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Comparison of TiN and CN_x coatings on orthodontic stainless steel: Tribological and biological evaluation

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ABSTRACT

Surface modification of orthodontic appliance materials has contributed to the development and popularization of orthodontic treatment. Important characteristics of modified materials include the coefficient of friction, antimicrobial activity, and biocompatibility. To investigate these characteristics, we coated a stainless steel (SS) substrate, which is used to manufacture orthodontic appliances, with a titanium nitride (TiN) or carbon nitride (CN_x) film. The coating thickness, elements, and surface morphology were characterized by scanning electron microscopy and energy-dispersive spectrometry. The coefficient of friction was measured using a universal micro-tribotester; the density of *Streptococcus mutans* was used to assess antimicrobial ability; and the viability of human periodontal ligament fibroblasts implanted on the samples was used to evaluate the biocompatibility of the different films. We found that the CN_x film exhibited a lower friction force, effective antimicrobial activity, and favorable biocompatibility compared to the uncoated and TiN-coated SS. In conclusion, a CN_x film is promising for modifying archwires to decrease friction and improve antimicrobial activity and biocompatibility.

1. Introduction

Stainless steel (SS) is often used in orthodontic appliances, including most types of brackets and archwires [1]. Its advantages are its low cost, high stiffness, and environmental stability [2]. However, its performance in terms of antibacterial activity and friction requires improvement [1,3,4] to improve the treatment efficiency [5,6] and oral health [7,8]. Wire–bracket friction could cause loss of orthodontic force and increase the risk of apical root resorption. Moreover, bacterial accumulation around orthodontic appliances leads to caries [7,9,10]. Therefore, modification of the surface properties of SS is of great importance in orthodontics. Coating with typical elements or materials is a direct route to surface modification [11]. CN_x, TiN, and TiO_2 are materials that have potential for biomedical material modification [12–14].

Because the hardness of β-C_3N_4 has been theoretically predicted to rival that of diamond, carbon nitride (CN_x) films have been extensively studied in recent decades [15,16]. Because of its extreme hardness, CN_x exhibits excellent friction and anticorrosion properties [12]. CN_x materials have structures similar to that of diamond-like carbon (DLC), which has been extensively studied for its mechanical properties and non-cytotoxic biocompatibility [4,5,17,18]. Furthermore, the nitrogen in CN_x stabilizes the sp^3 carbon, resulting in increased hardness, and is beneficial for its biocompatibility [19,20]. CN_x materials are also emerging as a new class of nanomaterials in bioimaging, sensing, drug delivery, and cancer therapy [21].

Titanium nitride (TiN) coatings have been widely applied to dental instruments, in particular, to improve the properties of rotary and endodontic cutting instruments [22]. TiN films have demonstrated favorable characteristics in terms of corrosion resistance, wear resistance, hardness, and improvement in the biocompatibility of bare NiTi alloys [13,23–25]. The use of metal nitride coatings could reduce bacteria attachment on surfaces; hence, such films possess considerable potential for the surface modification of medical implant materials [26].

Titanium and its alloys spontaneously form protective passive oxide films on their surfaces. Titanium dioxide (TiO_2), a photocatalytic antibacterial material, has considerable beneficial properties including chemical stability [27], biocompatibility [14,28,29], high potential for self-cleaning [30,31] and, importantly, high antibacterial activity [8,32,33]; TiO_2 is considered one of the most promising antimicrobial

Abbreviations: SS, stainless steel; TiN, titanium nitride; CN_x, carbon nitride; DLC, diamond-like carbon; TiO_2, titanium dioxide; IBAD, ion-beam-assisted deposition; hPDLCs, human periodontal ligament fibroblasts

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materials.

A film of an appropriate material, when applied on SS, can improve the surface properties and preserve the mechanical advantages of SS. However, most studies have focused on a specific characteristic of a single film [4,5,13,17,19], and each material has its own unique traits. Surprisingly, no studies have compared these films and comprehensively evaluated different film materials. Therefore, we designed experiments to compare and evaluate clinically used SS with TiN and CN_x films. TiO_2 films were also prepared and compared in terms of their antimicrobial properties.

