

A Comparative Study on Mechanical and Adhesion Properties of Calcinated and Non Calcinated Nanobioglass-Titania Nano Composite Coatings on Stainless Steel Substrates

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Abstract. Thick films of calcinated and non calcinated nanobioglass(NBG)-titania nanocomposite coatings were prepared on stainless steel substrates using an alkoxide sol-gel process. The prepared films were characterized by TEM, SEM, EDS, XRD and other methods. The composite films obtained from calcinated NBG particles were compared to the films obtained from non calcinated NBG particles. Here, we present a comparative study on the mechanical and adhesion properties of two types of film (TiO_2 -calcinated NBG and TiO_2 -non calcinated NBG). The prepared thick films were smooth and free of macro cracking, fracture or flaking. The grain size of these films was uniform and its nano scale confirmed using a TEM microscope. Adhesion tests were carried out according to the ASTM-D-3359-97 standard. The results showed that both calcinated and non calcinated NBG-titania films have very good adhesion properties. The hardness of the prepared films (TiO_2 -calcinated NBG and TiO_2 -non calcinated NBG) was compared by using a micro hardness test method. The results verified that the presence of calcinated NBG particles in a NBG-titania composite gradually enhanced the mechanical data of the prepared films.

Keywords: Nano bioglass (NBG); Sol-gel process; Titania sol; Adhesion properties; Composite.

INTRODUCTION

The field of nanocomposite materials has held the attention, imagination, and close scrutiny of scientists and engineers in recent years. This scrutiny results from the simple premise that using building blocks with dimensions in the nanosize range makes it possible to design and create new materials with unprecedented flexibility and with improvement in their physical properties. The concept of enhancing properties and improving the characteristics of materials through the creation of multiple-phase nanocomposites is not recent. The idea has been practiced ever since civilization

started, and humanity began producing more efficient materials for functional purposes [1].

Thin-film nanocomposites are films consisting of more than one phase, in which the dimension of at least one of the phases is in the nanometer range. These nanocomposite films can be categorized as multilayer films in which the phases are separated along the thickness of the film, or granular films in which the different phases are distributed within each plane of the film [2]. Granular nanocomposite films are those that contain both phases (metal and ceramic) in the same layer of the film and have no abrupt interfaces across the film thickness as found in multilayer films. Here, one phase can be in the nanosize range (similar to dispersions), or both phases can have nanocrystalline grains distributed contiguously and laterally in the film [2]. NBG-titania nanocomposite is a kind of granular nanocomposite coating; in this, the matrix phase is a titania and the dispersed phase is nanobioglass nano particles.

Due to their ability to form calcium phosphate (CaP) on their surface, sol-gel derived titania (TiO_2) coatings can be considered as an alternative for the

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more widely used bioactive ceramic-based coatings (hydroxyapatite, bioactive glasses) to ensure implant-bone contact [3]. Although sol-gel derived titania coatings provide interesting features, their potential in biomaterial applications has not been fully exploited. It was recently discovered that in addition to bone contact, sol-gel derived titania coatings facilitate direct soft tissue attachment (i.e. without fibrous capsule formation), making sol-gel derived titania coatings more widely applicable than coatings having only osteoconductive properties [4].

Bioactive glasses have been studied for more than thirty years, since Hench first invented bioglass [5]. Because of their good bioactivity, osteoconductivity and biodegradability [6], bioactive glasses (BG), as bone repair materials, have been used in clinics for more than ten years [7]. In addition, bioactive glass is the only one that can bond to hard and soft tissue [7]. However, due to their poor mechanical properties, these glasses cannot be used in load-bearing applications. Sol-gel derived titania and silica [8] has been shown to be bioactive. The use of mixed silica–titania films as implant coatings has not been extensively studied [8].

The aim of this study is to prepare a composite film constituted of a titania matrix with nanobioglass particles by the sol-gel process. Here, we have a comparative study on the mechanical and adhesion properties of two types of film, TiO_2 -calcinated NBG and TiO_2 -non calcinated NBG.

EXPERIMENTAL

Materials

The starting materials used in this preparation were analytical grade Tetraethyl orthosilicate (TEOS, Merck), Triethyl phosphate (TEP, Merck), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck), ammonia (Merk), nitric acid (Merck), commercial extra pure titanium isopropoxide (TTIP, Merk), isopropanol (iPrOH, Merck), and Diethanolamine (DEA, Merck). All materials were used as received without further purification.

