Enhancing the properties of bone China ceramics by treatment with microporous SiO$_2$ nanoparticles

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Abstract
In this study, microporous silicon dioxide nanoparticles (SiO$_2$–NPs) were used to improve the physical, chemical, and mechanical properties of bone China ceramics. Microporous SiO$_2$–NPs were prepared economically from sodium metasilicate (SMS) as a precursor with cetyltrimethylammonium bromide (CTAB) as a surfactant at different concentrations. The prepared SiO$_2$–NPs were characterized using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Raman spectroscopy to confirm the formation of microporous SiO$_2$–NPs. The optimum concentrations of the precursor and surfactant used in the SiO$_2$–NPs synthesis were set to be 1.5% and 2 g/200 ml, with a size range of 7–96 nm. SiO$_2$–NPs prepared at the optimum concentrations were incorporated into bone China at different concentrations to evaluate their effect on flexural strength and elasticity. The bone China prepared using 1% SiO$_2$–NPs (B$_1$) had the highest flexural strength and Young’s modulus values. Sample characteristics, including self-cleaning, differential scanning calorimetry, thermogravimetric analysis, bulk density (BD), apparent porosity (AP), and water absorption (WA), were investigated. The results revealed outstanding characteristic such as self-cleaning ability, remarkable increase in AP and WA, and a decrease in BD.

Keywords Bone China · Ceramics · Microporous silicon dioxide nanoparticles · Physical properties · Mechanical properties

Introduction
Bone China is a ceramic body that is traditionally used in the manufacture of translucent white tableware (Yahya et al. 2018; Toludare et al. 2019). Enhancement of the bone China body structure with nanomaterials is proposed to improve its properties and endow it with more functionality. The growing demand for bone China ceramic has led researchers to improve its physical, chemical, and mechanical properties for decorative and household applications as well as advanced applications (Toludare et al. 2019). The composition of bone China includes bone ash, kaolin, and feldspar at mass contents of 50%, 25%, and 25%, while bone China can be sintered at approximately 1250 °C (Nodeh 2017; Zhang et al. 2016). It is a highly crystalline material that contains approximately 70% crystalline components and 30% glass. The crystallinity of bone China is attributed to the presence of large amount of bone ash, which decomposes to CaO (lime), β-tricalcium phosphate (β-TCP), and H$_2$O at high temperatures (up to 1100 °C) (Toludare et al. 2019; Ahsan et al. 2012). The crystalline phases of bone China are formed fundamentally by anorthite (CaAl$_2$Si$_2$O$_8$), β-TCP (Ca$_3$(PO$_4$)$_2$), and calcium aluminosilicate glass (Yahya et al. 2018; Toludare et al. 2019; Bragança and Bergmann 2008). Because of these features, bone China bodies possess high flexural strength, high chipping resistance, and high modulus of rupture; however, the Young’s modulus is lower than that of hard porcelain owing to its high porosity (Batista et al. 2001).

Bone China contains recycled materials, such as bone ash (Bragança and Bergmann 2008; Carus and Bragança 2013). It has, therefore, become highly appealing because of the growing interest in recycling materials to maintain the environment. In recent decades, with the advantages of nanotechnology, researchers have made considerable efforts...
to enhance the properties of ceramics using nanomaterials. Improving the mechanical and physical characteristics of ceramics is challenging. The selection and concentration of nanoparticles (NPs) play a major role in controlling the material properties. There is an increasing interest in the characteristics of nanomaterials that may lead to the development of new ceramics with superior properties. Numerous studies have focused on the use of NPs, such as Al₂O₃, ZrO₂, TiO₂, and SiO₂–NPs, in ceramic bodies to improve their characteristics (Rambaldi et al. 2010; Ambrosi et al. 2014; Eliyan et al. 2021; la Garza et al. 2020; Aguilar-Elguézabal et al. 2017; Bi et al. 2017; Aly and Abd Elhamid, 2018). NPs can be applied to ceramic bodies in various ways, such as airbrush coating on green or fired specimens and the addition of NPs as raw materials (Rambaldi et al. 2010; Ambrosi et al. 2014; Eliyan et al. 2021; la Garza et al. 2020; Aguilar-Elguézabal et al. 2017).