2. Material and methods

2.1. Sample preparation

Commercial 304L SS disks (diameter, 20 mm; thickness, 1 mm) were provided by Hangzhou SHINYE Orthodontic Products Co., Ltd. (Hangzhou, China) and used as substrates for film deposition. Each disk was cleaned sequentially in ultrasonic baths containing acetone, ethyl alcohol, and deionized water, for 15 min in each bath, prior to deposition.

CN_x and TiN films were deposited by ion-beam-assisted deposition (IBAD) at the State Key Laboratory of Tribology, Department of Mechanical Engineering, Tsinghua University, Beijing, China. The IBAD system allows precise control of energetic particles by independent adjustment of the beam energy, beam current, and ion flux. Two Kaufman ion sources were used to sputter the targets and another assisting Kaufman ion source was used to bombard the deposited film. Before deposition, 304L SS disks were ultrasonically cleaned in acetone and alcohol and then in deionized water, each for 10 min, and dried with a hair dryer. In order to remove surface adsorbents and activate surface atoms, when the vacuum chamber was pumped to 5.0×10^{-4} Pa, the disks were bombarded for 20 min with an Ar^+ beam from the assisting ion source (beam energy, 800 eV; beam current, 60 mA; and ion flux, 9.6×10^{14} ions $cm^{-2} s^{-1}$).

The CN_x and TiN films were both deposited at room temperature. The base pressure was 4.0×10^{-4} Pa and the working pressure was approximately 1.5×10^{-2} Pa. To deposit the CN_x film, two carbon targets were simultaneously sputtered by an Ar^+ beam from the sputtering ion sources, for 60 min, with a beam energy of 2.5 keV, beam current of 80 mA, and ion flux of 2.4×10^{14} ions $cm^{-2} s^{-1}$. The deposited film was simultaneously bombarded by an N^+ beam with a beam energy of 200 eV, beam current of 30 mA, and ion flux of 4.8×10^{14} $cm^{-2} s^{-1}$, from the assisting ion source. For the TiN film, two Ti targets were simultaneously sputtered by an Ar^+ beam (beam energy, 2.5 keV; beam current, 80 mA; and ion flux, 2.4×10^{14} ions $cm^{-2} s^{-1}$) from the sputtering ion sources, for 60 min. The deposited film was simultaneously bombarded by an N^+ beam (beam energy, 200 eV; beam current, 30 mA; and ion flux, 4.8×10^{14} ions $cm^{-2} s^{-1}$) from the assisting ion source.

The TiO_2 film was prepared via a sol-gel process using spin-coating technology at the School of Materials Science and Engineering, Tsinghua University. The titanium alkoxide solution used for the spin coating contained 2 mL of C_2H_5OH, 350 µL of $C_{12}H_{28}O_4Ti$, and 100 µL of HCl (2 M). After coating the SS disk substrate using a commercial spin-coating apparatus (KW-4A, manufactured by the Institute of Microelectronics, Chinese Academy of Sciences, Beijing, China; spin speed: 3000 rpm, duration: 30 s), it was evaporated at 100 °C in a heater, and then sintered in air at ~500 °C for 30 min.

2.2. Morphology and elemental analysis

To measure the thickness and elemental composition of the film layer, and to observe the bonding between the film and substrate, film samples were cut by wire-cut electrical discharge machining and embedded in acrylic resin. Cross sections were sequentially polished using waterproof abrasive paper and polishing paste. The surface of the disk and its cross-sectional morphology were examined by scanning electron microscopy (SEM; QUANTA 200 FEG; FEI Company, Hillsboro, OR, USA) at 10 kV (for the surface) or 15 kV (for the cross-section). The elements in each layer were identified by energy-dispersive spectroscopy (EDS; FEI Company, Hillsboro, OR, USA). Surface morphological characteristics were measured using a MicroXAM-3D surface profiler (ADE Corp., Westwood, MA, USA).

