spectrum to identify the origin of Linqing brick: evaluation of the
influencing factors, assessing reliability, and providing scientific
advice

Zexuan Chen¹*, Long Zhang²*, Feng Hou³*, Jialiang Xie¹

&These authors contributed equally to this work and should be considered co-first authors

¹Tianjin International Engineering Institute, Tianjin University, Tianjin 300072, People’s Republic of China

²School of Architecture, Tianjin University, Tianjin 300072, People’s Republic of China

³Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of
Materials Science and Engineering, Tianjin University, Tianjin 300072, People’s Republic of China

* Corresponding authors:

Zexuan Chen: chenzexuan@tju.edu.cn, Long Zhang: arcdragon@163.com, Feng Hou: houf@tju.edu.cn
Abstract:

Linqing brick is quite popular in Chinese history. In 2008, “The manufacturing process of Linqing brick” was selected as the intangible cultural heritage list in China. Currently, identifying the origin of Linqing brick represents an important issue to be investigated in the field of archeology and architectural history research in China, as it could be used to verify certain assumptions regarding the history of heritage buildings, the resolution for which cannot be obtained by examining the historical documents. Hand Held X-ray fluorescence (HH-XRF) spectrometry enables the in-situ determination of the main elements and concentrations of Linqing brick in a rapid non-destructive manner. HH-XRF may prove to be significant in identifying the origin of Linqing brick. However, HH-XRF could be influenced by certain factors and may be capable of measuring only the element concentrations of the surface for the brick in situ. Which method would provide the most reliable data is an important concern. The aim of the present study was to verify the reliability of HH-XRF and to systematically evaluate the different factors influencing measurement precision and accuracy, in order to assist with scientific advice for the usage of HH-XRF. Four experiments were performed to determine the influencing factors and to assess reliability through cross-validation using inductively coupled plasma optical emission spectrometry (ICP-OES). Finally, the reliability of HH-XRF was ensured, and the scientific advice regarding its application in determining the concentrations of the main elements of Linqing brick was provided.
Keywords: HH-XRF, Linqing brick, origin, impact factors, reliability, scientific advice
1. Introduction

Linqing brick is quite popular in Chinese history. Several architectural heritages have been built mainly by using Linqing brick, such as the Forbidden City, the Temple of Heaven, Ming Tombs, Eastern Qing Tombs, and Western Qing Tombs. In 2008, “The manufacturing process of Linqing brick” was selected as the intangible cultural heritage list in China. Currently, the identification of the origin of Linqing brick is an important concern for the fields of archeology and architectural history in China. A small number of Linqing bricks have inscriptions which contain information regarding the origin. It is impossible to carry the Linqing bricks with inscriptions to the laboratory. Although, an accurate measurement of the main elemental concentrations of these Linqing bricks with inscriptions may be significant for the identification of the origin of Linqing bricks, as it may be used to verify certain assumptions regarding the history of the heritage buildings which cannot be resolved just through historical documents. Hand-Held X-ray fluorescence spectrometry (HH-XRF) allows the determination of the main element concentrations of bricks in a rapid and non-destructive manner. The element concentrations are determined in situ [1].

HH-XRF has applications in the field of archaeology, where it has been used to evaluate the source of archaeological items for several years. For instance, data from HH-XRF were used to divide the sources of obsidian, which assists in addressing the research questions concerning prehistoric mobility, exchange, and social networking in a specific area [2–4]. In consideration of its huge potential in evaluating the source
of obsidian, certain scholars have also conducted research on the influencing factors and reliability of HH-XRF when measuring the obsidian [1, 5, 6]. Speakman et al. even indicated several issues on the reliability of HH-XRF and also provided a few examples of HH-XRF measurements that are valid and reliable [7]. Besides obsidian, several other archaeological items may be studied using HH-XRF, such as the main ingredient of Roman military bronze equipment and the types of raw building materials used in distinct phases of construction [8, 9].

HH-XRF has also been used in combination with other scientific instruments, such as diffuse reflectance infrared Fourier transform and Raman spectrometers, in order to examine the building materials (e.g., bricks) for studying the diseases of buildings. Some scholars focused on estimating the impact suffered by the building materials and studying the degradation processes for the heritage buildings close to coastal areas [10, 11]. Others dedicated their research to study the influencing factors, such as urban atmospheres, infiltration water, and marine aerosol [12–16]. Moreover, rainwater composition and nitrate impact were also important as focus points [17–19].