A significant number of experiments have been conducted to prepare SiO₂–NPs due to their unique properties. SiO₂–NPs have lower toxicity than other NPs, and this increases their applicability, especially in biochemical fields such as drug delivery (Esim et al. 2019). SiO₂–NPs can be utilized to produce a strengthening filler for concrete and other construction composites (Jeelani et al. 2020). Furthermore, the nature of microporous SiO₂–NPs has a remarkable effect on CO₂ adsorption capacity due to their capillary pores as well as their photodegradation ability due to the available active sites found on SiO₂–NPs surface that react with dye molecules through redox reactions, especially during radiation exposure (Aguilar-Elguézabal et al. 2017; Rafigh and Heydarinasab 2017; Xu et al. 2021).

The effect of SiO₂–NPs on porcelain, whose chemical structure is close to that of bone China ceramics, was examined. Desoky et al. added 10% SiO₂–NPs during the preparation of porcelain and concluded that the application of these NPs led to a noticeable change in the density, porosity, and water absorption (WA) of the porcelain. The use of SiO₂–NPs has also been found to improve dielectric insulating characteristics (Desouky et al. 2020). Anil et al. reported that porcelain samples containing 2% colloidal SiO₂–NPs showed an increase in flexural strength and BD (Anil et al. 2009). However, the effect of SiO₂–NPs addition on the properties of bone China has not been studied.

In this work, we aim to synthesize microporous SiO₂–NPs with a suitable size and pores at the nanoscale and study their applicability at different concentrations in the production of bone China ceramics. Until now, and to the best of our knowledge, no study investigated the effect of the addition of microporous SiO₂–NPs to bone china body. In this respect, the physical, chemical, and mechanical properties of bone China were investigated before and after the addition of SiO₂–NPs to determine the effect of this addition on bone China characteristics.

### Experimental

#### Materials

Sodium metasilicate (SMS), cetyltrimethylammonium bromide (CTAB), sodium chloride, silver nitrate, methylene blue dye, polyvinyl methacrylate, and 37% hydrochloric acid were purchased from Sigma-Aldrich and used without further purification. The raw materials used in bone China preparation included sodium feldspar (albite; NaAlSi₃O₈; Minas Company, Cairo, Egypt), cattle bones from the local market, Cairo, Egypt, and kaolin (Al₂Si₂O₅(OH)₄) from Sedlecky Company, Bozicany, Czech Republic.

#### Methods

##### Preparation of microporous SiO₂–NPs

A modified method was used to prepare the microporous SiO₂–NPs (Abou Rida and Harb 2014). The precursor (silica wet gel) was prepared using SMS at concentrations of 0.15% and 1.5%. The cationic surfactant, CTAB, with different weights (1 and 2 g) was dissolved in 200 ml SMS solution. The temperature was adjusted to 55 °C under constant stirring at 300 rpm, and the mixture was neutralized using 2.5% HCl in two steps. First, HCl was added dropwise until the semi-gelatinous point at pH 9–9.5, and the mixture was stirred without HCl addition for 10 min to prevent the formation of a strong silica gel. HCl was then added to the mixture until it reached a pH of 3–3.5. NaCl (10 mL, 10%) was added to the mixture under constant stirring for 20 min. After this final addition, the silica wet gel was incubated at 50 °C for 24 h without stirring. The prepared silica wet gel was washed well with distilled water using a centrifuge at 5000 rpm until complete remove of the chloride ions, followed by drying in a microwave oven (800 W) for 10 min. This drying process was conducted seven times at 10 min intervals between microwave exposures. The dried samples were calcined at 650 °C for 3 h at a heating rate of 10 °C min⁻¹ and then milled to form a fine powder using a mortar.

