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Original Research

Novel and simplified functional grading technique with two different nanoparticles on three-unit zirconia prostheses: An In-vitro study

[1]Aditi Kanitkar, [2]Paresh V. Gandhi, [3]Ajay V. Sabane, [4]Aneesh.S. Kanitkar, [5]Vijaysingh More, [6]Rajashree Jadhav

[1]Assistant Professor, [2,5,6]Professor, [3]Professor and HOD, Department of Prosthodontics and Crown and Bridge, Bharati Vidyapeeth Dental College and Hospital, Sangli, Maharashtra, India;
[4]Associate Professor, Department of Prosthodontics and Crown and Bridge, Yogita Dental College, Khed, Maharashtra, India

ABSTRACT:
Aim: To evaluate functional grading technique to incorporate two different nanoparticles in three-unit fixed dental prostheses. **Setting and Design:** In -vitro intervention study. **Material and Methods:** Thirty-two three-unit monolithic zirconia prostheses (n=32) were machined and randomly assigned to four groups, each with similar specimens (n=8). All the four groups namely control (A)- without any nanoparticle, B- titania sol, C- silica sol, D- silica and titania nano sol. Grading with nanoparticles was carried out on pre-sintered monolithic zirconia and then were sintered. Evaluation of nanoparticles were seen under field emission scanning electron microscope (FE-SEM). Energy dispersive spectroscopy (EDS) was done to find an elemental composition of nanoparticles in zirconia. **Results:** Based on Scanning electron microscopy all the prosthesis after sintering showed the presence of nanoparticles. Energy dispersive spectroscopy (EDS) showed the elemental composition of nanoparticles in monolithic zirconia prostheses. **Conclusion:** Functional grading of monolithic zirconia with silica and titanium dioxide nanoparticles where the material composition is spatially varied to meet the performance demands of the fixed prostheses with non-ideal abutments.

Keywords: Nanotechnology, Titanium dioxide nanoparticle, silica nanoparticle, three-unit monolithic zirconia prostheses.

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Corresponding author: Aditi Kanitkar, Assistant Professor, Department of Prosthodontics and Crown and Bridge, Bharati Vidyapeeth Dental College and Hospital, Sangli, Maharashtra, India

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INTRODUCTION

Zirconia-based all-ceramic dental restorations have become more and more imperative, due to their outstanding biocompatibility and favourable aesthetics. The recent incorporation of monolithic zirconia into dentistry has amplified the spectrum of indications of fixed dental prostheses (FDPs) to eradicate the problem of chipping of porcelain in bilayered zirconia-based restorations[1,2] The monolithic zirconia restorations are used to eliminate veneer chipping in bilayered zirconia.[3] Tetragonal polycrystalline zirconia doped with 3mol% (3Y-TZP) is the dental material[4,5] of choice due to excellent biocompatibility and mechanical properties. Its construction was also quicker because the additional step of veneering was not necessary.

The focused problemsof monolithic zirconia are low-temperature degradation. [6,7] LTD and slow crack growth in the presence of water.[8,9,10]LTD is spontaneous formation of monoclinic phase at the surface in a nucleation. As the moisture fills oxygen vacancies flaws in the zirconia progress into the bulk of the material and affects mechanical properties as it involves the zirconia grains. [11,12,13,14] Fatigue fractures due to ageing occur when the inner stress surpasses the tensile strength of the material at that temperature. [15,16] Repeated thermal stressing and chewing forces facilitate subcritical crack growth in zirconia ceramics. This may cause an excessive transformation from tetragonal to monoclinic.[17] This may be one of the factors contributing to clinical failures, despite the high mechanical properties of zirconia-based restorations, especially adjoining to the pontic of fixed dental prostheses.