Using the measured elemental information, related inscriptions, and mathematical methods, one may develop a set of formulae connecting the origin and the elemental information, which would assist in identifying the origin of most of the ancient bricks without inscriptions on the cultural heritage buildings. However, a brick is not the same as obsidian. Meanwhile, when using HH-XRF to identify the origin of bricks, the factors to be considered, and the accuracy requirements for the data are quite different compared to when using HH-XRF to evaluate the building
diseases. Certain factors might influence the accuracy and reliability of HH-XRF, such as the measurement time [20]. Therefore, a scientific method for using HH-XRF to identify the origin of bricks must be established, which would ensure that the measured data are reliable for the next analysis. In the present study, four experiments were performed to assess the different factors influencing measurement precision and accuracy. The reliability was assessed through cross-validation using inductively coupled plasma optical emission spectrometry (ICP-OES). Finally, it was ensured that HH-XRF is a reliable technology and a scientific method to use it for the measurement of the main element concentrations of Linqing brick was determined.

2. Materials and Methods

2.1 Instrument

The instrument used in the present study was Niton XL2-960 GOLDD XRF Analyzer equipped with an Ag anode operating at a maximum of 45 kV and 100 uA. The spot size of the emitted X-Ray beam was 8 mm.

2.2 Samples and elements studied

Twenty bricks were used as samples (Table S1). In experiment 1 and experiment 2, only brick 4 was used. In experiment 3 and cross-validation, all the bricks were used. The main elements studied in the present research were Fe, Ca, K, Al, and Si, the elements with concentrations higher than 1%. However, in order to determine whether HH-XRF could measure all the elements, in experiment 1, the elements with a concentration higher than 0.1% were studied (Fe, Ca, K, Al, Si, Ba, Zr, Mn, Mg, Ti,
The elements studied in experiment 2, experiment 3, and cross-validation (Fe, Ca, K, Al, and Si) were the main elements of the present research.

2.3 Experiment 1: Evaluating the effect of measurement time

In order to evaluate the effect of the measurement time on precision, brick 4 was measured five times at a single point for 60, 90, 120, 150, 180, 210, and 240 s. The point was used for measurement after polishing with a sickle. The relative standard deviation (RSD) value for each element at each measurement time was used to determine the effect of the measurement time on the measurement precision. The US EPA criteria were used to evaluate data quality (Table 1).

2.4 Experiment 2: Evaluating the effect of rain on the day of measurement

In order to evaluate the effect of rain, HH-XRF measurements were performed prior to and after the brick 4 was washed in the rain. The point of measurement was polished with a sickle prior to commencing the measurement stages (prior to the rain and 0 s after rain).

The measurements were performed at 10 time points: prior to the rain, and 0, 1, 2, 3, 5, 7, 9, and 12 h after rain. The measurement conditions were as follows: rainfall 11.2 mm (1 day), the average temperature 24.3 °C (1 day), and average humidity of 69.2% (1 day).

2.5 Experiment 3: Evaluating the effect of surface conditions of the brick.

Providing a surface treatment method and verifying its reliability

In order to evaluate the effect of surface conditions on measurement accuracy and to propose a method for reducing error and verify the reliability of this method,
the following two experiments were performed:

2.5.1 Experiment 3-1: Uniformity of element distribution on the brick surface:

Direct measurement vs. measurement after polishing with a sickle

This experiment evaluated the effect of surface conditions on measurement accuracy and demonstrated how the error rate reduces after polishing with a sickle.

Ten points were identified on each brick surface for measurement. The measurements were performed under two surface conditions: first, a direct measurement (DM), and then a measurement after polishing with a sickle (MPS). The uniformity of the element distribution on the brick surface was determined through RSD for each element from the different points on the same brick.

2.5.2 Experiment 3-2: The difference in concentration between the brick surface and the brick interior

This experiment demonstrated the effect of surface conditions on measurement accuracy and verified the reliability of MPS.

Three fresh sections were cut for each brick that was subjected to measurements. The mean elemental concentrations of these three sections were compared with the mean elemental concentrations of the previous surface points polished with sickles obtained in the experiment 3-1.

2.6 Cross-validation using inductively coupled plasma optical emission spectrometry

The bricks were cut into small pieces, and each brick sample was subsequently ground into a fine powder with particle diameter less than 150 µm. Next, total
microwave digestion was used to digest the sample. The digested sample (500 mg) was placed in a PTFE reactor with 4 mL HNO₃ (70%), 1 mL H₂O₂ (20%), and 2 mL HF (40%). When the foam caused by the decomposition of organic matter disappeared, the container was capped and heated using a microwave digestion instrument named Solutions MD (Beijing Ying’an Meicheng Scientific Instrument company). The heating process was in accordance with a three-stage digestion procedure, which included the first step of three minutes to reach a temperature of 150 °C, the second step of 5 min at 180 °C, and the third step of 5 min to reach 200 °C. After the microwave digestion, the sample was heated in the acid-driven processor. Subsequently, the digest was transferred into a 50-mL flask and brought to volume with MilliQ water. Finally, the diluted digest was analyzed using a PerkinElmer ICP-OES Optima 8300.