2.3. Friction testing

A universal micro-tribotester instrument (UMT-5; UMT TriboLab, Bruker Nano Inc., Berlin, Germany) was used to measure the coefficient of friction of each film, using a standard GCr15 steel ball (diameter, 3 mm) as the counterpart (upper) sample. Tests were carried out at 25 ± 1 °C with a normal load of 1.47 N, sliding frequency of 5 Hz, and stroke length of 3 mm, to simulate the conditions of orthodontic treatment [34]. At least two samples were tested in each group. Frictional forces were recorded and the coefficients of friction were compared using Student's *t*-tests.

2.4. Antimicrobial testing

The SS substrate and SS samples coated with CN_x, TiN, and TiO_2 films were compared in antimicrobial tests. *Streptococcus mutans* plays a vital role in the progression of caries [35]; therefore, we used *S. mutans* strains from Peking University Hospital of Stomatology for the adhesion and viability tests. *S. mutans* cells were inoculated into 1.5 mL of brain heart infusion (BHI) broth and incubated for 24 h at 37 °C to obtain a cell density of approximately 1×10^8 mL^{-1}. In preparation for the adhesion tests, 20 µL of the broth that had been cultured overnight was transferred to 180 µL of BHI broth, and the samples were immersed therein; *S. mutans* was incubated with each sample for 2 h. Following this, samples to which the bacteria had adhered were carefully removed and immersed in 10% paraformaldehyde for 30 min to fix the cells. After dehydration through a gradient of ethanol treatments followed by gold spraying, the morphology of the bacterial adhesion was observed by SEM. The mean numbers of bacteria in five randomly selected views at a magnification of $\times 10^4$ were calculated and compared using Student's *t*-tests. At least two samples were used from each test group.

2.5. Biocompatibility testing

The behavior of human periodontal ligament fibroblasts (hPDLCs), provided by Peking University Hospital of Stomatology, on the sample films was evaluated in terms of cell viability/proliferation and cell adhesion. We used Cell Counting Kit-8 (CCK-8; ck04; DOJINDO Laboratories, Kumamoto, Japan) as a cell proliferation assay. The hPDLCs (P7) were seeded onto each test sample at a density of 2×10^6 mL^{-1} and then placed in an incubator under 5% CO_2 at 37 °C for 7 days. Subsequently, the samples underwent CCK-8 treatment at 37 °C for 2 h, following which the optical density (OD) of the culture medium was measured spectrophotometrically at 450 nm; three samples were used from each test group and OD values were compared using Student's *t*-tests.

After incubation, one sample was collected from each group and the adherent cells were fixed in 10% paraformaldehyde for 30 min and dehydrated in a sequential series of 30–100% ethanol. Cell adhesion morphology was observed via SEM.

3. Results and discussion

3.1. Surface morphology, elements, and roughness

The TiN layer appears as a single component with a uniform thickness of approximately 420 nm (Fig. 1(e, g)). However, the high-