##### SiO₂–NPs characterization

The surface morphology of the prepared SiO₂–NPs was observed using a scanning electron microscope (JEOL JSM-6510LB, Tokyo, Japan). Gold layer was used as a coating material for high-resolution imaging. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed to determine the elemental composition.
The sizes of the pores inside the prepared SiO$_2$–NPs were determined using a 200 kV transmission electron microscope (JEOL JEM-2100F, Tokyo, Japan) to confirm the formation of microporous SiO$_2$–NPs. The SiO$_2$–NPs powder was sonicated in distilled water, and the specimen was prepared for transmission electron microscopy (TEM) analysis using a drop of colloidal solution loaded onto a 400-mesh copper grid covered by an amorphous carbon film. The solvent was then evaporated at room temperature (Abou Elmaaty et al. 2018).

The crystallinity of the synthesized SiO$_2$–NPs was determined using an X-ray diffractometer (Bruker D8 ADVANCE, Karlsruhe, Germany). The crystallite size was determined using Scherrer’s Equation (Rauf et al. 2016) as follows:

$$B = \frac{K \lambda}{L \cos \theta}$$

where, $B$ = FWHM (Full Width at Half Maximum); $\theta$ = Bragg angle; $\lambda$ = wavelength radiation; $L$ = Crystalline size and $k$ = 0.9 (Scherrer constant).

The types of bonds present in the particles were determined using a confocal Raman microscope covering a range of 200–1000 cm$^{-1}$ at a laser wavelength and power of 531.95 nm and 7.2 W (Jasco NRS-4500, Tokyo, Japan). The Raman data were acquired and processed using the Jasco spectroscopy software suite.

**Preparation of bone China**

The cattle bones under study were boiled in water to remove adhering flesh and cartilage bits and then dried in sunlight for several days. This step was repeated thrice to completely clean the bones. The dried bones were calcined at 900 °C and then milled using mortar to obtain the bone ash. The bone ash, sodium feldspar, and kaolin were sieved using nylon sieve (45 μm). The mixture was grounded for 20 min and then mixed in powder mixing machine (Mxb-aoheng, USA) for 30 min at speed of 25 rpm/min.

A blank sample of bone China was prepared by mixing bone ash, feldspar, and kaolin in a weight mixing ratio of 50:25:25. These components were mixed with an appropriate amount of water to create a moldable mixture, which was then pressed into a rectangular acrylic mold (75 × 12 × 4 mm). The specimens were sintered inside an electric muffle furnace kiln at 1320 °C and then polished. These steps were repeated for the specimens prepared using microporous SiO$_2$–NPs, as described in Table 1.

| Bone ash (% w/w) | Feldspar (% w/w) | Kaolin (% w/w) | SiO$_2$–NPs (% w/w) |
|------------------|------------------|----------------|--------------------|
| 50               | 25               | 25             | 0                  |
| 49.5             | 24.75            | 24.75          | 1                  |
| 47.5             | 23.75            | 23.75          | 5                  |
| 45               | 22.5             | 22.5           | 10                 |
| 42.5             | 21.25            | 21.25          | 15                 |

**Chemical composition analysis of the raw materials in bone China**

The chemical composition of the starting raw materials used in bone China preparation was determined using X-ray fluorescence (XRF). Samples of the raw materials were ground through a 200-mesh sieve, and polyvinyl methacrylate was used as the binding agent. The samples were pressed manually for up to 5 t using a Herzog pressing machine (TP 60/2D, Hamburg, Germany).

Quantitative determination of the oxides, including SiO$_2$, Al$_2$O$_3$, CaO, MgO, TiO$_2$, Fe$_2$O$_3$, Na$_2$O, K$_2$O, P$_2$O$_5$, Cr$_2$O$_3$, MnO, SrO, and SO$_3$, was accomplished via computerized XRF (Philips PW-1400, Amsterdam, Netherlands).

**DSC and TGA analysis**

The thermal behavior of the prepared bone China samples was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC analysis was performed to identify the difference in the amount of heat required to increase the temperature of the prepared SiO$_2$–NPs and the bone China samples. TGA was conducted to identify weight loss during the sintering process. A differential scanning calorimeter (Setaram S60/58986, Lyon, France) was used for both DSC and TGA analyses. Then, 20 mg of each sample was analyzed in a N$_2$ atmosphere. Alumina powder was used as a reference material, and the heat rate was maintained at 10 °C min$^{-1}$.

