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Improved functional performances of traditional artistic pottery by sol-gel nanoparticles deposition

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Abstract

This work is focused on the realization of a new manufacturing process based on the introduction of TiO_2 nanostructured coatings on the surface of red earthenware pottery for domestic use. The aim of the study is to improve the technical properties of the product made from lime and iron-rich clays used to produce traditional artistic Tuscan pottery (Italy). The identified strategy involves the application of nanoparticles onto the surface of ceramic substrates via a sol-gel based process; the initial porosity of the Earthenware promotes the insertion of inert nanoparticles in the outermost part of the ceramic material by simple immersion of bisqueware in the colloidal solutions of nanoparticles. Morphological investigation of the functionalized surfaces has been carried out by scanning electron microscope and atomic force microscopy, while the effectiveness of the treatment was checked by evaluating the water absorption capacity in compliance with the standard method AS-1012.21-1999. The obtained results show a reduction of surface porosity, which turns into a reduced water uptake respect to the traditional pottery, maintaining, at the same time, identical aesthetical characteristics.

1. Introduction

Tableware and ornamental items represent about the 6% of the European ceramics industry market, with a value close to € 28 billion [1]. The same study, however, shows a trade deficit for European ceramic sector: low-cost imports (predominantly from China) represents about 60% of the market, while European ceramics manufactures sell outside the European market about 30% of their production [1]. These data suggest that European earthenware productions still represent an important industrial sector and a remarkable business, which economical sustainability is strictly related to excellent design and high technical standard. The traditional 'made in Tuscany' artistical pottery is characterized by the historical and the traditional style of the ancient productions distinguishing itself for the aesthetic quality. However, due to the high competitiveness of the markets, these productions cannot compete only because of aesthetic aspects and become mandatory an improvement of their functional properties. Traditional pottery [2] for domestic use is generally glazed [2] in order to reduce water absorption and to increase the mechanical resistance.

Earthenware are realized by firing a mixture of raw materials, for such reason these materials are generally classified on the ground of their chemical (Fe_2O_3 content) and mineralogical composition (phyllosilicates and carbonates), on which it depends their plasticity, the vitrification ability and resulting porosity extent, reached in result of the firing process. Therefore, ceramic bodies can be divided, depending on the final color of the product, in dark-firing (from pink to dark brown, high Fe_2O_3 content) and light-firing (from white to light brown, low Fe_2O_3 content) clay [3] and in porcelain, stoneware or earthenware according to their vitrification and water absorption degree [4].

Earthenwares are glazed ceramic materials of low vitrification degree resulting in an opaque, porous and finely textured crystalline structure [4]. Made of clays, silica, feldspar, feldspathic fluxes and/or calcium carbonate, these materials are characterized by tiny pores and grains that generally does not reach 150 μm, resulting not detectable to the naked eye [4]. Unglazed ceramic body is usually white (distinguished in calcareous earthenware or feldspathic earthenware) or colored by Fe_2O_3 presence (red Earthenware) [5].

The 'Italian majolica' is a glazed brownish-red earthenware, made from a mixture of clays containing 3%–5% Fe_2O_3, 20%–30% limestone, quartz and feldspar. In addition to the typical color, iron oxide promotes the vitrification [6] which improves the mechanical strength while limestone constitutes the flux and it is responsible for the open porosity [6]. As consequence of the relatively high limestone content, the porosity is high leading a water absorption higher than 10% [6] by weight, which dramatically reduces the thermal shock resistance if comparted with other feldspathic earthenware in which water absorption can be as down as 3% [4]. The reduction of the water uptake down these limits would improve the 'Italian majolica' allowing its use to a much larger and wide context, such as restaurant, catering and canteens, which require greater resistance to more severe conditions, in term of dishwasher temperatures and detergent aggressiveness.