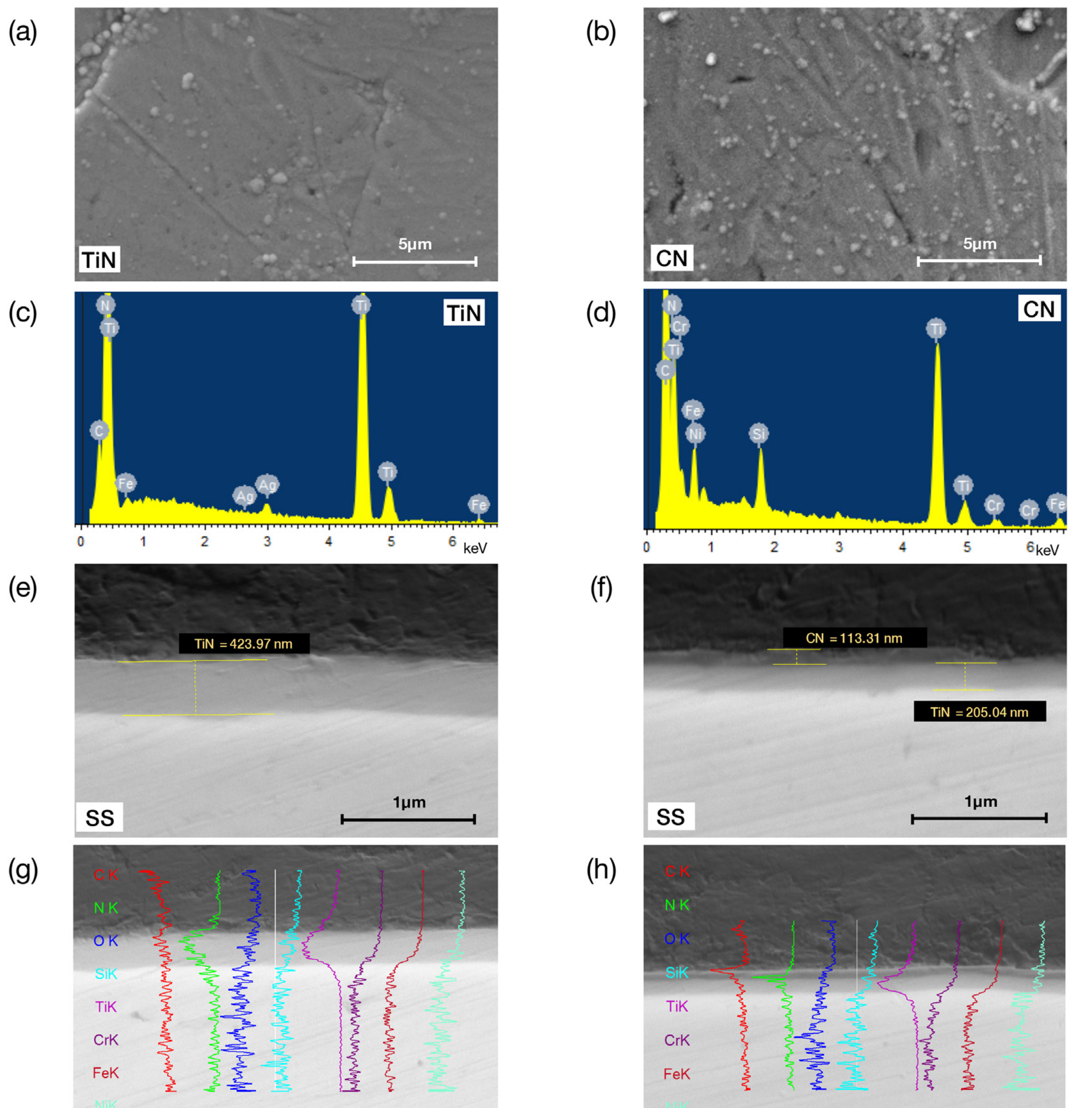


Fig. 1. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) results for titanium nitride (TiN) (a, c, e, g) and carbon nitride (CN_x) (b, d, f, h) coatings. (a, b) Surface morphology of TiN and CN_x coatings, in which cracks, scratches, and sporadic small particles are evident (magnification: 5000×; voltage: 10 kV). (c, d) Coating surfaces consisting mostly of N and Ti (TiN) and N, C, and Ti (CN_x). (e, f) Cross-sectional morphology of single-layer TiN (thickness: 450 nm); the cross-sectional morphology of CN_x includes an inner TiN layer (thickness: 200 nm) and an external coating layer (thickness: 100 nm) so that the total thickness is 300 nm (magnification: 50,000×; voltage: 15 kV). (g, h) Chemical compositions of single-layer TiN and two-layer CN_x coatings.

magnification SEM images show that the surface of the film is not flat or smooth; the film is too thin to smooth the roughness and scratches on the substrate, and occasional small particles are also observed (Fig. 1(a, c)). Due to the manufacturing process and equipment, the CN_x film exhibits two layers: an inner TiN layer of approximately 200 nm and an outer CN_x layer of 100 nm (Fig. 1(f, h)). The TiN interlayer and CN_x upper layer are distinct, and the two-layer structure appears to be dense. Overall, the CN_x film is approximately 300 nm, and its surface is also not flat (Fig. 1(b, d)).