Compressive layers protect and strengthen the surface, preventing microcracks from forming. Different methods have been reported in the literature to create compressive layers. Mechanical pre-treatment methods [18] have been proposed in literature which includes airborne particle abrasion. After the mechanical pre-treatment method with air abrasion, flaws may develop deeper than the compressive layer [19] affecting the surface integrity of the zirconia. Another way of introducing a compressive layer is the 'Functional grading technique'. Functionally graded materials [20] (FGM), which has an innovative property of exhibiting variation in material properties showing improved resistance to contact, flexural strength, and fatigue damage of graded ceramic relative to their ungraded structures. Functionally graded zirconium with Glass/silica infiltration [21] prevents water entry into the grain contours and reduces low-temperature degradation. The surface of graded zirconium has a better stress distribution [22] and good flexural strength. Functional grading with silica infiltration [23] promotes bonding between zirconia and resin cement without affecting its mechanical properties due to structural homogeneity and wettability of the material. A glass/zirconia multilayer formed by the sol-gel method of grading imparts greater load-bearing capacity [24] than an ungraded surface.

In recent years, sol-gel derived titania (TiO_2) [25] coatings have been shown to enhance the bioactivity of zirconia surfaces. Micrometre-scale particles have been reduced to nano meter-scale particles for a broad range of applications in different materials. The presence of nanostructures may improve the interaction between resin cement and zirconia ceramics at the adhesive interface. Dos Santos [26] reported that titania nanotubes can be incorporated on the zirconia surface. A variety of zirconia surface treatments have been described to enhance bond strength. Studies reported in literature [27] are devoid of any apprises about the investigation of fracture resistance of silica and titanium dioxide nanoparticles graded monolithic zirconia. Mezarina-Kanashiro[28] evaluated the shear bond strength of resin cement to zirconia after different methods of titanium dioxide nanotubes incorporation. Thus, titanium dioxide nanotubes incorporation improved bond strength without the need for sandblasting. There is a dearth of literature available on the functionally graded monolithic zirconia with titanium dioxide and silica Nanoparticles. This highlights the importance and the necessity of conducting more research in this field.

The Objectives of this study were 1. To accomplish functional grading with silica and titanium dioxide nanoparticles in monolithic zirconia (3Y-TZP). 2. To evaluate different nanoparticles in monolithic zirconia(3Y-TZP) three-unit fixed dental prosthesis under Field emission Scanning electron microscopy.

This is an experimental in vitro comparative study. The present study was approved by an institutional review board. IRB number BVDU/DCH/404/2021. The sample size was estimated using "G power" software Version 3.1.9.2 (Heinrich Heine University, Dusseldorf, Germany). ES = Effect size was calculated from the reference article- Villefort RG[23] et al, considering the mean and standard deviation values of the fatigue limit of the two groups – GZG, and SSG, which was found to be 2.06. Confidence intervals 99% and power 90%.ES = m1 - m2 / SDp

SEQUENCE OF EXPERIMENTAL PROCEDURES

Thirty-two mandibular three unit Fixed dental prostheses (FDPs) were fabricated. Prostheses were randomly assigned to four groups each group with equal specimens(n=8). All four groups except the control group were graded with silica and titanium nanoparticles as shown in Figure 1.

Preparation of Nano sol for functional grading: (a)Titania Nano-sol synthesis [29]: Solution A: A homogenous solution was made using 0.5 wt % titania dioxide nanoparticles of size 50 to 80 nm (ISO 9001:2015 NRL research lab, Jharkhand India) mixed in 95% ethanol. Solution B: ultrapure water, ethanol, and nitric acid were mixed. This solution was then added to solution A with constant stirring drop by drop and the resultant solution was stirred vigorously and was left to age at room temperature for 24 hours. The entire process of synthesis was carried out at ambient atmospheric pressure. (b)Silica Nano-sol synthesis: Silica sol prepared according to Campos et al [22]. The silicic sol was obtained by adding sodium metasilicate (Na2SiO3·5H2O) aqueous solution (10% m/m) to 0.5 wt% silica nanoparticles (NRL research lab, Jharkhand India).

Manufacturing of tooth analogues: The patient's cast was selected to simulate oral anatomy. Tooth preparation was done on the selected cast on the surveyor and scanned by 4-axis optical scanner (Meditidentica blue, Seoul, Korea). Thirty-two composite tooth analogues were designed on exocad software (exocad GMBH, Darmstadt, Germany) and milled with Ruthenium (Ruthenium dental products Pvt ltd., new Delhi, India) to simulate three-unit FPD with the second premolar and the second molar as the abutment teeth and mandibular left first molar as pontic as depicted in Figure 1.