Preparation of Nano-Bioactive-Glasses (NBG)

NBG was prepared by an alkali-mediated sol-gel method. In a typical preparation of nano-bioactive 58S glass [9] (SiO_2 : CaO : P_2O_5 =58:23:9, weight ratio), TEOS (21.6 ml), distilled water (13.9 ml) and 2 M HNO_3 (2.8 ml) are dissolved in ethanol (50 ml) and stirred at room temperature for 30 min. TEP (2.2 ml) is then dissolved into the prepared acid silica sol. After stirring for 20 min, the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (14.04 g) is added into the acid sol. A certain concentration (2.0 mol/l) of ammonia solution (10 ml) is dropped into the acid sol while vigorously stirring after the

Table 1. The bioactive glass composition (weight ratio, %).

	SiO_2	CaO	P_2O_5	Impurity
Design	58	33	9	0.07
Experiment	58.39	34.5	6.5	

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is completely dissolved. The sol swiftly gelled. The obtained gel was stirred using a magnet in order to avoid forming bulk gel and, then, the resulting gel was kept in the oven at 60°C for 1 day to remove the residual water and ethanol. The dry gel powders were calcinated at 600°C in air for 2 h. The heating rate of calcinations was fixed at $3^\circ\text{C}/\text{min}$. The glass composition was analyzed by an x-ray fluorescence method (PW2404, PHILIPS). The analysis result (Table 1) showed that the composition of obtained glass was almost consistent with the designed composition.

Preparation of Titania Sol

A 0.5 M solution of TTIP (7.5 ml) in iPrOH (47.9 ml) was prepared and, subsequently, a suitable amount of DEA (9.15 ml) was added to the solution. A molar ratio of $\text{DEA}/\text{TTIP} = 4$ was used. The solution was stirred at room temperature for 2 h. Subsequently, water (0.86 gr) was added, drop by drop, under vigorous stirring. A molar ratio of $\text{H}_2\text{O}/\text{TTIP}=2$ was used. A clear sol was obtained. This sol was stable at room temperature and no changes were observed, even after storage for many months.

Preparation of Nanostructured Bioactive Glass/Titania Composite Coating

The nanostructured bioactive glass/titania composite was prepared by addition of 70 grams/liter of calcinated and non-calcinated NBG powders. The powder was added slowly with vigorous stirring (at 50°C for 3 h) to prevent the formation of agglomerates. A thick, white, viscous solution was obtained. This solution settled slowly over a period of two weeks. To prevent settling, the modified sol was stirred constantly while in storage between experiments. The stainless steel substrates 316 L (with 15 mm diameter) to be coated were cleaned with ethanol and then washed ultrasonically in distilled water. This cycle was repeated 5 times and then the substrates were dried at 125°C for 4 h. Two stainless steel disks of 15 mm diameter were placed in two beakers. The beakers with the stainless steel were filled with the composite sol (one with calcinated NBG powder and the other with non-calcinated NBG) and allowed to stand for ten minutes. Subsequently, the sol was drained; the beakers were dried in air at room temperature for 24 h and then heat-treated. After

heat treatment and cooling, the disks were removed and put back in the beaker prior to coating again. Heat treatment for all samples was done using a multi-segment programmable furnace (Exciton 1500). The furnace temperature was increased at a ramp rate of 3°C per minute until it reached 100°C and was held at 100°C for 1 h. Subsequently, the temperature was increased at a ramp rate of 3°C to 600°C and held for 1 h. Finally, the furnace was allowed to cool down naturally to room temperature. The cooling down period took approximately 12 h.

Characterization of Nano-Composite Coating

The microstructure of NBG powder was investigated using a Hitachi600 transmission electron microscope. A scanning electron microscope (Phillips XL 30) was used to determine the thickness and morphology of nanostructure composite films on substrates. The same instrument was also used to perform electron diffraction spectroscopy (EDS) quantitative analysis of nanostructure composite films. The prepared films were characterized by a Philips X'pert MPD diffractometer, using Cu K α generated at 40 kV and 40 mA. The samples were scanned from 10° to 90° with a step size of 0.02° and a count rate of 3.0°/min.