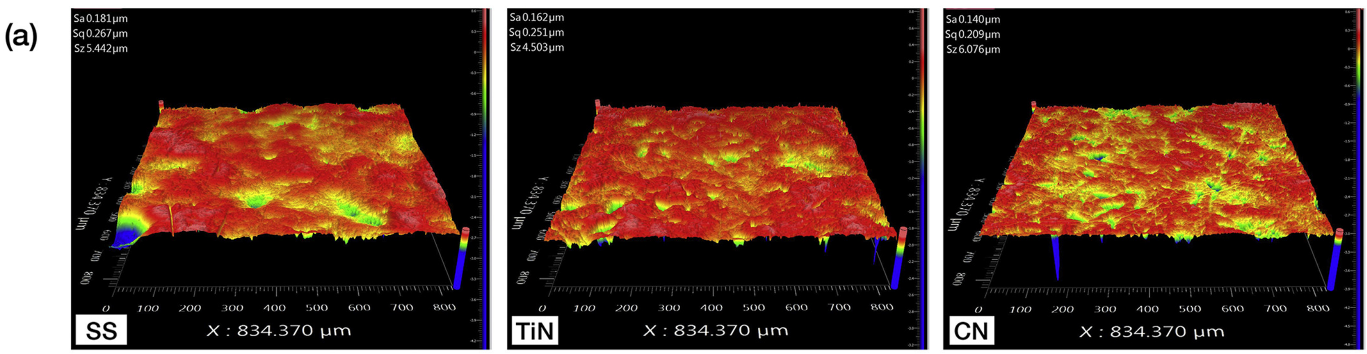
The films slightly reduce the surface roughness parameter (Ra). For the SS substrate, Ra is 0.181 μm, whereas for the CN_x and TiN films, Ra values are 0.140 and 0.162 μm, respectively. Overall, surface quality has improved with the addition of the films (Fig. 2(a)).

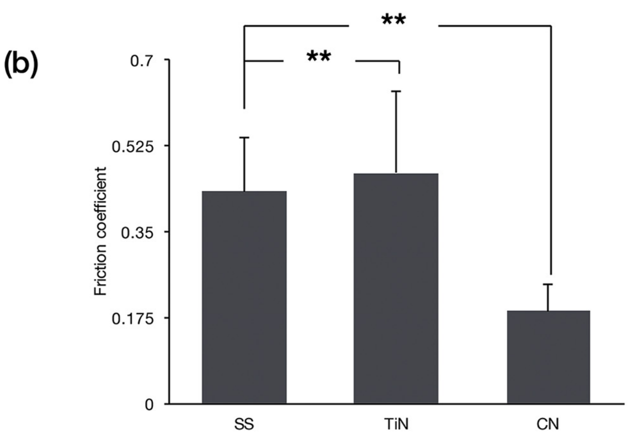
3.2. Tribological properties

The coefficient of friction of the SS substrate is 0.431 ± 0.109; the addition of the TiN film slightly improves the coefficient, to 0.469 ± 0.165 ($P < 0.05$). However, addition of the CN_x film significantly reduces the coefficient to 0.188 ± 0.056 ($P < 0.05$) (Fig. 2(b)).

Friction is a major clinical challenge that must be handled appropriately in orthodontic practice. The orthodontic literature notes numerous variables that affect friction levels at the bracket–archwire interface; these are mainly mechanical factors such as archwire and bracket materials and biological factors such as saliva, plaque, acquired pellicle, corrosion, and food particles [36]. Future studies should investigate the modification conditions, including a proper counterpart material, lubrication condition, and test instrument, in order to reflect clinical conditions.