Figure.1 -Study design
a) Preparation Nano sol of Tio2 and silica from nanoparticles.
b) Tooth analog to receive monolithic three-unit fixed prosthesis
c)Designing and milling of three-unit fixed prostheses
d)Grading of zirconia prostheses with Nano sol
e) Sintering of fixed prostheses
f) Evaluation of nanoparticles under scanning electron microscopy

MANUFACTURING OF MONOLITHIC ZIRCONIA PROSTHESIS

The three-unit tooth analogues were scanned (Meditidentica blue, Seoul, Korea) and the monolithic zirconia ceramic prostheses were designed. Design parameters for anatomically shaped monolithic zirconia were: 1 mm breadth of material and space for luting agent of 25 µm, optimum connector dimensions [30] as 3x3 mm^2. A total of Thirty-two identical three-unit prostheses were milled from (3Y-TZP) monolithic zirconia blanks of 12 mm thickness (Ivoclarzenostar, Ivoclarvivadent AG, Liechtenstein, Germany) in full-contour design using a milling unit (Zenotec mini, Ivoclar Vivadent, Germany) equipped with rotary tools.

Functional grading technique: To incorporate silica and titania sol in a pre-sintered monolithic zirconia prosthesis ‘The Brush infiltration method’ [31]was used to carry out functional grading[32,33]of monolithic crowns at the pre-sintered stage. The brush was directed from the mesial to the distal surface of the prosthesis twice with a brush (CAMELIN no.9). Group B and Group D specimens were graded twice with nano titania sol using a thick brush. Group C and Group D samples were graded twice with a brush with silica sol prepared at (The national chemical laboratory, Pune). Nano-sol of titanium dioxide was applied first and then nano silica-sol was applied for group D.

SINTERING PROTOCOL

As the grading with titania and silica sol was completed, all the thirty-two prostheses were sintered at 1450^0c as per manufacturers instruction in a sintering furnace. After that, the margins were manually adjusted with a dental micromotor (MARATHON3, SAEYENG MICROTEK, KOREA).

MICROSTRUCTURAL ANALYSIS

Prostheses of monolithic zirconia were fixed with carbon tape and a portion of their surface was coated with gold sputtering (Emitech gold sputter) to provide surface conductivity. SEM images made from the surface at different magnifications with QUANTA 200(Hillsboro, Oregon, USA). The grain size of the nanoparticle was estimated from ‘Field emission scanning electron microscopy’ (FE-SEM) images made from FEI NOVA NANOSEM 450(Hillsboro, Oregon, USA) under a high vacuum with 20.00 kV.

RESULTS

Microstructural analysis: Based on Scanning electron microscopy all the prostheses after sintering showed the presence of nanoparticles. Energy dispersive spectroscopy (EDS) showed the elemental composition of nanoparticles in monolithic zirconia prostheses.Figure 2 depicts SEM examinations of occlusal surfaces of the representative specimens of each group. Field Emission scanning micrographs (FE-SEM) at 80,000x magnification showed the presence of nanoparticles.

Figure.2 - Representative scanning electron micrographs of the fractured surfaces of Group A, Group B, Group C, Group D.

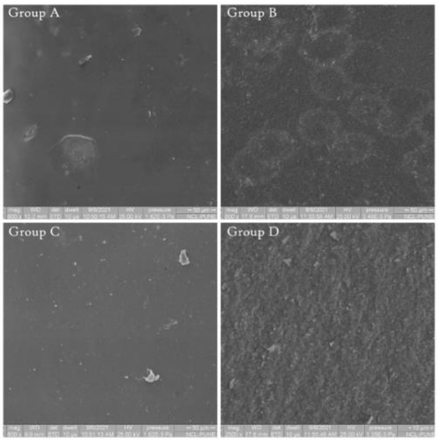


Figure 3 displays the average particle size of 69.56nm of the titanium dioxide and silica nanoparticles infiltrated in monolithic zirconia of Group D at different magnification.

