photocatalytic antibacterial properties of the scaffold were evaluated under 365 nm ultraviolet (UV) light and dark conditions. In addition, the mechanical properties and biocompatibility of the scaffold were studied.

Materials and methods

Materials

Tetra-butyl titanate (purity>98.0%), hydrofluoric acid (HF, purity>40.0%) and rhodamine B (RhB, purity>99.0%) were got from Shanghai Aladdin Biochemical Technology Co., LTD (Shanghai, China). GO nanosheets (purity>99.9%) were provided by Chengdu Organic Chemical Co., LTD (Chengdu, China). PLLA powders (purity>99.0%) were bought from Shenzhen Polymtek Biomaterial Materials Co., LTD (Shenzhen, China). Phosphate-buffered saline (PBS), anhydrous ethanol and deionized water obtained from Sinopharm Holding Chemical Reagent Co., LTD (Beijing, China).

Synthesis of TiO_2@rGO nano powders

The hydrothermal method was employed in synthesizing the composite powders. Firstly, 150 mg GO was ultrasonically dispersed in anhydrous ethanol to obtain 3 mg/ml GO ethanol solution. Following the gradual addition of tetra-butyl titanate (7 ml) and HF solution (0.8 ml) into the solution, it was stirred for 10 min before reacting in a Teflon-lined reaction vessel at 180°C for 24 h. When finished, the TiO_2@rGO product was washed twice with water and obtained (centrifugation step at 6000 rpm, 10 min), and dried for 24 h. Pure TiO_2 nanoparticles were also prepared following the above procedure, in which the reaction was carried out in the absence of GO.

Preparation of scaffold

To prepare PLLA/TiO_2@rGO (PTG) composite powders, TiO_2@rGO powders were firstly weighed and dispersed ultrasonically in ethanol for 30 min. Then, a certain amount of PLLA powders were weighed and mixed into the dispersing liquid for ultrasonic dispersion for 15 min (mass ratio of PLLA to TiO_2@rGO was 19:1), and then magnetically stirred for 3 h to achieve uniform dispersion solution[29]. After centrifuging the mixture (6000 rpm ,8 minute), the PLLA/TiO_2@rGO composite powders were collected after drying and grinding. PLLA/TiO_2 (PT) composite powders were prepared using the same procedure.

Three-dimensional (3D) porous scaffold was prepared using a SLS system[30]. The specific steps were as follows[31-33]: First, the 3D model was designed and converted into stereolithography (STL) file, which was then imported into the SLS system where the system automatically calculated the bracket section data[34]. After that, a layer of powders with a thickness about 0.1 mm was evenly dispersed on the platform using a roller. The laser beam proceeded to sinter the powders following a predetermined path which was guided by the slicing data of the scaffold model using a laser power of 1.8 W and a scanning speed of 120 mm/s. Upon completing each path, the platform would move vertically to about the height of a single powder layer, and a new layer of powders was spread. This process was repeated systematically until the desired scaffold was obtained through layer-by-layer sintering.

Characterizations

X-ray diffractometer (XRD): XRD (Rigaku Ultima IV, Tokyo, Japan) was utilized for detecting the crystal structure of the samples from $2\theta=5$ to 80° with a scanning speed of 2 °/min. Fourier transform infrared spectroscopy (FTIR): FTIR spectrometer (Thermo Scientific Nicolet iS5, Massachusetts, USA) was employed for studying the functional groups of the samples, from 400-4000 cm^{-1}. Raman spectroscopy: Raman spectrometer (Horiba LabRAM HR Evolution, Kyoto, Japan) was conducted to detect the structure of the samples at room temperature, from 50-4000 cm^{-1}. Scanning electron microscope (SEM)：SEM (Phenom-World BV, Eindhoven, Netherlands) was used to observe the microscopic morphology of the sample after sputtering with platinum for 120s. X-ray photoelectron spectroscopy (XPS): XPS spectrometer (Thermo Scientific K-Alpha, Massachusetts, USA) was employed to ascertain the chemical bond binding energy in the samples. The excitation source was Al Kα ray (hv= 1486.6eV). The working voltage was 12 kV and the filament current was 6 mA. Electrochemical impedance spectroscopy (EIS) and transient photocurrent: Electrochemical workstation (CHI760E, Shanghai, China) was used to test the EIS and transient photocurrent response of the sample in a three-electrode system using platinum foil, the as-prepared TiO_2@rGO, and saturated calomel electrode (SCE) as the counter, working and reference electrodes, respectively. When testing the intensity of photocurrent, the illumination interval was 20 s with the irradiation wavelength <400 nm. EIS were conducted using a frequency range from 100 kHz to 0.1 Hz. Photoluminescence (PL): Fluorescence spectrophotometer (FLS1000, Edinburgh, Britain) was used to measure the PL response. The excitation wavelength was 325 nm. UV-visible diffuse reflectance spectra: UV-visible spectrophotometer (UV-3600, Shimadzu, Japan) was employed to explore the absorbance of the samples at 200 nm-1000 nm. Electron spin resonance (ESR): ESR spectrometer was used to detect ROS at ambient temperature