Oxide nanoparticles (NPs) are currently used for several applications, ranging from biology and medicine [7] to architecture [8] and construction industry [9, 10]. Their peculiar properties mainly arise from the reduced particles dimensions and consequently to the altered chemical and electronic behavior of these confined portion of matter [11, 12]; in particular, the enhanced chemical reactivity have attracted the ceramics community aiming to the development of NPs-functionalized ceramic surfaces. Indeed, the use of oxide NPs, such as SiO_2, ZrO_2, Al_2O_3 and TiO_2 to functionalize ceramic and glass products/manufacts is rapidly growing [13, 14]. For example, due to its photo-catalytic properties, TiO_2 has been applied in architecture [15] and it has been exploited to realize self-cleaning coatings on tiles [16–18] and natural stones (travertine) [19]. SiO_2 NPs have been applied for architectural and cultural heritage conservation[20, 21], as well as to support silver particles to improve the antibacterial properties of ceramic tiles [22], while, metal oxide-based NPs have been embedded in the bulk of cement based materials increasing their mechanical resistance and durability [23]. ZrO_2 NPs have been successfully added to concrete increasing its compressive, tensile and flexural strengths [24]. Analogously, enhancement of stoneware's mechanical-physical properties have been obtained by adding NPs to the body mixes for tile [25, 26]. Limiting the treatment to surface alone would allow to minimize the costs of the required 'high tech' raw materials. From this point of view, NPs have been applied for surface treatments of several stone-wares [27, 28]. However, to the best of our knowledge, there is no reports focused on the improvement of technical performances of domestic earthenware items such as tableware.

Here, we aim to close this gap by showing how non-toxic metal oxide NPs can be effectively employed to reduce the porosity of the 'Italian majolica' tableware improving the technical properties of the traditional ceramic products. We propose the use of titanium oxide NPs as an intermediate waterproof coating of the unglazed fired red earthenware (bisque ware), obtaining a new product featuring unaltered aesthetical properties of the historical 'Ceramica Montelupina' [29] but characterized by improved functional properties as a consequence of the decreased water absorption (figure 1). The proposed method is intended for food industry applications, therefore, both high chemical stability and non-toxicity criteria have been considered to select the NPs suspensions and buildup process (i.e. solvent use must be limited to water or to mixture of water/ethanol). The new productive process described here takes advantage of the porosity of bisque ware, which permits the interlaying of inert NPs in semi-finished products by simple dipping in a TiO_2 NPs suspension (figure 1) and therefore can be easily adapted to an industrial process.

Nanostructured functional coatings are generally obtained by using plasma treatments [30] or other expensive physical or chemical vapor techniques [31, 32].

These processes are generally complex, limiting their appeal for industrial applications. Alternatively, sol-gel processes yield to sustainable approaches to functionalize surfaces with NPs [33–35]. However, NPs handling poses some major threats to worker's health [36–38]since it can easily be dispersed in air leading to a short term exposure risk; therefore, the factors of risk related to NPs exposure need to be considered during the procedure development. For these reasons, in this work we adopted a dipping technology [39] for the treatment of ceramic items with the nanostructured coatings in order to reduces the use of dangerous solvents. Unlike spraying [40, 41], this method does not require any special equipment and, unlike self-assembly based coatings [42], it limits the additionally required working time.

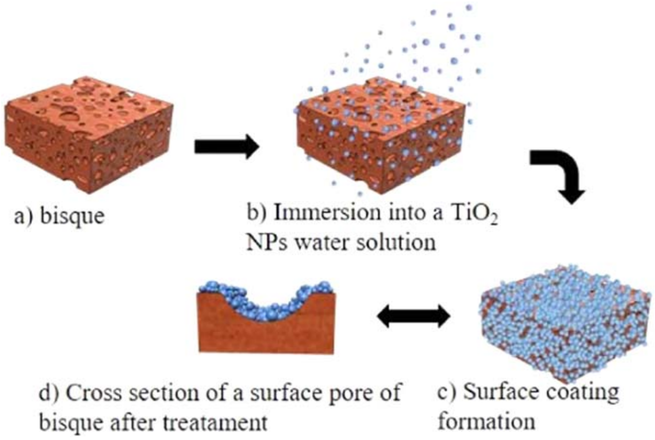

Figure 1. Functionalization mechanism (a) porous bisque ware substrate (b) immersion of bisque ware in colloidal solution of TiO_2 NPs (c) NPs interaction with substrate and coating formation (d) NPs enter and fill them.