**Determination of AP, BD, and WA**

The apparent porosity ($AP$), bulk density ($BD$), and water absorption ($WA$) were determined based on the Archimedes method according to ASTM C373 (2006).

The test specimens were dried in an oven at 150 °C until constant mass and then cooled in a desiccator to then obtain the dry weight ($W_D$). The specimens were placed in a pan and boiled in distilled water for 5 h. They were submerged in water while boiling and then soaked in water completely for an additional 24 h without touching the sides of the vessel. After impregnation of the test specimens, the suspended
weight \( (W_S) \) of each specimen suspended in water was determined. Then, all excess water was removed lightly from the surfaces of the specimens using a moistened, lint-free linen or cotton cloth, and the saturated weight \( (W_M) \) was obtained. The exterior volume \( (V) \), in cubic centimeters, was calculated using Eq. (1).

\[
V = W_M - W_S
\]  

\( (1) \)

AP, WA, and BD were calculated using Eqs. (2), (3), and (4):

\[
AP = \left[ \frac{(W_M - W_D)}{V} \right] \times 100
\]  

\( (2) \)

\[
WA = \left[ \frac{(W_M - W_D)}{W_D} \right] \times 100
\]  

\( (3) \)

\[
BD = \frac{W_D}{V}
\]  

\( (4) \)

Three-point bending strength test

A three-point bending test was conducted using a Lloyd LRXPlus material testing machine based on ASTM C1341 (2018) at room temperature and preload speed of 21 mm/min to evaluate the flexural strength of the bone China ceramic samples. Three replicates were used for each sample to carry out bending test through the compression direction.

Self-cleaning test

The photodegradation ability of the prepared bone China was also evaluated. The samples were stained by immersing in a methylene blue dye \( (0.2 \, \text{g L}^{-1}) \) for 5 min, and then dried and exposed to sunlight for 24 h. The change in color strength was determined as \( K/S \) value in the stained samples using a spectrophotometer (CM3600A; Konica Minolta, Japan). The Kubelka–Munk equation was used for the \( K/S \) value calculation in Eq (5) as follows:

\[
K/S = \frac{(1 - R)^2}{2R}
\]  

where \( R \) represents the reflectance of the stained samples, \( K \) is the absorption coefficient, and \( S \) is the scattering coefficient.

A decrease in the \( K/S \) value at 600 nm indicates dye degradation, which is expressed as the self-cleaning capacity (SCC) according to Eq. (6) as follows:

\[
SCC = \left[ \frac{(K/S)_b - (K/S)_a}{(K/S)_b} \right] \times 100
\]  

where \((K/S)_a\) and \((K/S)_b\) represent the color strengths before and after exposure to sunlight, respectively (Ibrahim et al. 2017).

### Results and discussion

#### SiO₂–NPs characterization

The size and morphology of the prepared SiO₂–NPs were characterized using scanning electron microscopy (SEM) after the calcination process. The results showed that the SMS and CTAB concentrations used in the SiO₂–NPs preparation evidently affected the SiO₂–NPs size, as displayed in Table 2.

The SiO₂–NPs prepared using 1.5% SMS and 1 g CTAB ranged from 34 to 385 nm in size, while the change in SMS concentration to 0.15% caused a decrease in their diameter to 15–370 nm. CTAB at different concentrations \( (1 \, \text{and} \, 2 \, \text{g/200 ml SMS}) \) was used as a nonionic surfactant to control the SiO₂ particle size at the nanoscale. The SiO₂–NPs diameter decreased noticeably with increasing CTAB concentration, as shown in Table 2 and Figs. 1 and 2. The diameter of the SiO₂–NPs synthesized using 2 g CTAB/200 ml SMS (1.5%) ranged from 7 to 96 nm. The formation of SiO₂–NPs was also confirmed by EDX analysis, which revealed the presence of both silicon and oxygen, as illustrated in Fig. 2. The SEM micrographs showed a clear variation between the traditional silica and the prepared SiO₂–NPs. The prepared SiO₂–NPs diameter ranged from 7 to 479 nm, while the size of traditional silica particles was in the range of 1883–28,872 nm, as shown in Fig. 1.