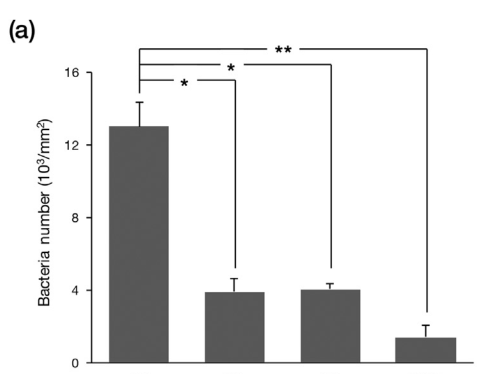
DLC coating is an effective method to reduce frictional forces, as has been well-documented [5]. Recently, CN_x coating has been shown to generate even lower coefficients of friction and wear rates [37,38]. The low friction of CN_x films has been attributed to the formation of a carbonaceous transfer film with low shear strength on the mating surface [39]. The sp^2 C-rich structure of the CN_x film as well as its protection function for the archwire is reported to be responsible for the low friction of the wire-bracket sliding system [12]. Cheng and Zheng





Friction coefficient	SS	TiN	CN
Mean	0.431	0.469	0.188
SD	0.109	0.165	0.056

Fig. 2. (a) Three-dimensional morphology and surface roughness, as measured by the MicroXAM-3D surface profiler, and (b) coefficients of friction for the uncoated stainless steel (SS) sample, and TiN- and CN_x-coated SS samples. TiN-coated SS (CN_x-coated SS) shows a higher (lower) coefficient of friction compared with the uncoated SS sample (both $P < 0.05$).



Bacteria Number ($10^3/mm^2$)	SS	TiN	CN	TiO_2
Mean	13.002	3.888	4.030	1.368
SD	1.304	0.724	0.268	0.691

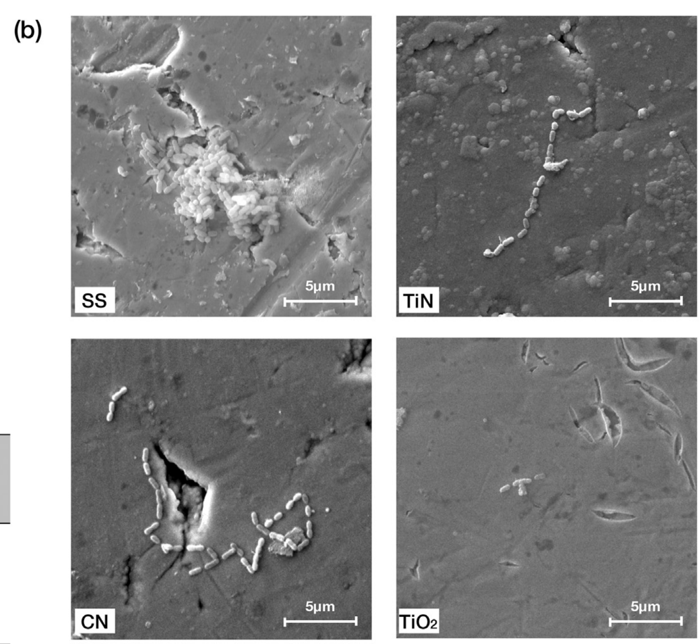
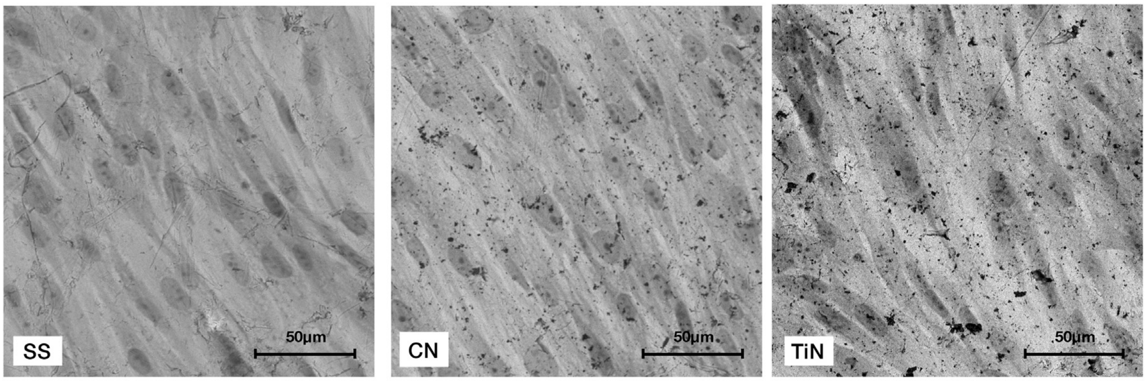
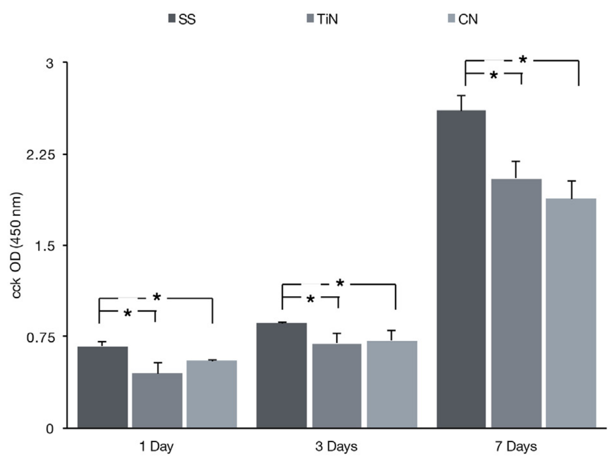