Microhardness and Adhesion Tests

The hardness of the films obtained by 2 dip coating/heat treatment cycles was determined with a Vickers microhardness measuring device (FischerScope HM2000 S), as described in DIN-EN-ISO-14577. The reported values are averages of 10 measurements performed at different locations in the center section of each sample. The thickness of all coatings is more than ten times the maximum indentation depth of 1 μ m, in order to reduce the effects of the substrates.

The adherence of the TiO₂-NBG calcinated and non calcinated films was tested using the tape stripping method (ASTM-D3359-02). The most prevalent test for evaluating coating “adhesion” is the tape-and-peel test, which has been used since the 1930's. In its simplest version, a piece of adhesive tape is pressed against the deposited film and the resistance and degree of film removal are observed when the tape is pulled off. Since an intact film with appreciable adhesion is frequently not removed at all, the severity of the test is usually enhanced by cutting a figure X or a cross hatched pattern into the film before applying and removing the tape. Adhesion is then rated by comparing film removed against an established rating scale. If an intact film is peeled cleanly by the tape, or if it debonds just by cutting into it without applying tape, then, the adhesion is rated simply as poor or very poor.

An X-cut is made through the film to the substrate; a pressure-sensitive tape is applied over the cut, removed, and the adhesion is assessed qualitatively on the 0 to 5 scale. In this study, extra strength transparent scotch tape strips were pressed to a 9 cm×22 cm stainless steel substrate coated with TiO₂-NBG films. The tape was allowed to remain for 10 minutes and then pulled off both slowly and quickly. The X-cut area was inspected for removal of coating from the substrate or previous coating and the adhesion was rated in accordance with the following scale:

- 5A: No peeling or removal,
- 4A: Trace peeling or removal along incisions or at their intersection,
- 3A: Jagged removal along incisions up to 1.6 mm (1/16 in.) on either side,
- 2A: Jagged removal along most incisions up to 3.2 mm (1/8 in.) on either side,
- 1A: Removal from most of the area of the X under the tape, and
- 0A: Removal beyond the area of the X.

RESULTS AND DISCUSSION

NBG Powder Characterization

TEM images revealed that the NBG particles are sphere-shape with uniform morphology. The particles have an average size of approximately 50–60 nm, which is suitable for cell attachment (Figure 1) [10]. According to the literature, the cell responses enhance in the presence of ceramic nanoparticles of less than 100 nm in diameter [10]. The enhanced cell response

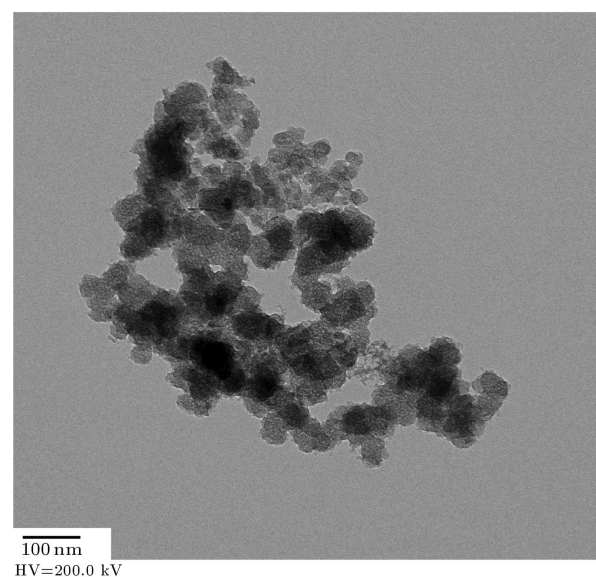


Figure 1. TEM image of NBG powders.

may result from the prerequisite protein adsorption, which is also influenced by the nanodimensions [10]. The TEM Energy Dispersive Spectroscopy (EDS) of calcinated NBG powders showed the presence of Ca and Si and O in the samples. The Cu signal is from the TEM grid. The XRD study confirmed that the calcinated and non calcinated glass generally existed in an amorphous state, as no diffraction peaks could be observed except a broad band between 15° and 40° (2θ) (Figure 2).