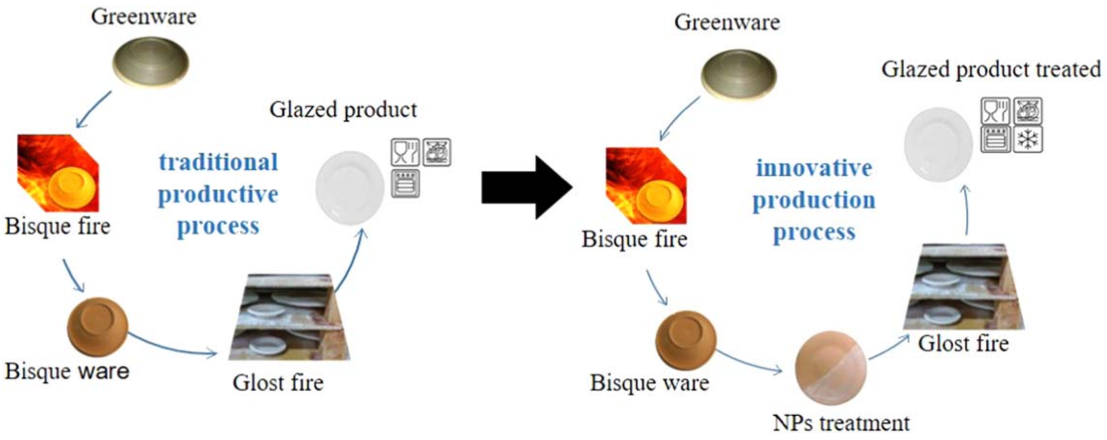

Figure 2. Scheme of the introduction of the NPs functionalization step in a traditional production protocol, to the right is depicted the traditional schematized industrial process and to the left the new industrial process.

Being not toxic in case of skin contact [43], and widely used as food and personal care additive [44], titanium dioxide NPs constitute an ideal candidate for this application. Moreover, a common procedure for synthesis of TiO_2 NPs utilizes organometallic precursor- titanium in acidic ethanol aqueous solution [45, 46], that offer a good perspective for industrial applications in owe to the possibility to supply commercially available colloidal solutions. As a consequence, the developed strategy is perfectly compatible with the traditional production process [47] of 'Italian majolica' (figure 2).

2. Materials and methods

Sol was prepared using titanium isopropoxide (97%) as titania source, by mixing 1:1 molar ratio with acetic acid (Sigma Aldrich, Milano, Italy) in inert environment [48]. Distilled water, nitric acid (Carlo Erba, 65%), and Triton® X-100 (0.86×10^{-3} M, Sigma Aldrich, Milano, Italy), were added to obtain a 0.1 M TiO_2 sol. The mixture thus obtained was kept under vigorous stirring until a clear solution was observed: nitric acid was added as peptizer, and no precipitate formed. Glycidoxypropyltrimethoxysilane (Glymo) (Sigma Aldrich, Milano, Italy) was finally poured in the sol (0.03 M) and stirred overnight. The resulting acidic solution ($pH = 1.28$) was diluted 1:10 with distilled water before the application on the bisque ware. The bisque ware (Ceramiche Virginia s.r.l, Montespertoli (Fl), Italy) was processed by molding on a commercial shape and size (coffee cup dish, 10 cm diameter) avoiding, in this way, scale effects that could happen on lab prepared substrates.