Fig. 3. Attachment of bacteria to uncoated SS, and TiN-, CN_x -, or TiO_2-coated SS. (a) Average number of attached bacteria ($10^3\ mm^{-2}$) on each sample. TiN-coated ($P < 0.05$), CN_x-coated ($P < 0.05$), and TiO_2-coated ($P < 0.01$) SS show fewer attached bacteria compared with the uncoated SS sample. (b) SEM image of *Streptococcus mutans* on the surfaces of the samples following culture for 2 h.

(a)



(b)



cck OD (450 nm)	SS	TiN	CN	TiO_2
1 Day	0.669	0.446	0.550	0.669
3 Days	0.858	0.694	0.717	0.858
7 Days	2.606	2.046	1.884	2.606

Fig. 4. (a) Proliferation and viability of human periodontal ligament fibroblasts (hPDLCs) on test samples over a 7-day period of incubation obtained as the optical density (OD) value after CCK-8 treatment. There is no significant difference between the TiN- and CN_x-coated SS samples; however, all coated samples show OD values lower than those of the uncoated SS sample ($P < 0.05$). (b) SEM images of hPDLCs on the surfaces of each sample after the 7-day culture.

[40] have reported that when TiN compounds are coated onto the surface of NiTi alloys by plasma immersion ion implantation and deposition methods, the coefficient of friction is reduced and the wear resistance of the NiTi alloy is improved. However, reports of TiN application on SS are rare, although some studies have indicated that a specific thickness is vital for effective TiN coating [41,42]. Xiao Huang et al. [43] have reported that the elastic modulus and hardness mismatch between coating and substrate affect the friction and wear properties of a TiN coating system. Our results indicate that at similar thicknesses, a CN_x film reduces the coefficient of friction of an SS substrate, whereas a TiN film increases it. Therefore, a TiN film is not suitable for SS modification to decrease the friction coefficient.

In orthodontic treatment, precise size of the brackets and archwires plays important role [44]. Hence, the thickness of surface modification films should be controlled in order to maintain the precision of the appliance and achieve the required performance. Low-friction appliance materials are favored in orthodontic treatment.

Although both the films we studied were able to reduce the surface roughness, they had opposite effects on the coefficient of friction. The surface roughness, therefore, was not the dominant factor determining the tribological properties of the material. However, in clinical practice, a smoother surface will hinder food particle and bacterial plaque accumulation, thus reducing friction. Therefore, a smoother surface is favorable if biological factors are taken into consideration.

The TiO_2 film has the loosest structure among all the tested coatings. Typical elements of TiO_2 are not detected in the EDS of the cross-sections, but are detected on the coating surface. The average film thickness is ~500 nm. The coating surface is also not smooth or flat, and scratches but no small particles are observed (Supplementary Fig. 1). Note that the TiO_2 film wore out in a few seconds in the friction test, due to which an accurate coefficient could not be recorded (Supplementary Fig. 2), probably because of the weak adhesion between the film and substrate or weak film structure. Considering the demands for clinical applications, a loose structure and weak adhesion are disadvantages of this coating.