The histogram of the SiO₂–NPs revealed that the NPs prepared using 2 g CTAB/200 ml SMS (1.5%) showed the narrowest size range (7–96 nm) in comparison with the other prepared SiO₂–NPs. In contrast, the SiO₂–NPs synthesized using 1 g CTAB/200 ml SMS (1.5%) had the largest diameter, ranging from 34 to 385 nm, as shown in Fig. 2. In addition, the histogram showed a variation in NPs diameters

| Table 2 Effect of SMS and CTAB concentrations on SiO₂–NPs size |
|---------------------|------------------|-----------------|
| SMS (%)  | CTAB (g/200 ml SMS) | SiO₂–NPs diameter (nm) |
|----------|---------------------|------------------------|
| 1.5      | 1                   | 34–385                 |
| 1.5      | 2                   | 7–96                   |
| 0.15     | 1                   | 15–370                 |
between the NPs prepared using CTAB at the concentration of 1 g/200 ml, and SMS at different concentrations of 0.15% and 1.5%. The most of SiO$_2$–NPs prepared with 0.15% SMS were around 50 nm, while the most of the NPs synthesized using 1.5% SMS and CTAB (1 g/200 ml) were around 150 nm. The histogram bins were 100 nm wide and centered at 50, 150, 250, and 350 nm, as shown in Fig. 2a. Furthermore, the histogram bins of the SiO$_2$–NPs prepared using 2 g CTAB/200 ml SMS (1.5%) were 20 nm wide and centered at 10, 30, 50, 70, and 90 nm. SiO$_2$–NPs with diameters of 20–40 nm were considered altogether as particles with a diameter of 30 nm, as illustrated in Fig. 2b.

**TEM analysis**

SiO$_2$–NPs can be classified into three types depending on the pore diameter: microporous (less than 2 nm), mesoporous (2–50 nm), and macroporous (more than 50 nm) [26]. TEM analysis was conducted to confirm the microporous nature of the prepared SiO$_2$–NPs. The TEM micrographs showed the formation of microporous SiO$_2$–NPs, including pores with diameters ranging from 1 to 2 nm, as shown in Fig. 1. The porous nature of the prepared SiO$_2$–NPs increases the specific area and porosity because of the nanopores that impeded inside, enabling SiO$_2$–NPs capillary action and higher water absorption capacity than traditional SiO$_2$–NPs (Jafari et al. 2019; Gu et al. 2016).

**Raman spectrum analysis**

The Raman spectrum of the SiO$_2$–NPs showed peaks at approximately 233 and 577 cm$^{-1}$, indicating the presence of SiO$_2$. The broad peak at 577 cm$^{-1}$ refers to the formation of amorphous SiO$_2$–NPs (Biswas et al. 2018; Shabir et al. 2011), as shown in Fig. 3. The observed peak in the region 380–445 cm$^{-1}$ may be corresponding to O–Si–O signal in SiO$_2$. Another peak appeared around 470 cm$^{-1}$ may be attributed to Si–Si bond (Melinon et al. 1998).
Chemical composition of raw materials

The chemical compositions of the raw materials (bone ash, feldspar, and kaolin) were determined using XRF and are listed in Table 3. Feldspar gave the highest SiO₂ percentage (75.10%), followed by kaolin (48.16%) and bone ash (0.98%). Kaolin and bone ash had the highest concentrations of Al₂O₃ (37.04%) and CaO (40.46%). Moreover, bone China raw materials contained other components in small quantities, as tabulated in Table 3. The obtained results revealed that a higher loss of ignition (LOI) was observed in kaolin (12.98%), followed by bone ash and feldspar. Tironi et al. (2012) reported that the LOI of kaolin was 13.3%, which agrees with the results obtained in this study.