Chemical composition (from F to U) of the bisque were determined by x-ray fluorescence spectroscopy (XRF) analysis using a Rigaku Primus II spectrometer equipped with wavelength dispersive x-ray fluorescence (WDXRF) spectrometer with a Rh tube, automatic sample changer, detectors scintillation counter for heavy elements and flow proportional counter for light elements. Powder pellets were mixed with wax binding agent (SpectroBlend® 44 μ Powder, Breitlander GmbH, binder to sample weight ratio 1:5).

The NP functionalization was obtained by dipping the bisque wares into the TiO_2 colloidal suspension for 30 s and then letting to dry the samples in a temperature-controlled environment at 80 °C for 30 min.

Surface characterization was carried out by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM analysis were performed by coating the samples with a thin Au/Pd (80/20) layer and the obtained images were processed with ImageJ software, version 1.51 K, to extrapolate dimensional values of present structures. The size of the pores was evaluated by measuring the distance between the edges (the diameter) at the widest point of the pore. SEM (Hitachi, Model S-2300) is equipped with energy dispersion spectrometry (EDS) controlled by PATHFINDER software (Thermo Scientific Inc.). AFM (P47 Solver Pro, NT-MDT, Russia) operated in in tapping mode in air with a sharp silicon probe (model NSC36/AIBS), scanning data were processed and analyzed with Gwyddion software, version 2.47.

Phase analysis of the sample's surface was performed by means of gazing angle XRD. The spectra were collected using Bruker New D8 Da Vinci spectrometer operating in Bragg-Brentano mode with an Cu x-ray source and a Theta-Theta goniometer.

After functionalization, the bisque wares were glazed by using a standard industrial process. According to the usually adopted processing steps, the glassy coating was applied by immersion in a glaze suspension (CE394/193.5 Glaze Wetm White Artw pp25Kg, Vetriceramici-Ferro Spa) and then matured in a glost firing operation until 1080 °C.

Water absorption was determined as stated by AS-1012.21-1999 standard [49] providing an indication on the porosity degree of the examined material. This method was preferred to the BN ES 1217, indicated in PAS 54:2003 (Specification for domestic ceramicware and glassware—Article intended for contact with foodstuffs, and vases), because it does not require samples fragmentation which would compromise the nanostructured coating effect. AS-1012.21-1999 method is based on the following standardized procedure: samples were dried at 110 °C (+/−5 °C) for approximately 24 h, let to cool down to room temperature and weighted evaluating the 'dry mass'. Then, the samples were completely immersed in deionized water (23 ± 2 °C) for 24 h, removed from the water, dried with slightly moist smooth cotton cloth in order to remove surface water and weighed again. The percentage variation between the two weights led to an estimation of the porosity of the object (amount of water absorbed).

3. Results and discussion

Industrial bisque wares are intrinsically heterogeneous; therefore, an appropriate reference protocol was realized synergically exploiting several analytical techniques that allowed us to monitor the morphology and properties of the samples as function of the different functionalization procedures.

3.1. Morphological investigation

Figure 3(a) depicts SEM images of the bisque ceramic's sectional structure, highlighting the interconnected structure responsible for the elevated water absorption. Figure 3(b) depicts the surface of the bisque characterized by a very irregular morphology and variable chemical composition as determined by EDS (see supplement data figures S1(a) and (c) is available online at stacks.iop.org/MRX/6/025032/mmedia). SEM was also used to determine the shape and size of the superficial pores by acquiring and inspecting, five images, representative of the samples variability. These images were analyzed returning the histogram of pores size distribution depicted in figure 3(c).

The reference bisque ware was also compared to a similar sample heat-treated without the NPs functionalization in order to simulate the chemical and physical transformations that happens during the firing of the glaze. SEM analysis performed on this sample (see supplement data figure S2) does not evidenced significant changes in both, the surface and the body morphology of the ceramic attributable to the heat treatment.

Functionalization by means of TiO_2 NPs can easily be monitored via chemical analysis by EDS (see supplement data figure S1) since titanium is nearly absent to the biscuit composition as proved by XRF measurements (See supplement data table S1).