3.3. Antibacterial activity

SEM analysis shows large numbers of bacteria adhered to the SS sample surface, at an average density of $13.002 \pm 1.304 \times 10^3\,\text{mm}^{-2}$, whereas fewer bacteria have adhered to samples coated with the film over short timescales. After 2 h, all three film groups show fewer bacteria than SS. TiO_2 exhibits the best antibacterial action against *S. mutans* ($P < 0.01$). The other two films also show fewer bacteria than SS ($P < 0.05$) (Fig. 3).

The antibacterial properties of TiO_2 have been attributed primarily to the surface generation of reactive oxygen species (ROS) and free metal ion formation [45]. Bacterial colonization on a surface is a complex process. In the initial phase, bacteria adhere to the biomaterial substrate and plaque begins to grow. The adhesion of bacterial cells to a surface is determined by the interplay of electrostatic and hydrophobic/hydrophilic interactions, which would be influenced by the structure and chemical bond, such as the transformation of the sp^2/sp^3 ratio [46]. Plaque formation is largely influenced by parameters such as the surface roughness and chemical composition. Rougher surfaces facilitate bacterial colonization and rapid biofilm maturation, whereas smoother surfaces provide a less suitable substrate for bacteria [47]. Both, the CN_x and TiN films, reduce the surface roughness. Coatings with nitrides such as zirconium nitride (ZrN) and titanium nitride (TiN) have attracted attention because they limit bacterial colonization, in comparison with other implant abutment materials used in clinical practice [48,49]. That indicates that the influence of chemical composition also plays a role. A combination of smoothness and chemical modification was responsible for the antibacterial activity of the TiN-coated samples. In DLC, the ratio of sp^3 to sp^2 carbons has been reported to influence bacterial adhesion [46]; a similar mechanism may also occur for CN_x. The antibacterial mechanisms of CN_x and TiN films remain unclear, but our results provide promising avenues for future research.

However, the antibacterial efficiency of CNx and TiN is not as high as that of a traditional antibacterial agent. Nowadays, nanomaterials and organic materials are showing promise. Guanhui Gao et al. [50,51] have provided inspiring ways to modify hybridized nanocomposites with silver nanoparticles, a traditional and impressive antibacterial nanomaterial, to promote their antimicrobial activity and stability. Based on known antimicrobial materials, new nanocomposites should be explored more for clinical applications.

3.4. Biocompatibility

In the biocompatibility test results, the measured OD values represent cell numbers and viability. During the 7-day incubation, hPDLCs proliferate well with almost no difference between the population on the CN_x and TiN-coated SS samples ($P > 0.05$). However, cell viability on the coated samples is lower than that on the SS substrate, for the 7-day incubation ($P < 0.05$). The SEM image illustrates the shape and density of cells on the coated and uncoated samples (Fig. 4(a)). The measured OD values are influenced by material cytotoxicity as well as surface properties. Surface roughness [45] and energy [49] would, to some extent, determine whether a surface is suitable for cell attachment, spreading, or proliferation. Elements released by the coating may not play a dominant role here, because DLC, Ti, and nitride are all reported to be biocompatible [20,27].

4. Conclusions

Although all biofilms have unique characteristics and advantages, an optimal film in terms of all surface properties is required. In this study, we compared the microscopic characteristics as well as the antimicrobial and biocompatibility properties of CN_x and TiN films to identify future directions for developing biofilms. The TiN and CN_x films were plated using IBAD. These films had similar thicknesses in the range of 300–500 nm. Both films reduced the surface roughness of the SS substrate. Overall, the CN_x film had the best surface properties among the tested samples, including a significantly lower and more stable coefficient of friction, effective antimicrobial properties, and biocompatibility with normal human cells. Compared to SS, the TiN film provided a higher frictional force, but better antimicrobial properties, and also showed adequate biocompatibility.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.surfcoat.2019.01.072.

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Conflicts of interest

Mengqi Zhang, Xiaomo Liu, Hongfei Shang, and Jiuxiang Lin declare that they have no conflicts of interest.

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