Examination of bone China surface

SEM analysis

The surfaces of samples (B₀ and B₁) were examined using a scanning electron microscope as shown in Fig. 4. Sample B₀ did not contain SiO₂-NPs, while B₁ contained SiO₂-NPs, which revealed the stability of the SiO₂-NPs in the bone China ceramic after thermal treatment at 1320 ºC. The
SiO$_2$–NPs found on the surface of the B$_1$ sample were distributed well and were spherical in shape. Furthermore, the surfaces of fractured bone china samples were examined using SEM analysis to confirm the presence of SiO$_2$–NPs inside the bone china structure and to compare the microstructure of the B$_0$ and B$_1$ samples. The obtained SEM micrographs showed that microporous SiO$_2$–NPs are found on the B$_1$ sample either on the surface or inside its body, comparing to that of B$_0$, which was clear from the prepared SiO$_2$–NPs.

### XRD analysis

X-ray diffraction (XRD) analysis was conducted for the bone China samples sintered at 1320 °C to identify the different phases formed during the sintering process. B$_0$ showed peaks related to β-TCP, anorthite, and quartz, as shown in Fig. 5 (Biswa et al. 2018; Kara and Stevens 2002; Bimson 1969). The XRD spectra of the SiO$_2$–NPs showed a broad peak in the range of 19.68°–27.32°, indicating the formation of amorphous SiO$_2$–NPs (Rafigh and Heydari-nasab 2017; Ghani et al. 2017). The weak and single peak appeared around 27.88° after the broad peak may be attributed to small amounts of crystalline SiO$_2$–NPs. Tsukimura et al. reported that the amorphous nanoparticles are slowly transformed to a crystalline phase because the crystalline phase is more stable than amorphous nanoparticles and found that crystalline SiO$_2$ particles show a strong and sharp peak around 27° (Tsukimura et al. 2021).

The fired and sintered sample B$_1$ showed peaks with lower intensities than B$_0$. In addition, B$_1$ exhibited lower crystallite size (46.83 nm) than B$_0$ (47.43 nm), indicating the decrease in bone china crystallinity nature as a result of SiO$_2$–NPs addition. The low decrease in crystallite size and crystallinity phases may be also due to the low concentration of SiO$_2$–NPs present in B$_1$ sample. (El-Didamony et al. 2020) reported similar results and found that the intensity of the quartz phase in ceramic engobes decreased due to the addition of SiO$_2$–NPs.

### Characterization of bone China under study

#### Bending test

The mechanical characteristics of the bone China samples with SiO$_2$–NPs at different concentrations (1, 5, 10, and 15%) were identified via a bending test in comparison with those of bone China free of SiO$_2$–NPs. Figure 6 shows the effect of the SiO$_2$–Nps concentration on the flexural strength, which is defined as the maximum bending stress that can be applied to a material before it yields in a flexure test. B$_1$ showed a remarkable improvement in flexural strength, which increased to 38.38 MPa compared with B$_0$ (35.46 MPa). On the other hand, the addition of SiO$_2$–NPs at concentrations of 5, 10, and 15% led to a notable decrease in the flexural strength, as shown in Fig. 6. SiO$_2$–NPs at a concentration of 1% may recover the macropores found inside the bone China body, which enhances the flexural strength (Alrumaih 2019). SEM micrographs of the surface of the fractured B$_1$ sample confirmed the presence of microporous SiO$_2$–NPs in the macropores of bone china body as shown in Fig. 4. Therefore, the addition of SiO$_2$–NPs at low concentration (1%) enhances the bone china strength. However, the