(Bruker EMX PLUS, Karlsruhe, Germany), with a microwave power of 6.325 mW, a scan range of 100 G, and a field modulation of 1 G, for the detection of spin adducts.

Mechanical properties

The mechanical properties of the scaffold were evaluated by a mechanical testing machine (YAW-300C, Shandong, China) setting the loading speed as 0.5 mm/min. The scaffold samples used for tensile testing were dumbbell-shaped (12×3 mm^3), and for compression testing were cylindrical (diameter 6 mm, height 10 mm). Under continuous loading, the samples fractured during tensile testing and exhibited severe deformation with 30% strain during compression testing. The stress-strain curves were obtained, and the modulus was calculated. Each experiment was conducted five times.

Photocatalytic activity

Photocatalytic activity of the PLLA, PT and PTG scaffolds was detected by RhB degradation. Square samples (9×9×1 mm^3) were produced in sheet form by SLS technology. The PLLA, PT and PTG scaffolds were added to three tubes that contained 4 mL RhB solution (8 μg/mL), respectively, while the fourth tube contained no scaffold and was used as a blank control. After irradiated with UV light, the supernatant was collected every 25 min, and measured using a visible spectrophotometer (V-1800, Shanghai, China). Photocatalytic degradation curves of RhB were obtained for each type of scaffolds.

Antibacterial properties

S. aureus and *E. coli* strains were thawed from the -78 °C refrigerator and cultivated in the autoclaved LB medium to activate the strains. Next, the activated strains were streaked onto solid LB medium using an inoculating loop to get a single colony, and then cultivated in LB medium for 1 d at 37 °C. The bacterial suspension was prepared by diluting the culture in sterile saline to a concentration of 10^8 CFU/mL for later use. In the bacterial standard plate counting assay, the initial bacterial solution was diluted in a gradient to 10^6 CFU/mL. The PLLA, PT and PTG scaffolds were placed in EP tubes, to which 100 μL of the 10^6 CFU/mL bacterial solution and 900 μL of LB liquid medium were added. A separate group without scaffold was used as the blank control. The bacterial solution was irradiated with UV light (365 nm) for 30 min and then incubated 24 h. The resulting bacterial solution was diluted 10^5 times, and 100 μL of the solution was uniformly coated on a solid LB medium. After further incubation at 37 °C for 24 h, colonies were counted using ImageJ software. Control experiments were conducted in parallel with a darkness group serving as the control. The PLLA group in dark was selected as the negative control group, while the others were selected as the experimental group. The bacterial survival rate was determined through theutilization of the following formula[35]:

$$Bacterial\ survival\ rate = {}^{A_1}\!/_{A_0} \times 100\%$$

where A_0 and A_1 represent the bacterial counts in the negative control group and the experimental group, respectively. The antibacterial activity was 1-*bacterial survival rate*.

To measure the destruction of biofilms through photocatalysis, live/dead staining was used. The PLLA, PT and PTG scaffolds were placed in EP tubes, and 100 µL of a bacterial solution (10^6 CFU/mL) and 900 µL of LB liquid medium were added. At 37 °C, the samples were then cultivated for 24 h, followed by irradiating with UV light for 30 min. Live/dead staining was performed using a SYTO9/PI Double Stain Kit (MKBio, MX4234), and images were captured with a fluorescence microscope (Olympus IX73, Japan). SEM was used to assess the effect of the scaffold material on bacterial biofilm. After the experiment, the scaffold was carefully removed from bacterial solution, and the biofilm was washed using PBS. The cleaned biofilm was then fixed overnight at 4 °C using a 2.5% glutaraldehyde solution. The bacteria were subsequently dehydrated for 15 min, and then air-dried for 24 h. Finally, the samples were characterized using SEM after sputter-coating.