No drastic surface morphology modification is detectable as a consequence of the bisque immersion in the colloidal solution (figure 4(a)), only small, Ti-rich, fractured areas become present (figure 4(a) upper right red box).

The same holds for the subsequent heat treatment at 1080 °C required for glost fire; even in presence of NPs the surface does not displays drastic changes (figure 4(b)), however, it is possible to observe the formation of large aggregates (figure 4(b), bottom left) in small and confined areas of the sample. These features have already

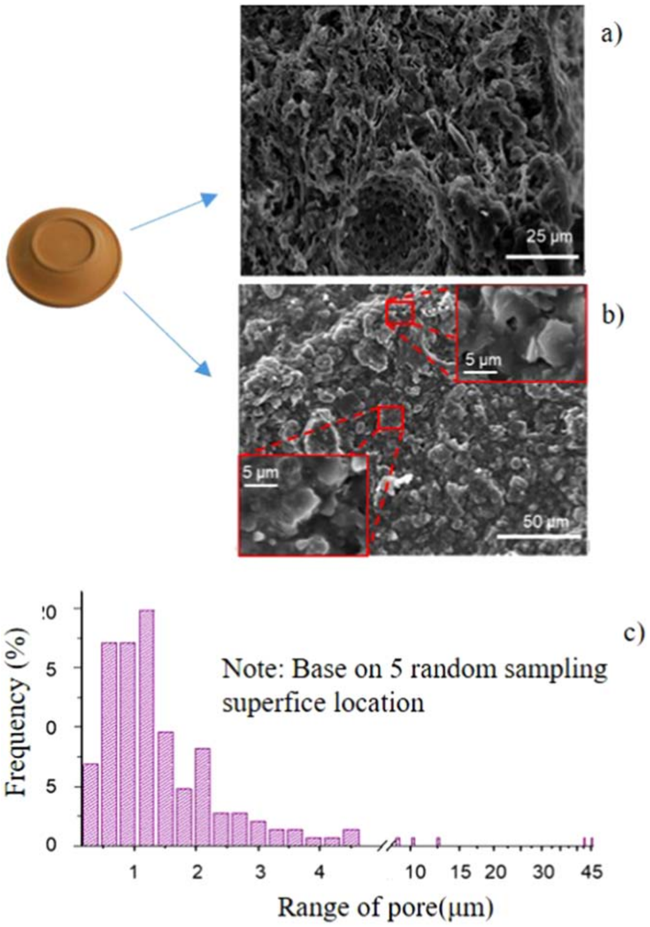

Figure 3. Bisque ware SEM images analysis (a) red bisque ware section (b) red bisque ware surface (c) pore size distribution, classes are divided by a range of 0.3 μm. Measurement based upon 5 random samplings of surface.

been observed by Elfanaoui and coworkers, in TiO_2 film annealed at 400 °C and attributed to surface tension in the film [50].

The presence of large aggregates in the functionalized samples treated at 1080 °C could be interpreted as partial sintering and coalescence of the NPs during kiln-firing. Before the firing process, the areas marked by higher surface concentrations of TiO_2 NPs, presents TiO_2 islands. This hypothesis is supported by the observed behavior in specimens immersed in more concentrated colloidal solutions of TiO_2, where islands have been found even before the kiln-firing and the distance between them would result increased as consequence of the heat treatment (see supplement data figure S3 and S4).

AFM characterization was carried out to evaluate the effect of these treatments at nanometer scale. Images collected on untreated bisque ware (figures 5(a) and (b)) confirm the presence of porous and irregular structure even at local level.

As shown by AFM data reported in figure 5, the heat treatment at 1080 °C induces a texture refinement of the surface, wich roughness pass from $Rms = 8.22$ nm to $Rms = 11.7$ nm and, more importantly, introduces significant structural variation respect to the untreated surfaces (figure 5(a)).