#### Table 3

| Chemical composition of the raw materials used in bone China preparation | Chemical components | Bone ash SD | Feldspar SD | Kaolin SD |
|---|---|---|---|---|
| SiO$_2$ | 0.98 ± 0.04 | 75.10 ± 1.83 | 48.16 ± 0.89 |
| Al$_2$O$_3$ | 1.40 ± 0.14 | 15.10 ± 0.21 | 37.04 ± 1.13 |
| CaO | 40.46 ± 0.57 | 1.12 ± 0.12 | 0.09 ± 0.01 |
| MgO | 2.83 ± 0.26 | 1.04 ± 0.04 | 0.05 ± 0.01 |
| SO$_3$ | 0.32 ± 0.03 | 0.17 ± 0.02 | 0.26 ± 0.07 |
| TiO$_2$ | – | 0.03 ± 0.01 | 0.75 ± 0.06 |
| Cl$^-$ | 0.27 ± 0.08 | 0.05 ± 0.01 | – | – |
| Fe$_2$O$_3$ | 0.06 ± 0.01 | 0.28 ± 0.02 | 0.28 ± 0.04 |
| Na$_2$O | 2.00 ± 0.15 | 3.25 ± 0.25 | 0.01 ± 0.00 |
| K$_2$O | 0.04 ± 0.01 | 2.20 ± 0.30 | 0.03 ± 0.01 |
| P$_2$O$_5$ | 0.32 ± 0.09 | 0.47 ± 0.08 | 0.32 ± 0.06 |
| Cr$_2$O$_3$ | – | 0.03 ± 0.01 | – | – |
| MnO | – | 0.01 ± 0.00 | – | – |
| SrO | 0.03 ± 0.01 | – | – | – |
| Loss on ignition (LOI) | 1.43 ± 0.25 | 1.12 ± 0.09 | 12.98 ± 0.32 |
increase in SiO$_2$–NPs concentrations of 1% maximizes the porosity, which decreases the bone China flexural strength because of the porous nature of SiO$_2$–NPs (Gu et al. 2016).

Figure 6 also shows the effect of the SiO$_2$–NPs on Young’s modulus of the bone China ceramics. Young’s modulus describes the elastic properties of a solid material undergoing compression or tension in only one direction. The Young’s modulus of B$_1$ exhibited an evident increase (to 10%) compared with that of B$_0$. Moreover, the bone China samples containing SiO$_2$–NPs at concentrations of 5, 10, and 15% (B$_5$, B$_{10}$, and B$_{15}$, respectively) showed a noticeable decrease ranging from 11 to 60% in comparison with the bone China samples that did not have the SiO$_2$ NPs, as shown in Fig. 6. The decrease in Young’s
The modulus may be due to the reduction in the anorthite (CaO·Al$_2$O$_3$·2SiO$_2$) content caused by the addition of SiO$_2$–NPs. Pabst et al. reported that the elastic constant (Young's modulus) of dense, single-phase, isotropic polycrystalline plagioclase depends on the anorthite content (mol.%) and found that the elastic constant increases with the anorthite content (Pabst et al. 2015). In the current study, the addition of SiO$_2$–NPs at a low concentration (1%) led to an increase in elasticity, which reveals that SiO$_2$–NPs could be added at low concentrations to improve the mechanical properties of bone China in a cost-effective process. Based on bending test, the optimum concentration of SiO$_2$–NPs in bone China preparation was 1%, so B$_1$ specimens were selected to be subjected to the following tests.

Fig. 5 XRD spectra of biscuit-fired bone China (B$_0$), bone China with SiO$_2$–NPs (B$_1$), and SiO$_2$–NPs

![XRD spectra](image)

Fig. 6 a Flexural strength, b Young’s modulus of pure and nanostructured bone China ceramic samples with SiO$_2$–NPs concentrations of 0%, 1%, 5%, 10%, and 15%
Physical characteristics

The effect of the addition of SiO₂–NPs at the optimum concentration (1%) on the physical characteristics of B₀ and B₁, namely, BD, AP, and WA, was investigated. The AP and WA percentages of B₁ were higher than those of B₀, as shown in Table 4. The addition of SiO₂–NPs caused a decrease in the BD value compared to the original bone China (prepared without SiO₂–NPs addition). El-Didamony et al. studied the physical effect of nano-silica on ceramic engobes and found that BD decreases with an increase in nano-silica concentration, which agrees with the results of the present work (El-Didamony et al. 2020). A slight decrease in BD may be due to the low concentration (1%) of SiO₂–NPs used in B₁ preparation, which did not significantly affect the BD of bone china. Furthermore, the capillary forces existing in the nanopores filled them with water (Kumar et al. 2015) and led to the increases in WA and AP due to the use of microporous SiO₂–NPs, as seen in the TEM micrographs and displayed in Fig. 1.