Cytocompatibility

To evaluate the cytocompatibility of the scaffold, the proliferation status of hBMSCs (American Type Culture Collection, Manassas, USA) was assessed. By using Dulbecco's Modified Eagle's culture medium (DMEM) enriched with 10% fetal bovine serum and 1% antibiotics, hBMSCs were seeded onto sterile scaffold samples (1×10^5 cells/cm^2). Following incubation at 37 °C and 5% CO_2 for 1, 3 and 7 d, they were washed thrice using PBS, and subsequently fixed with 2.5% glutaraldehyde at room temperature. After dehydration with graded ethanol solutions and air-drying at 35 °C, SEM was utilized for observing cell adhesion on the sample surface. To evaluate cell viability, the cells were stained using Calcein-AM/PI Double Stain Kit (Beyotime) in PBS at 37 °C for 30 min. The Cell Counting Kit-8 (CCK-8, Beyotime) was utilized to assess the proliferation of hBMSCs on the scaffold. At each evaluation time point, the medium was removed, and the scaffolds were washed with PBS before being transferred to fresh medium containing 10% CCK-8 and cultivated for an additional 2 h. Next, the microplate reader (Thermo Multiskan FC) was used to measure the optical density (OD) of the supernatant. The stained samples were ultimately visualized using a fluorescence microscope (Olympus Corporation, Tokyo, Japan), where green fluorescence indicated living cells, and red fluorescence indicated dead cells.

Statistical analysis

All quantitative results were presented as the mean±standard deviation. Statistical analysis was carried out using Statistical Products and Services Solutions (SPSS, Version 19, IBM Corporation, Armonk, USA), with significant levels of $p<0.05$ and $p<0.01$ used to denote significant differences, represented by * and **, respectively.

Results and discussion

Characterization of TiO_2@rGO

The hydrothermal method was utilized to synthesize the composite powders, as shown in Fig. 1(a). SEM was used to examine the microstructure of synthesized TiO_2 nanoparticles and TiO_2@rGO composite powders, as illustrated in Figs. 1(b) and (c). Although the images of the two samples were almost similar, the TiO_2@rGO had a pinnate two-dimensional structure, showing the difference with TiO_2 nanoparticles. The morphology analysis also clearly showed that the pinnate two-dimensional structure observed in TiO_2@rGO was due to the present of rGO.

The XRD patterns of GO, synthetic TiO_2 and synthetic TiO_2@rGO were illustrated in Fig. 1(d). The location of the observed peaks was consistent with previous reports. The peak at $2\theta=11.25°$ of GO corresponded to the (001) crystal plane[36]. About the TiO_2, the peak at 25.28° corresponded to the (101) crystal surface of anatase phase TiO_2, indicating that the prepared TiO_2 nanoparticle was anatase phase. The specific diffraction peaks of TiO_2 at $2\theta=37.91°$, 47.86°, 53.75° and 62.68° could also be attributed to the (004), (200), (211) and (204) reflections of TiO_2 nanocrystalline surfaces (JCPDS No. 21-1272), respectively[37, 38]. This indicated that the TiO_2 nanoparticle had been successfully synthesized. For the TiO_2@rGO, the characteristic reflection peaks corresponding to each crystal surface of anatase phase TiO_2 were observed, but no specific reflection of GO was observed, indicating that all GO had been successfully reduced to rGO in the hydrothermal reaction process. The characteristic peak of rGO was not observed, probably because its characteristic peak at about 27° was close to the (101) crystal peak of TiO_2. The functional groups of GO, TiO_2 and TiO_2@rGO samples were analysed by FTIR, as illustrated in Fig. 1(e). The 3450 cm^{-1} peaks in all spectra indicated C-OH group's O-H stretching vibration. The peak at 1627 cm^{-1} observed in GO was attributed to the C=C skeleton vibration, while the 1400 cm^{-1} and 1087 cm^{-1} peaks corresponded to the C-OH and C-O-C vibrations, respectively[38, 39]. Absorption peaks at 500-800 cm^{-1} were observed in the TiO_2 sample, which resulted from the Ti-O-Ti stretching vibration. For TiO_2@rGO sample, a peak caused by the skeleton vibration of rGO was observed at 1627 cm^{-1}. The disappearance of the peak corresponding to C-O-C in rGO at 1087 cm^{-1} indicated that GO was successfully reduced to rGO.