NPs functionalization leads the increases of the submicrometer surface roughness, reasonably attributable to the formation of NPs aggregates. The roughness reduction observed after the thermal treatment (figure 5(d)) (figure 5(b)) would be interpreted as a partial sintering of TiO_2 NPs, which turns in a decrease of the surface porosity (see next paragraph). This hypothesis is in agreement with the data reported by Peña-Rodríguez and coworkers on red clay ceramic tiles coated with fly ash powders [51]. In accordance with our observation, the aforementioned study demonstrated a direct correlation between water absorption and soubstrate roughness of the ceramic material

The AFM data here reported, both confirm the decrease of the bisque wares porosity as result of the partial NPs sintering during the process of glost firing as represented in the scheme of figure 6.

On the other side XRD data collected in both, bragg brentano (see supplement data figure S5) and grazing incidence mode (GIXRD) (see supplement data figure S6), confirm the presence of titanium oxyde (anatase

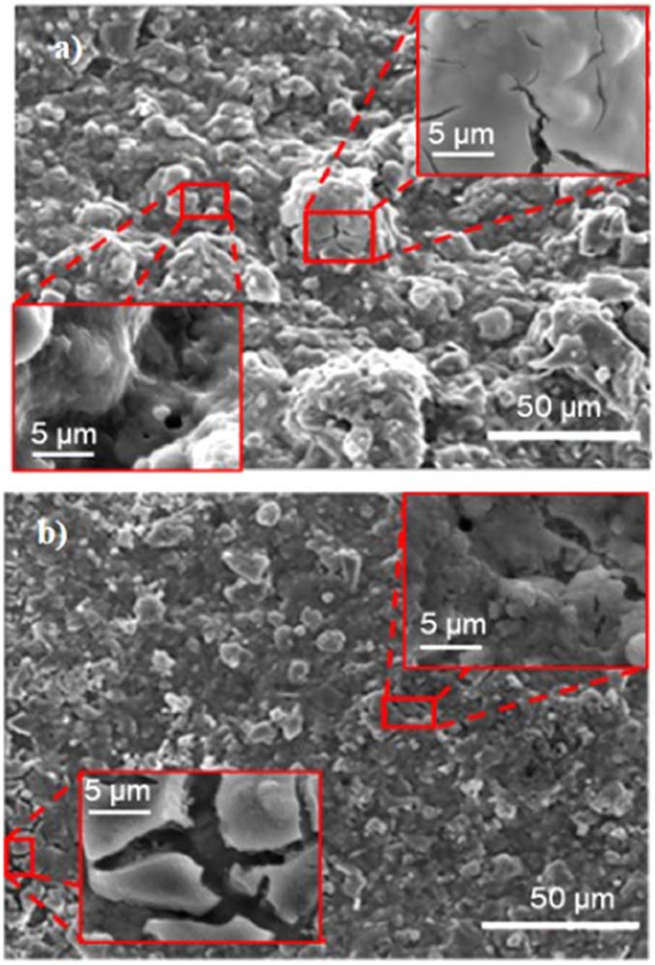

Figure 4. Compared SEM images. (a) bisque ware dipping in TiO_2 colloidal solution (b) bisque ware dipping in TiO_2 colloidal solution and firing at 1080 °C.

phase) at the surface of the functionalized samples, that, as expected, turned into rutile after firing [52] (see supplement data figure S6).

3.2. Water absorption tests

Through the water absorption measurements, it is possible to evaluate the relative porosity and eventually the effect of the NPs treatment.

Due to the relatively large variability of the material, the test was performed on a representative set of samples (57) and the data obtained were statistically analyzed (see figure 7). The reference group is constituted by the bare bisque wares which presents absorption ranging from 15% and 11.3% with an average of 13.3% (standard deviation = 0.8). In order to establish the actual improvement of the performance due to the NPs treatment, an average value of water absorption reduction attributable to the glazing process was defined. The same bisque wares used in estimation of the average absorption of ceramic substrate were later used for every next samples preparation. Some samples were only glazed and used to establish water absorption reduction attributable to the glazing process alone. That returned an average absorption reduction of about 3% (standard deviation = 0.4) attributable to the glaze alone. Then, the water absorption reduction attributable to the NPs was determined by glazing the functionalized samples. The overall data analysis showed an improvement in the performance for the finite product corresponding to a reduction in water absorption of about 20%. From a finished gazed product characterized by an average water absorption of 10% to a finished product with average water absorption of 8% (standard deviation 0.8, figure 7) if treated with NPs.