NANO COMPOSITE CHARACTERIZATION

Figure 3 shows the XRD patterns of NBG-titania films. Diffractograms confirm the formation of an anatase phase in both calcinated and non calcinated NBG-titania films on stainless steel substrates. They also indicate that as the number of coatings increase the amount of anatase increases, as is evident from the peaks. Titania exists mainly in three polymorphs: rutile, anatase and brookite. Rutile is considered the stable form of titania. Anatase is metastable and converts to rutile at high temperatures accompanying grain growth. It has been suggested that titania has different properties depending on its micro-structure. Compared to rutile titania, anatase titania has unique properties and advantages for medical applications. Anatase exhibits stronger interactions with metal compared to rutile, and the surface of anatase titania can absorb more OH^- and PO_4^{3-} than that of rutile

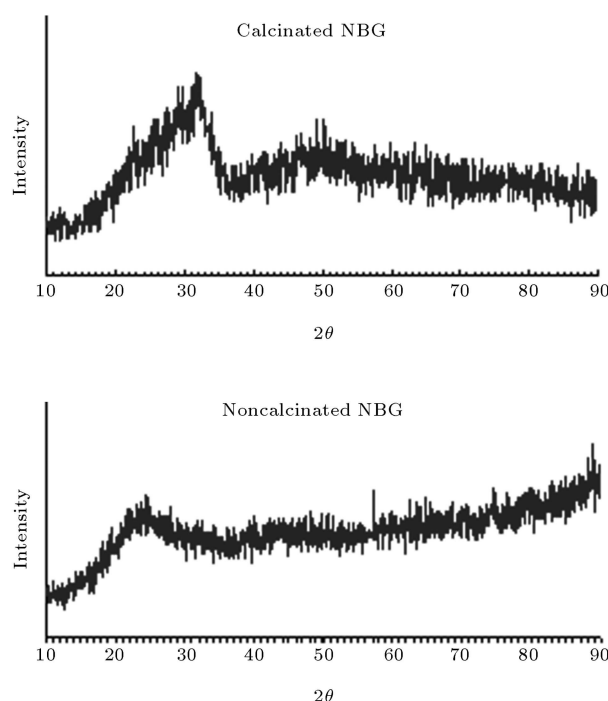


Figure 2. WAXRD pattern of calcinated and non calcinated NBG particles, heat treated at 600°C in air.

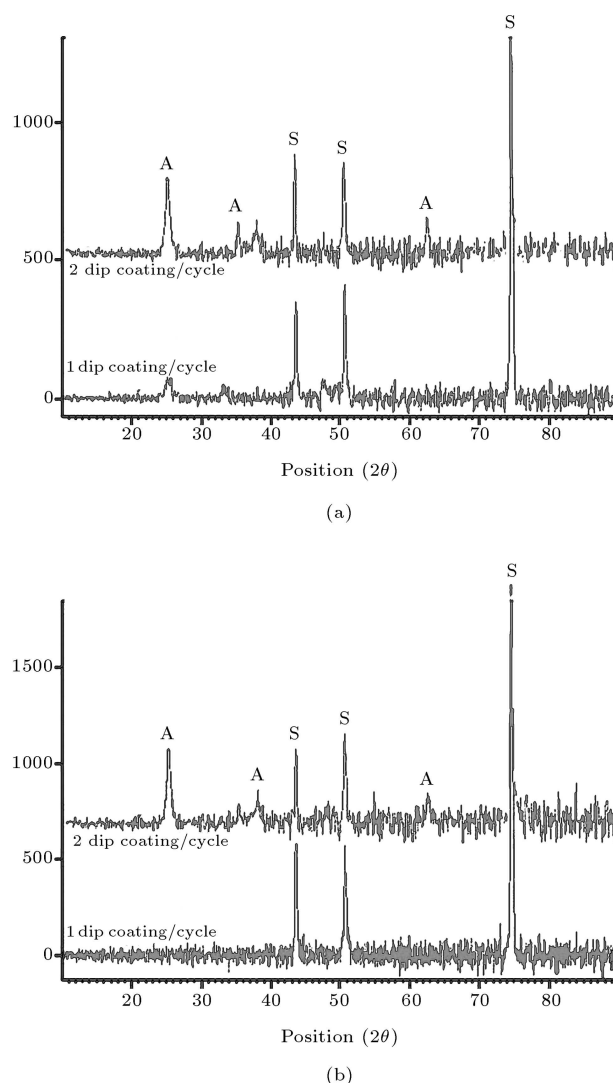


Figure 3. X-ray diffractogram for stainless steel substrates coated 2 times with (a) calcinated NBG-titania nanocomposite sol, and (b) non calcinated NBG-titania nanocomposite sol, heat treated at 600°C (A: anatase, S: substrate).

titania in body fluid, which is in favor of depositing a bone-like apatite [11].