The vibration modes of the three samples were studied using Raman spectroscopy, as illustrated in Fig. 1(f). Two well-defined peaks were observed in the GO sample at 1349 cm^{-1} and 1595 cm^{-1}, which were attributed to the D and G bands, respectively[38]. The D band, which was a typical characteristic of sp^3 defects in carbon, and the G band, which furnished valuable insights into the in-plane vibrations of sp^2-bonded carbon atoms of graphene, were both discernible features in the sample[40, 41]. Some oxygen-containing functional groups combined at the boundary of the graphite layer, resulting in a large number of defects C (sp^3) and impurities, which destroyed the crystal structure of graphite. About the TiO_2 samples, it showed the peaks of typical anatase phases at 147 ($E_{g(1)}$), 391 (B_{1g}), 512 (A_{1g}) and 633 ($E_{g(2)}$) cm^{-1}, respectively. The TiO_2@rGO sample displayed the characteristic peaks of graphene, with the D (1349 cm^{-1}) and G (1595 cm^{-1}) peaks being detected, respectively. Strength ratio (I_D/I_G) of 1.21 was much higher than that of GO (0.85), indicating that GO had been successfully converted to rGO[42]. The peaks of TiO_2 (141, 386, 506 and 634 cm^{-1}) were also existent, indicating the synthesis of TiO_2@rGO composite powders.

XPS was conducted to analyze the composition of TiO_2 and TiO_2@rGO samples. Analysis of the obtained spectra revealed the existence of O, Ti, and C elements, and the outcomes were presented in Fig. 1(g). The high-resolution XPS spectra of C, Ti and O were analyzed and displayed in Figs. 1(h)-(j). C 1s binding energy peaks measured in the TiO_2 sample were at 284.8 eV (C-C), 286.4 eV (C-O) and 288.3 eV (C=O), while that of the TiO_2@rGO was at 284.6

eV, 286.5 eV and 288.9 eV[38]. However, an additional binding energy peak located at 285.6 eV was observed in the TiO_2@rGO sample. Combined with the above characterization experiments, it was judged to be a C-O-Ti bond, indicating that TiO_2 and rGO had chemically bonded, which was advantageous for facilitating the transfer of photogenerated charge carriers. The binding energies of Ti $2p^{1/2}$ and Ti $2p^{3/2}$ in TiO_2 were 464.4 eV and 458.6 eV, respectively, while those of the TiO_2@rGO moved to 465.2 eV and 459.7 eV, respectively. It indicated that there was electronic transfer from TiO_2 to rGO, and led to an increase in TiO_2 binding energy. As shown in Fig. 1(j), the binding energies of O 1s of the TiO_2 sample were located at 529.9 eV (Ti-O bond) and 530.7 eV (C-O bond), while the binding energy peaks of the TiO_2@rGO sample moved to 530.7 eV (Ti-O bond) and 531.2 eV (C-O). The C=O bond at 533.2 eV was also observed. The results of XPS analysis confirmed a bonding connection was established between TiO_2 and rGO, which promoted electron transfer. In short, these indicated the adhesion of TiO_2 nanoparticles on rGO, and the successful synthesis of the TiO_2@rGO, which was conducive to the transfer of photogenerated carriers in the photocatalytic reaction. Previous studies indicated that the migration of photogenerated carriers was crucial in the photocatalytic production of ROS[43].