Figure.3- FE- SEM photographs with average nanoparticle size

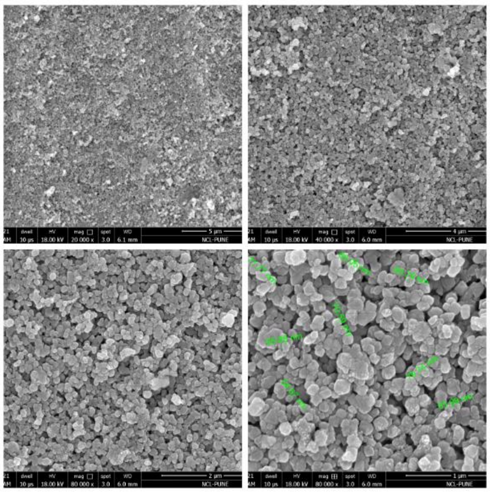
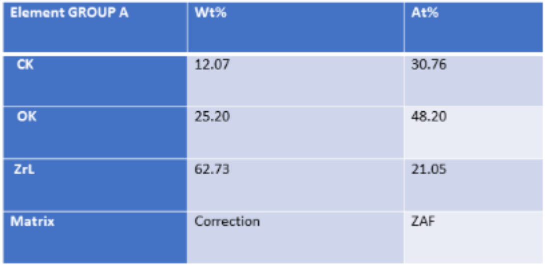


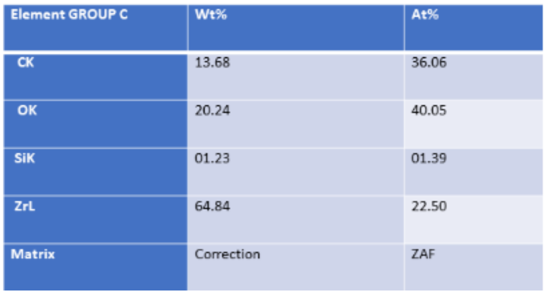
Figure 4 analyses the elemental composition of the prosthesis, scanning electron microscopy (SEM) was supplemented with energy–dispersive X-ray spectroscopy (SEM-EDS).

Figure.4 - EDS analysis of occlusal surfaces after fracture resistance testing of all groups

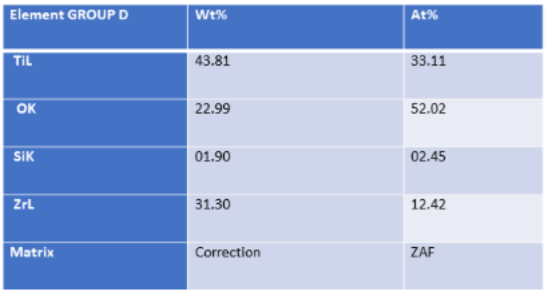


Element GROUP A	Wt%	At%
CK	12.07	30.76
OK	25.20	48.20
ZrL	62.73	21.05
Matrix	Correction	ZAF

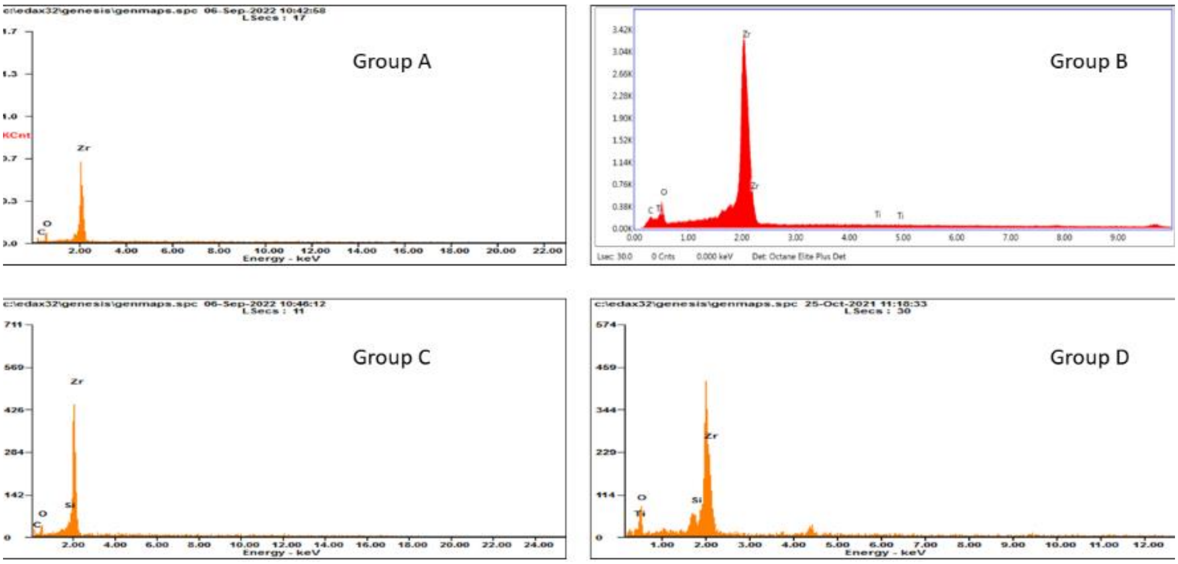
Element GROUP B	Wt%	At%
C K	6.61	18.26
O K	27.88	57.82
ZrL	65.23	23.72
TiK	0.28	0.19
Matrix	Correction	ZAF