SEM morphologies of prepared films coated on stainless steel substrate are shown in Figure 4. The morphology appears rough and homogeneous with some submicron pores and cracks due to small residual compressive stresses [12]. The extent and frequency of the micro cracks increases with the number of dip coating/heat treatment cycles. These stresses are caused by chemical reactions during drying, and also the difference in thermal expansion coefficients between the substrate and the TiO_2 films. When crystallization occurs, large compressive stresses are generated [13]. When grain growth and densification of the film occurs the stresses are reduced [13]. The densification that accompanies grain formation is directly proportional

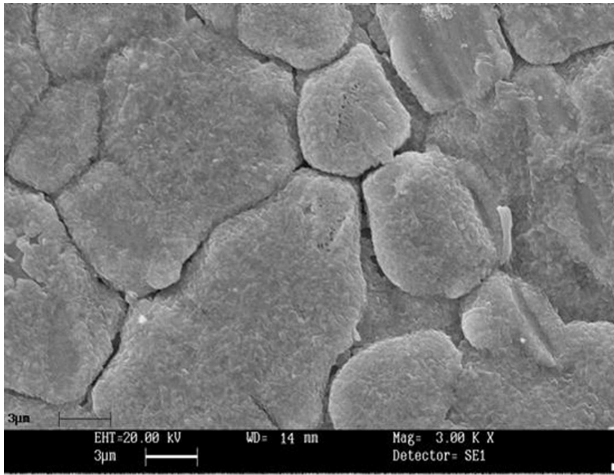


Figure 4. SEM micrograph of stainless steel coated with NBG-titania sol after 2 dip coating/heat treatment cycles at 600°C.

to grain size [13]. Since the nanobioglass particles provide an initial grain growth site (≈ 30 nm), growth takes place fairly quickly and, consequently, compressive stresses are reduced quickly. Also, the stainless steel substrate has a higher coefficient ($17 \times 10^{-6} \text{ }^\circ\text{C}$) of linear thermal expansion than the TiO_2 films ($2.1 - -2.8 \times 10^{-6} \text{ }^\circ\text{C}$) [13]. On cooling, the stainless steel substrate shrinks more than the TiO_2 films, leading to further reduction of compressive stresses, and these reduced compressive stresses lead to the formation of small micro cracks.

Hardness and Adhesion Tests

Table 2 presents the Vickers hardness values of NBG-titania films. The average value of 10 measurements at different places on the films was recorded (Figure 5). Figure 6 clearly indicates that calcinated NBG-titania films have a higher hardness than non calcinated NBG-titania films, due to the dense structure and morphology of calcinated NBG-titania films. On the same grounds, it can be assumed that increasing the bond strength of the ionic link in calcinated NBG particles would be expected to strengthen the glass structure and, consequently, increase the Vicker's hardness [14]. It is obvious that the mechanical properties of sol-gel derived bioglass 58S are enhanced by the high hardness and strength of the titania matrix.

Table 2. Vickers micro hardness test results for TiO_2 -NBG films.

Sample	Vickers Hardness Numbers	Load (gr)
TiO_2 -Calcinated NBG film	358.7	15.15
TiO_2 -Non calcinated NBG film	291.5	15.15

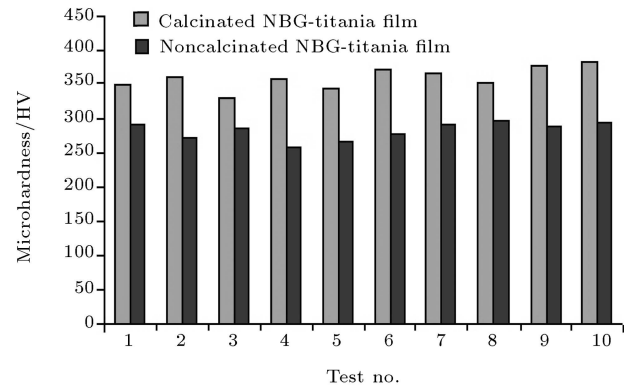


Figure 5. Microhardness/HV investigations at different places on the NBG-titania films.