The photocatalytic activity of the above two samples was investigated and characterized. The light absorption characteristics of them were measured using UV-vis spectroscopy, as illustrated in Fig. 2(a). The absorption band edge of the TiO_2 sample was around 390 nm, similar to TiO_2@rGO, which was consistent with previously reported results[44]. rGO did not significantly broaden the optical response range of TiO_2. Subsequently, the photocatalytic activity was characterized under UV light at 365 nm. The effect of rGO on photogenerated electron-hole pair separation was demonstrated by transient photocurrent response and Electrochemical Impedance Spectroscopy (EIS) measurement[45, 46]. An equivalent circuit diagram was obtained through EIS measurement and was shown in Fig. 2(b), with the measured results presented in Fig. 2(c). The diameter of the Nyquist circle was positively correlated with the impedance, which reflected the relative size of the electrochemical impedance[45, 47]. The TiO_2@rGO sample exhibited a shorter Nyquist circle diameter than the TiO_2 sample, indicating much smaller interfacial charge transfer resistance and better charge transfer efficiency.

The efficiency of photogenerated carriers' separation and conversion in the photocatalyst was studied through a series of experiments. Photoluminescence (PL) is an effective technique to evaluate the efficiency of photoluminescence electron-hole separation[45, 48]. When the photocatalyst absorbs light energy to produce photogenerated carriers, the subsequent recombination of these charge carriers results in the emission of light. Generally, the intensity of photoluminescence is directly proportional to the degree of separation of photogenerated electron-hole pairs. Higher carrier separation efficiency causes lower PL intensity, resulting in more efficient photocatalytic behavior. The PL spectra of the two samples at atmospheric temperature under a 365 nm UV light were presented in Fig. 2(d), featuring a broad emission peak centered at 435 nm. The higher PL strength of the TiO_2 indicated that the holes and electrons in TiO_2 were easier to recombine, confirming that the addition of rGO was conducive to the inhibition of carrier recombination[49].

Transient photocurrent responses of interfacial charge separation were studied by collecting multiple switching cycles under a 365 nm UV light, as shown in Fig. 2(e). As is known, a high separation rate of photon-producing carrier supports photocatalytic efficiency. The stronger index of photocurrent intensity, the higher the photocatalytic efficiency and activity. As illustrated in Fig. 2(f), the photocurrent density increased when the power was turned on and the illumination started, while the current density decreased when dark. The superior photocurrent intensity observed in TiO_2@rGO compared to that of TiO_2 suggested that the rGO effectively enhanced the separation efficiency of photogenerated carriers[50]. In addition, as shown in Figs. 2(g)-(i), ESR was used to detect the ROS produced by the TiO_2@rGO under photocatalytic conditions. The signal of $\bullet OH$ was the strongest, followed by that of $\bullet O_2^-$, while there was almost no signal of $^1O_2$[45]. It indicated that $\bullet OH$ was the main product of the TiO_2@rGO photocatalysis, with a small amount of $\bullet O_2^-$, and both of these were the main factors contributing to the photocatalytic antibacterial activity.

Characteristic of scaffold

The PLLA powders, the prepared PT and PTG composite powders were processed into scaffolds with personalized porous structure using the SLS technique, as shown in Fig. 3(a). The designed porous support was shown in Fig. 3(b). The scaffold was cylindrical (diameter 12 mm, height 12.5 mm) and had a number of through-holes distributed on the upper front, as well as a large number of lateral holes on the side[51, 52]. These features were conducive to nutrient delivery and cell proliferation[53, 54]. FTIR and XRD were utilized to analyze the scaffold's composition, and the corresponding results were illustrated in Figs. 3(c) and (d), respectively. In the FTIR spectra of PTG exist a peak at 500-800 cm^{-1} indicating the presence of TiO_2. Similarly, in the XRD patterns, the peak observed at $2\theta=25.3°$ for the PT and PTG samples indicated the presence of TiO_2 in the scaffolds. The results of FTIR and XRD confirmed that the scaffolds were successfully prepared.

The mechanical properties of the PLLA, PT and PTG scaffolds were evaluated by tensile and compression tests, and the relevant results were shown in Figs. 3(e) and (f) and Figs. 3(g) and (h). The scaffolds containing TiO_2 and TiO_2@rGO exhibited enhanced tensile strength and modulus. Specifically, the PTG scaffold demonstrated a notable increase in tensile strength from 474 MPa to 640 MPa compared to the PLLA scaffold, while the modulus was only slightly elevated. Moreover, the compressive strength and modulus of the scaffolds containing TiO_2 and TiO_2@rGO were also enhanced. Specifically, the PTG scaffold was demonstrated an increase in compressive strength from 130 MPa to 230 MPa and an increase in compressive modulus from 14.73 MPa to 18.77 MPa, resulting in a 76.9% and 27.4% improvement, respectively, compared to the PLLA scaffold. Incorporating TiO_2 and TiO_2@rGO as reinforcement phases resulted in an improvement of the mechanical properties of the PLLA scaffold.