2.7 Quality Assurance

The RSD used in experiment 1 and experiment 3-1 is calculated by dividing the standard deviation by the arithmetic mean of the data from the same measurement time or the data from different points on the same bricks. RSD is used to evaluate the precision of measurement time and the uniformity of the brick surface.

The data generated using HH-XRF were assessed using established criteria through cross-validation (Table 1). The RSD, R², and inferential statistics were used to assess a data quality level comparable to the relationship between HH-XRF and ICP-OES.

For the linearity level, if the coefficient of determination (R²) obtained in the
linear regression analysis between HH-XRF and the validation method was greater than 0.7, a Q2 quality level would be achieved. In order to achieve a Q3 quality level, $R^2$ must be greater than 0.85 (Table 1).

In regard to precision requirements, if $RSD \leq 10\%$, a Q3 quality level is achieved. In addition, $RSD = 20\%$ serves as the threshold between the Q2 and Q1 quality levels. $RSD$ is calculated by dividing the size of residual standard error by the mean (Table 1).

In regard to inferential statistics, only the gradient of the line is close to 1, and the y-intercept is approximately 0, indicating a Q3 quality level, implying statistical similarity (Table 1).

If the linear model quality achieves one of the three levels, all three standards should meet the requirement for that level. For instance, if $R^2$ is 0.90 and $RSD$ is 8.0%, while the gradient of the line is close to 0.8, this is a Q2 quality level, implying that the relationship $y = mx$ or $y = mx + c$ would be accepted.
### Table 1 Criteria for characterizing data quality (US EPA)

| Data quality level | Statistical requirement |
|--------------------|-------------------------|
| Definitive Q3      | $R^2 = 0.85$–1. Relative standard deviation (RSD) $\leq 10\%$. Inferential statistics (test for gradient of line = 1 and y-intercept = 0) must indicate the two datasets are statistically similar (at the 95% confidence level), i.e., relationship $y = x$ accepted. |
| Quantitative screening Q2 | $R^2 = 0.70$–1. Relative standard deviation (RSD) $<20\%$. Inferential statistics indicate the two datasets are statistically different; i.e., relationship $y = mx$ or $y = mx + c$ accepted. |
| Qualitative screening Q1 | $R^2 = \text{less than 0.70}$. Relative standard deviation (RSD) $> 20\%$. Inferential statistics indicate that two datasets are statistically different. |

3. Results and Discussion

3.1 Evaluating the effect of measurement time on measurements

Measurement time is important for the accuracy of the obtained data. If an unsuitable measurement time is used, the element concentration in each measurement would be quite different even when the same point is subjected to measurement. Principal components analysis (PCA) is a practical method to analyze the data concerning element information in archaeology. However, if a wrong measurement time is used, the difference obtained between different element information data may not be due to the origin and rather due to the instrument itself.

Certain previous studies have demonstrated that increasing the measurement time could achieve higher precision with lower RSD values [21, 22]. However, RSD does not decrease linearly with measurement time, and an extended analysis may not
result in tangible improvements in measurement precision [23].

A few studies reported using a fixed measurement time, such as 45 s [24] or 60 s [22].

The present study demonstrated that an optimal measurement time is strongly dependent on the element under investigation (Fig. 1). In the case of Fe, Ca, K, Al, and Si, the main research elements of the present study, RSD was less than 5% for each measurement time (Fig. 1a). In the case of Ba, Zr, and Mn, RSD was less than 10% for each measurement time (Fig. 1b). Therefore, it is suggested that 60 s should be selected as the measurement time for Fe, Ca, K, Al, Si, Ba, Zr, and Mn (Table 2). However, for Mg, RSD was 64.93% when 60 s was selected as the measurement time. The RSD value obviously decreased from 64.93% for 60 s to 11.42% for 180 s. This rule was also applicable to Ti (Fig. 1c). Therefore, it is suggested that 180 s be selected as the measurement time for Mg and Ti (Table 2). In the case of Cl, RSD values fluctuated, covering a wide range; at certain times, the values were larger than 30%, while at other times, the values were smaller than 5%, without exhibiting any relationship with the corresponding measurement time (Fig. 1d). Therefore, it was inferred that using a Niton XL2-960 GOLDD XRF Analyzer to measure Cl in a Linqing brick is inappropriate.
Fig. 1 Relationships between measurement time and RSD on precision for Fe, Ca, K, Al, Si, Ba, Zr, Mn, Mg, Ti, and Cl.