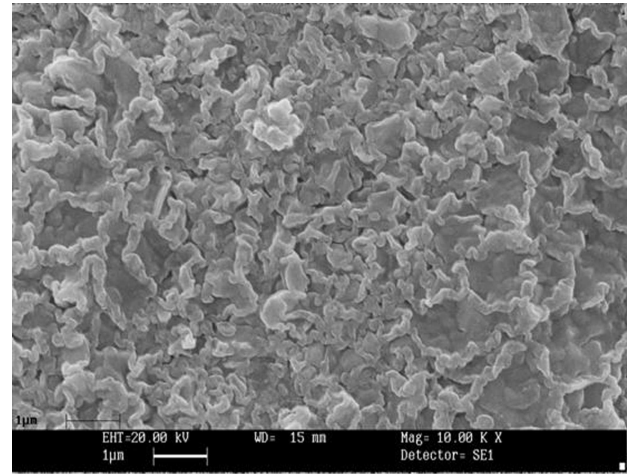


Figure 6. Dense structure and morphology of calcinated NBG-titania films.

Adhesion test experiments using the tape stripping method confirmed that even after 10 applications and removal from the NBG-titania coated samples, no TiO_2 -NBG was observed on any of the strips, nor was the film surface visibly disturbed in any way (degree of film removal: 5A). When a flexible adhesive tape is applied to a coated rigid substrate surface and then removed, the removal process has been described in terms of the “peel phenomenon,” as illustrated in Figure 7. Peeling begins at the “toothed” leading edge (at the right) and proceeds along the coating adhesive/interface or the coating/substrate interface, depending on the relative bond strengths. It is assumed that coating removal occurs when the tensile force generated along the latter interface, which is a function of the rheological properties of the backing and adhesive layer materials, is greater than the bond strength at the coating-substrate interface (or cohesive strength of the coating). In actuality, however, this force is distributed over a discrete distance ((O-A) in Figure 7), which relates directly to the properties described, not concentrated at point (O) in Figure 7, as in the

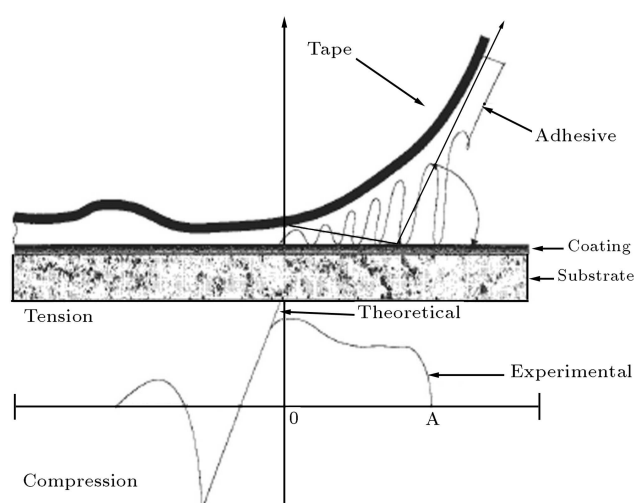


Figure 7. Peel profile according to ASTM D 3359-2 standard.

theoretical case, though the tensile force is greatest at the origin for both. A significant compressive force arises from the response of the tape backing material to being stretched. Thus, both tensile and compressive forces are involved in adhesion tape testing. The absence of any flaking off suggests that the film obtained from both calcinated and non calcinated NBG particles firmly bonded to the substrate and cannot be easily removed.

CONCLUSION

In this research, novel NBG-titania composite films were successfully prepared on 316L disks using a sol-gel route. The major findings of this study are presented below:

- The micro hardness tests indicated that calcinated NBG-titania films have a greater hardness than non calcinated NBG-titania films.
- The tape stripping method results indicate that both calcinated and non calcinated NBG particles firmly bonded to the substrate and cannot be easily removed.

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