Photocatalytic activity of scaffold

The photocatalytic activities of the PLLA, PT and PTG scaffolds were determined by the RhB degradation method, as shown in Fig. 4(a). RhB belongs to the xanthene dye family, which can be degraded by photobleaching and N-desulfurization through TiO_2 photocatalysis[55, 56]. The PLLA, PT and PTG scaffolds were submerged in RhB solution respectively, and irradiated with UV light to observe color fading of the solution, as shown in Fig. 4(b). The absorbance of the solution at different time points was measured using a visible spectrophotometer at a wavelength range of 450-650 nm, as illustrated in Figs. 4(c)-(f). The color of the RhB solution in the PTG scaffold became lighter, and the absorbance decreased after 75 min of UV irradiation[48]. The absorption curves of the PLLA scaffold and blank control group were basically unchanged, indicating that the PTG scaffold produced ROS and degraded RhB under UV irradiation. The same trend was observed in the PT scaffold, but to a lesser extent. The changes in the absorption peak and area under the curve were analyzed, as illustrated in Figs.

4(f) and (g). The PTG scaffold had the fastest degradation rate, and the highest degree of RhB under UV irradiation, which resulted from the ability of rGO to separate electron holes and improve the photocatalytic efficiency of TiO_2.

Photocatalytic antibacterial effect *in vitro*

To investigate the antibacterial ability of the PLLA, PT and PTG scaffolds, antibacterial experiments were conducted *in vitro*. The impact of the scaffolds on the proliferation of *E. coli* and *S. aureus* were observed by fluctuations in bacterial population on the petri dish, as shown in Figs. 5(a) and (b). Taking the PLLA scaffold in dark as the negative control group, the number of bacterial colonies on the PT scaffold decreased slightly, and that on the PTG scaffold decreased significantly. This indicated that TiO_2 had a photocatalytic antibacterial effect, and the addition of rGO effectively improved the photocatalytic antibacterial effect of TiO_2. As biofilm formation is a crucial factor in implant-associated infections, we examined the scaffolds' ability to eliminate biofilms. The live/dead staining experiment of bacteria biofilm treated by photocatalysis showed that UV irradiation of the PTG scaffold had a strong destructive effect on the bacterial biofilm, as illustrated in Figs. 5(c) and (d). However, only a small amount of the bacterial biofilm was destroyed under UV irradiation alone. The bacterial counts of each group in the plate counting experiments were counted and the survival rate was calculated, as shown in Figs. 5(e) and (f). Under dark conditions, both the PT and PTG scaffolds had a weak inhibitory effect on bacteria due to the presence of TiO_2 and rGO. Compared to dark conditions, UV irradiation led to a slight decrease in the survival rate of both bacterial strains. Upon exposure to UV irradiation, the PTG scaffold exhibited a considerable reduction in bacterial survival rate, with *E. coli* and *S. aureus* displaying survival rates of 40% and 29%, respectively, compared to survival rates of 62% and 45% for *E. coli* and *S. aureus* in the PT scaffold. This indicated that rGO enhanced the photocatalytic activity of TiO_2 in producing ROS, thereby enhancing the antibacterial effect. The antibacterial effect was not ideal, and the possible reason was that UV light has weak penetration ability, and the antibacterial substances are encapsulated in PLLA, making it difficult to release [42]. In the future, it was planned to utilize certain methods to promote the release of antibacterial substances, such as enhancing the degradation rate of the scaffold; or shifting the absorption range of titanium dioxide towards longer wavelengths to improve its photocatalytic efficiency. These measures aim to enhance the antibacterial properties of the scaffold.