Element GROUP C	Wt%	At%
CK	13.68	36.06
OK	20.24	40.05
SiK	01.23	01.39
ZrL	64.84	22.50
Matrix	Correction	ZAF



Element GROUP D	Wt%	At%
TiL	43.81	33.11
OK	22.99	52.02
SiK	01.90	02.45
ZrL	31.30	12.42
Matrix	Correction	ZAF



DISCUSSION

Zirconia is a chemically inert, non-etchable polycrystalline material. [34] Low temperature degradation[35] or ageing results in undesirable transformation, microcracking, grain pull-out, and loss of strength.The kinetics of degradation depends on the exact parameter of the hydrothermal environment (temperature, humidity, and pressure) and on the exact material characteristics (grain size, amount of yttria, porosity and surface residual stresses). Various surface pre-treatments[36,37,38] were carried out to reduce surface degradation. Zirconia ceramics are known to exhibit the 'Transformation toughening mechanism' and can be toughened during grinding, machining [39,40] and ageing. The transformation toughening mechanism cannot enhance the strength for all applications, especially when there is excessive transformation due to presence of water. The functional grading technique makes the zirconia impervious to the surface flaws by incorporating compressive stresses[41]. Functionally graded zirconia may lower the risk of fatigue failure. This belief is supported by the findings of former studies.[42,43,44]

Nanotechnology deals with objects of nanometer-sized particles. Nanoparticles are different from macro-sized particles. Nanoparticles differ in their physical, chemical and biological properties due to their high surface-to-volume ratio. In addition to having a high elastic modulus and titanium oxide nanoparticles [45] are inexpensive nontoxic semiconductors with melting temperatures of approximately 1870° C. Titanium dioxide has been used to improve the fracture resistance of endodontically treated teeth. [46] Incorporation of nanoparticles in pre-sintered zirconia is possible as the zirconia has a porous structure. In a few studies, it was observed that the addition of titania to zirconia decreases the ultimate mechanical property. [47,48] Most of the studies [49,50] on the graded zirconia\titania\silica were executed for improving the bond strength of the prosthesis or to increase the bioactivity of zirconia implant.Based on the literature reviewed, the present study was amongst the first few studies that proposed to use innovative functional grading technique to incorporate nanoparticles on three-unit graded monolithic zirconia prosthesis.

Titania coatings on zirconia substrates have been previously shown to be effective at attaching soft tissues. [51,52,53] Different methodologies have been reported in the literature for infiltrating titania to monolithic zirconia. One way of infiltrating titania is by the sol–gel route. [49] Another route is mixing commercial powders of zirconia and titania. The sol-gel technique has several steps and is thus time-consuming but it results in more homogeneous materials. On the contrary, mixing commercial powders could alter the mechanical properties present in the already existing material. This was based on the pretext that the zirconia material which already has a reputation for exhibiting good mechanical properties need not be modified. Nano sol was used in the present study to functionally grade the monolithic zirconia with nanoparticles in a pre-sintered stage. Thus, incorporating nanoparticles in a pre-sintered stage is an effective technique which can be carried out during routine CAD\CAM processing laboratory when compared to different methodologies mentioned in the literature.

Also, the nano sol-gel titania coating developed in our study forms a transparent coating on the zirconia specimen. The new graded material disclosed no perceptible colour differences when compared to non-graded monolithic zirconia. The grading on zirconia prosthesis is by brush which is a less technique-sensitive method than the dip coating processing method which has several steps. Nano titania and silica sol application on the monolithic pre-sintered fixed partial denture helps maintain a homogeneous layer compared to titania nanotubes [26] on zirconia.