Self-cleaning

The photodegradation ability of B₀ and B₁ samples was evaluated against methylene blue dye by direct exposure to ultraviolet radiation from sunlight. Photocatalytic activity is affected by the particle size, crystalline structure, porosity, and specific surface area of the material (Zuo et al. 2014). In photocatalytic activity, UV and visible rays were used to motivate redox reactions via activating the photocatalyst (Zhou et al. 2021). B₁ showed an obvious decrease in the blue color and a degradation percentage value of 88.23%, indicating the applicability of the prepared bone China with SiO₂–NPs as a photodegradable material. The photocatalytic activity of SiO₂–NPs may be due to their porosity and particle size (Abou Elmaaty et al. 2021). The B₁ sample showed a lower degradation percentage value of 79.83% than the B₁ specimen, indicating that the presence of SiO₂–NPs in the microstructure of bone china improved its photodegradation ability.

DSC and TGA

TGA/DSC analysis was performed on B₀ and B₁, as shown in Fig. 7. The bone China samples were subjected to a temperature range of 20–1550 °C at a heating rate of 10 °C min⁻¹ to evaluate their thermal performance. The TGA/DSC curves of B₀ showed four endothermic peaks at 272.5, 370.6, 575.3, and 1435 °C. The first and second peaks (272.5 °C and 370.6 °C, respectively) were due to the removal of water. The endothermic peak at 575.3 °C was a major peak related to the removal of the crystalline water of bone China porcelain minerals, which is the first step in the composition of bone China porcelain structures (Chakraborty 2014; Guo et al. 2020). The endothermic effect at 1435 °C is related to the crystallization of the cristobalite phase (Colombo et al. 2018; Ajanaku et al. 2016; Gualtieri 2007).

The TGA/DSC curves of B₁ showed nine endothermic peaks at 66.8, 265.1, 576.4, 776.6, 942.9, 1042.3, 1260, 1369.9, and 1427.3 °C, as illustrated in Fig. 7. The first peak (66.8 °C) may correspond to moisture loss (Belhouchet et al. 2019). The second peak (265.1 °C) was due to the removal of water. The peaks at 576.4 °C and 776.6 °C were related to the removal of any chemically bonded water with bone China minerals and to the formation of meta-kaolinite from kaolinite (Chakraborty 2014; Ajanaku et al. 2016). The peaks observed at 942.9 °C and 1042.3 °C may be due to the crystallization of apatite (Riaz et al. 2014). The endothermic peak at 1260 °C signaled the transformation of the spinel phase to the mullite phase (Colombo et al. 2018; Gualtieri 2007). Finally, the endothermic peaks at 1369.9 °C and 1427.3 °C were related to the appearance of the cristobalite phase and the emergence of SiO₂–NPs in the sample (Colombo et al. 2018; Ajanaku et al. 2016; Aras and Kristaly 2019; Yang et al. 2012).

Conclusion

In this study, microporous SiO₂–NPs were utilized to improve the physical, chemical, and mechanical properties of bone China ceramics. They were prepared using a cost-effective method utilizing SMS as a precursor in the presence of CTAB as a surfactant. The optimum concentrations of SMS and CTAB required for SiO₂–NPs preparation at the nanoscale were investigated. The SEM and TEM micrographs, XRD patterns, and Raman spectrum confirmed the formation of microporous SiO₂–NPs. These SiO₂–NPs were added to the raw materials of bone China at various concentrations to study their effect on bone China ceramic properties. The obtained results showed that B₁ had the highest flexural strength and Young’s modulus values among all the bone China samples and was selected for further tests. B₁ showed a remarkable increase in AP and WA, whereas BD decreased. In addition, the photodegradation ability of B₁ specimens was evaluated against methylene blue dye, which decomposed clearly on
the B₁ surface after exposure to sunlight. Moreover, the thermal behavior of the B₀ and B₁ samples was studied using TGA/DSC analyses.

The obtained results revealed that SiO₂–NPs addition may enable bone China ceramics to be used in new fields, such as filters, bio-scaffolding, and drug delivery. Bone China contains recycled materials; therefore, it is an eco-friendly and sustainable material that can be used in advanced applications.

**Declarations**

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

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