The morphological changes of the bacteria on the PLLA, PT and PTG scaffolds without or under UV irradiation were studied by SEM characterization, as shown in Figs. 5(g) and (h). The untreated *E. coli* and *S. aureus* in the control group were along with smooth and intact cell walls. In all the unilluminated groups, the morphologies of the bacteria remained almost unchanged. The PT scaffold was irradiated by UV light, and a few bacteria were damaged, and the surface became wrinkled. However, the PTG scaffold experienced serious damage to bacteria after UV irradiation, resulting in unclear bacterial boundaries, different degrees of surface depression and even cell wall damage. These results demonstrated that the PTG scaffold could destroy existing biofilms and prevented biofilm formation under UV irradiation. The photocatalytic antibacterial mechanisms of the PTG scaffold were shown in Figure 6[57]. The PTG scaffold contained TiO_2@rGO, in which the electrons in the valence band of TiO_2 absorbed photon energy and transferred to the conduction band to be activated, and left holes in the valence band under the irradiation of UV light. Further, due to the superior electrical of rGO, the electrons in the conduction band were transferred to rGO surface, preventing the recombination of electrons and holes[58, 59]. Oxidation-reducing electrons and holes reacted with H_2O and O_2 in the environment, respectively, to produce ROS including •OH and $\bullet O_2^-$. ROS oxidized the bacterial membrane structure to break it, and further destroyed the bacterial genetic material to achieve scaffold photocatalytic antibacterial function.

Cytocompatibility

Cell assays were conducted to assess the biocompatibility of the PTG scaffold, with the PLLA scaffold serving as the control. Fig. 7(a) depicted SEM images of human bone marrow stem cells (hBMSCs) cultured on the scaffolds for 1, 3 and 7 days. Within 1 day, hBMSCs on the PLLA scaffold exhibited a slim spindle shape with distinct separation from one another. Some filamentous pseudopodia extensions were observed on the PTG scaffold. After 3 d, cells coverage area increased and an irregular polygonal shape emerged as the filamentous extensions intermingled. After 7 d, hBMSCs had grown and extended on the PTG scaffold to form a cell layer. It suggested that the PTG scaffold had a better cytocompatibility, indicating that the addition of rGO and TiO_2 in PLLA could promote cell adhesion[60, 61].

Cell viability for both PLLA and PTG scaffolds was assessed via fluorescent staining techniques to distinguish living (green) and dead (red) cells, as illustrated in Fig. 7(b). Obviously, living cells spread well and increased over time, as the filamentous pseudopodia grew, and there were few dead cells in the scaffolds. Additionally, consistent with the cell adhesion experiment, the PTG scaffold showed higher cell viability than the PLLA scaffold at each sampling time. It suggested that TiO_2@rGO could promote cell proliferation of PLLA. In addition, the relative cell area, cell density and CCK-8 result of each group were statistically analyzed and calculated, as shown in Figs. 7(c)-(e). The superior ability of the PTG scaffold to promote hBMSCs growth may attribute to several factors[62]. Firstly, the incorporation of TiO_2@rGO improved the scaffold's hydrophilicity, which facilitated cell adhesion and proliferation[63, 64]. Additionally, the rough and large surface area of the TiO_2@rGO offered more sites for cell adhesion, and the presence of Ti element was beneficial for stimulating cell growth.

Conclusions

In summary, TiO_2@rGO composites were prepared by hydrothermal method and introduced into PLLA, and the photocatalytic antibacterial bone scaffold was prepared by SLS technique. With UV irradiation, the free electrons in the conduction band of TiO_2 transferred to the surface of rGO, avoiding recombination with holes, which improving the photocatalytic activity of TiO_2. The main photocatalytic products of TiO_2@rGO were •OH and $•O_2^-$. Compared to the PT scaffold, PTG scaffold showed better antibacterial properties with antibacterial rates against *E. coli* and *S. aureus* of 60% and 71%, respectively. Additionally, the incorporation of TiO_2@rGO also improved the mechanical properties and biocompatibility of the scaffold. This study provides a feasible strategy for the antibacterial functionalization of bone scaffold and expands the antibacterial application of TiO_2.

Author contributions

FPei Feng, Haifeng Tian and Cijun Shuai produced original idea. Pei Feng, Haifeng Tian, Feng Yang designed the experiment. Haifeng Tian, Feng Yang, Shuping Peng, Hao Pan performed experimental synthesis and characterizations. Pei Feng, Haifeng Tian, Feng Yang, Shuping Peng, Hao Pan, Cijun Shuai discussed the results and analyzed experimental data. Pei Feng, Haifeng Tian revised the manuscript. All the authors read and approved the final manuscript.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human or animal subjects performed by any of the authors.

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