The presence of titanium dioxide and silica nanoparticles under the 'Field Emission - scanning electron microscope' (FE-SEM) (Fig. 3) and Energy dispersive spectroscopy (EDS) of the occlusal surface of the prosthesis supports the findings of the present study. The addition of nano-sized ductile particles to oxide ceramics reduces subcritical crack growth by deflecting the crack and aids in crack bridging.This may improve fracture resistance can be attributed to the same and findings are supported by previous studies. [54,55,56] Zirconium titanate formed in the present study could withstand mechanical loads that allow force transmission and prevents crack propagation into the underlying substrate. Sintering of milled zirconia prosthesis facilitates attraction between particles which reduces porosity and densifies the material. The grain size of titania has a smaller ionic radius compared to the radius of Zirconia [57] this supports the findings of the present study. Functional grading with nanoparticles decreases pores which reduces stress concentrators and fracture origins. This proves improvement in fracture resistance of graded zirconia.

With the extensive use of monolithic restorations in posterior regions; degradation of zirconia needs to be dealt with due to cyclic loading during mastication and exposure to water in the oral environment. Previous studies done on titania addition on zirconia are on disc-shaped specimens or flat geometry. The shape of a fixed prosthesis is variable as the geometry of the teeth and alignment, its contour has a complex combination of various convexities and concavities.The present study is the first study to the author's knowledge on a three-unit monolithic prosthesis graded with silica and titania nanoparticles. Normal mastication load values are ranging from 50 to N and paand parafunctional behaviour of 500–880 N has been reported, [58] bruxism cases may also be as high as 1000 N. [59]Further studies can be done to evaluate fracture resistance of nanoparticle graded prostheses.

Fatigue failure and surface flaws are one of the etiologic factors influencing fractures in zirconia prostheses. The grading of zirconia was found to have improved ageing resistance and fewer flaws than non-graded zirconia. Mechanical properties were also maintained with graded zirconia. [60] The rate of phase transformation and content of the monoclinic phase was reduced with graded monolithic zirconia. Consequently, this graded glass/zirconia structure may lower the risk of fatigue failure. This hypothesis is supported by the findings of previous [61]studies. Therefore, it can be speculated that this nanoparticle-graded prosthesis will be superior to its ungraded prostheses in restoring posterior regions.

Following are few limitations of current study. The present study did not perform fracture resistance after thermal and mechanical loading. Clinically the monolithic prosthesis will be subjected to dynamic as well as oblique loading. Thus, clinical trials with graded zirconia on long-span fixed prostheses are required. Future recommendations for clinical studies are needed with a longer follow-up period to confirm the results of the present study. Nanoparticle-graded monolithic zirconia can be evaluated for the small connector size restorations and implant-supported monolithic prosthesis. This can assess the evaluation of nanoparticle-graded monolithic zirconia prostheses in thinner sections. Microstructural analysis should be done to explicate the relationship between crystalline phase assemblage and the reliability of functionally graded zirconia.

CONCLUSION

Within the limits of this in vitro study; the following conclusions were drawn

1) Silica or titanium dioxide nanoparticles can be incorporated in three-unit fixed dental prosthesis with single step Functional grading technique. 2) Two different nanoparticles can be evaluated with their elemental composition on the surface of monolithic zirconia.

CLINICAL SIGNIFICANCE

The functional grading technique to incorporate nanoparticles used is an easy, simple, less technique-sensitive, and single-step method, to incorporate titania nanoparticles when compared to different methodologies in literature. Integrating nanoparticles in pre-sintered stage is an effective technique which can be carried out during routine CAD\CAM processing laboratory when compared to different methodologies mentioned in the literature. The Functional grading technique can promote better stress distribution and increase the clinical longevity of monolithic restorations.

LIST OF ABBREVIATIONS

LTD - low-temperature degradation

3Y-TZP- 3 mol% yattria stabilized tetragonal zirconia polycrystals

SEM-Scanning electron microscopy

FE-SEM-Field emission -scanning electron microscopy

SEM-EDS- Scanning electron microscopy -energy dispersive spectroscopy

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