4. Conclusion

TiO_2 nanoparticles were introduced on the surface of bisque ware via sol-gel process. The formation of the coating was obtained by immersion of the commercial bisque ware into a TiO_2 NPs colloidal aqueous solution.

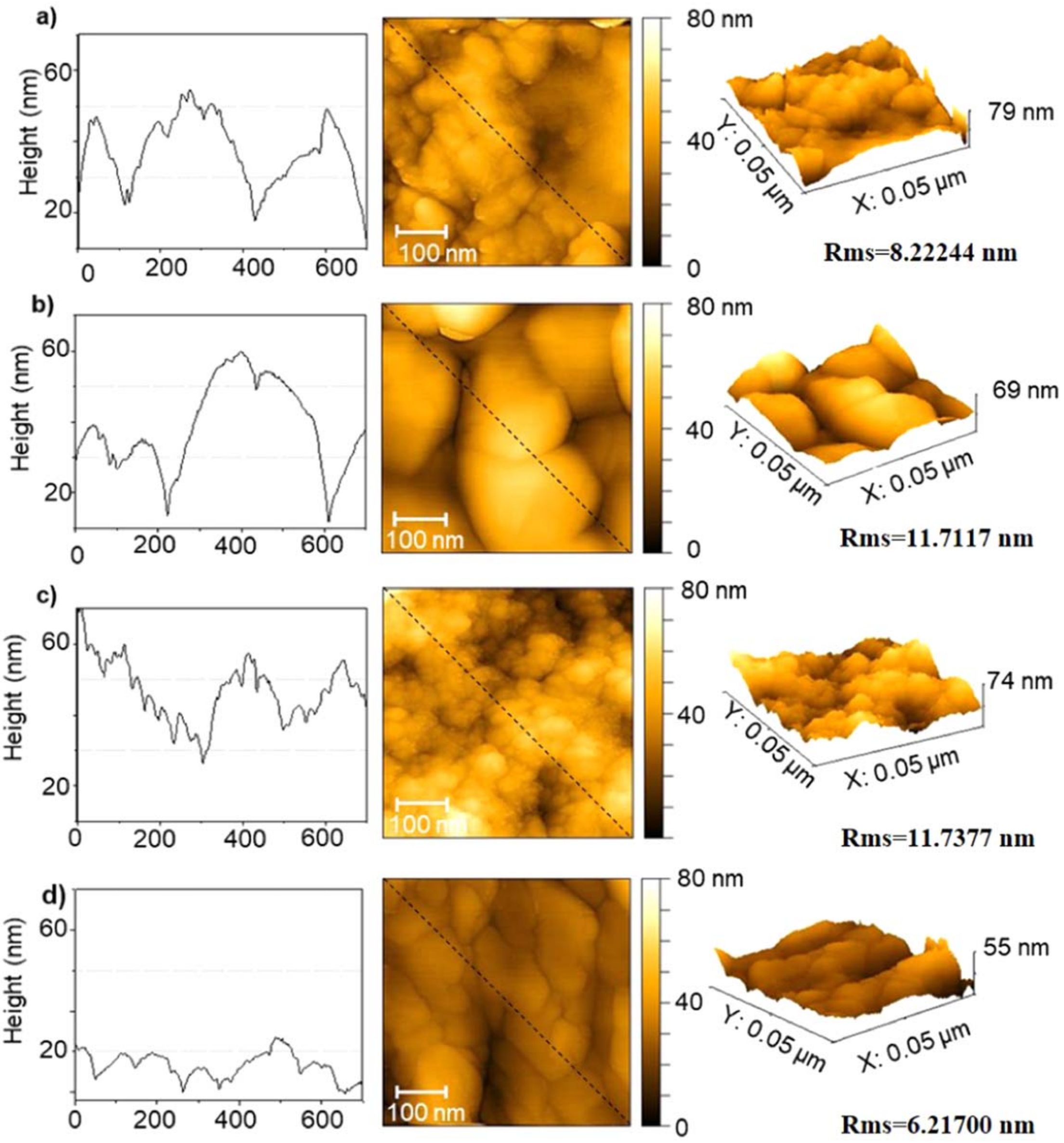

Figure 5. AFM topographic images and respective roughness data (profile of line shown in topography image and height topography 3D) of a 0.5 μm × 0.5 μm section of the bisque ware surface (a), (b) and of the TiO_2 coatings (c), (d), before (a), (c) and after (b), (d) firing at 1080 °C.

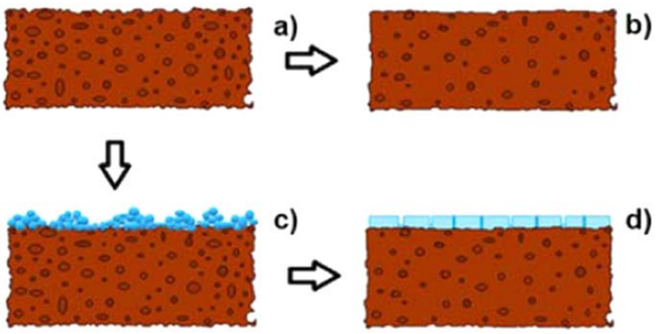

Figure 6. Schematic drawing of surface modifications occurring during the glost fire, related to the presence of NPs. Bisque ware without (a) and with (b) NPs treatment. Figure (b) and (d) represents bisque after heat treatment, in absence and in presence of TiO_2 NPs respectively.

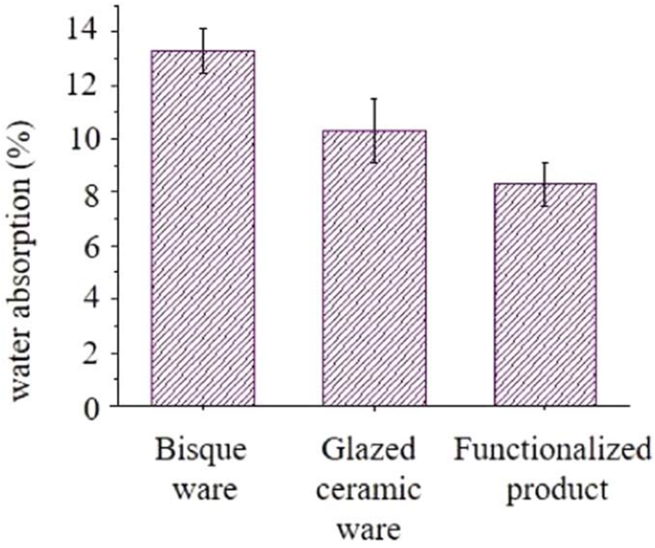

Figure 7. Comparison of the average water absorption as a function of the surface treatment.

During the dipping process, NPs partially permeate inside the pores of ceramic material and stick to the surface. After glazing, the functionalized red earthenware display a substantial improvement of their technical characteristics. According to these results, the surface of bisque ware become covered by NPs and part of the pores were successfully sealed during the glazing and firing process leading a reduced water absorption capacity.

Although the NPs treatment presented in this study does not allow to reach the feldspathic earthenware pottery features in term of water absorption degree (3% wt ca.), the performances improvement is such as to suggest its use in external systems, as well as traditional uses but with less precautionary measures.

Further developments, due to its flexibility, may arise from integration with others manufacturing process approaches.

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