Table 2 Suggestions for element measurement times

| Element | Fe  | Ca  | K   | Al  | Si  | Ba  | Zr  | Mn  | Mg  | Ti  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Measurement time | 60 s | 60 s | 60 s | 60 s | 60 s | 60 s | 60 s | 60 s | 180 s | 180 s |

In general, fixing a single precise measurement time for every element is inappropriate. Different elements require different measurement times. Therefore, it is essential to conduct preliminary tests on the element using specific samples to determine the appropriate measurement time for that particular element, which would assist in fulfilling the precision requirements for the survey data.

3.2 Evaluating the effect of rain on measurements

If the brick is washed in rain, photoelectric absorption and scattering will
increase, which may increase the baseline values (noise) and lower the emission peaks (signal), leading to higher limits of detection and reduced apparent concentration [23]. Rain, therefore, exerts a huge influence on the accuracy of measurements conducted using HH-XRF.

The present study demonstrated that all the investigated elements, with the only exception of K, are greatly influenced by rain, and that it takes a long time for the concentrations of these elements to return to the pre-rain values (Fig. 2). In the present study, it took approximately 7 h to return to the concentration value prior to the rain (Rainfall: 11.2 mm; Average temperature: 24.3 °C; Average humidity: 69.2%).
Fig. 2 Variety of concentrations of each element, and their comparison with the concentrations before being washed

Correction of the effect of rain is difficult because determining the appropriate correction factors requires laboratory analysis of the unaffected bricks with a matrix similar to the bricks affected by the rain in the ancient buildings. This analysis would be a complicated procedure difficult to be conducted in the case of in-situ portable testing.

Therefore, it is crucial to perform the measurements on a sunny day, when it has not rained for the previous three days. Meanwhile, if conditions permit, it is better to select measuring bricks located at the inside of the rooms.

If the rain arrives prior to performing measurements, the measurements must be halted. When the rain is over, preliminary tests should be conducted on the brick affected by the rain, and comparison should be made with the concentration value measured prior to the rain to ensure the reliability and accuracy of the obtained data.

3.3 Evaluating the effect of surface conditions of the brick on measurements, providing a surface treatment method, and verifying the reliability of that method
The bricks on the exterior wall of the ancient buildings have been exposed to the external environment for several hundred years, being affected by several factors such as acid rain, humidity [12], dry and wet depositions [15, 16, 19], freeze-thaw cycles [25], and infiltrations by aqueous solutions [17] during the process. These sources of deterioration may promote efflorescence formation, loss of material, and crystalline bloom, particularly on the brick surface [15]. Such factors may greatly influence the surface of the brick. Meanwhile, it is possible to perform measurements on the brick surface only when HH-XRF is used for the in-situ measurements. Therefore, to improve the precision and accuracy of the measurements, an applicable surface treatment method is required to ensure that the measured data could be used to represent the element concentration of the entire brick.

3.3.1 Evaluating the uniformity of element distributions on brick surfaces: DM vs. MPS

It is clear that, regardless of the element under investigation, using MPS may cause the concentrations between every point on the same brick to become similar (Table S2-S6). Interestingly, the differences between the maximum and minimum concentrations within 10 points were under 0.4% for almost all the bricks investigated for elements Fe, K, and Al, while for Si, the differences were under 1%. Only a few points did not satisfy this condition, such as point 1 in brick 1 for K (Table S4); these specific values should be ignored as exceptions. In regard to Ca, certain cases are similar to those for Fe, K, and Al, while in other cases, the concentration difference between points is huge (Table S3), which might be led by the concentration
distributions for the bricks itself. Therefore, if this phenomenon occurs, the value
measured for this element of this brick should be discarded.

In order to ensure the accuracy of the measurements, 10 points must be selected
on each brick for measurement. The mean concentration value of these 10 points
would represent the elemental concentration of the brick (ignore the specific value). If
the concentration difference for the element between each point is huge, then that
brick should be discarded for this element. Each point must be polished with a sickle
prior to performing the measurement, as it may improve the accuracy of the
measurement.

3.3.2 Evaluating the concentration differences between brick surfaces and
interiors

In order to verify the reliability of MPS, just observing the uniformity of the
surface is not sufficient. In order for a phenomenon such as efflorescence, loss of
material, and crystalline bloom to occur, the differences between the surface element
concentrations and the internal element concentrations of the brick must be larger than
those of a new brick. Therefore, it is crucial to analyze the concentration differences
between the surfaces and the interiors of the ancient brick.

It is clear that the value differences between the sections and the points were not
much large for most cases. However, for K and Ca, there were a few cases that
exhibited large differences between the sections and the points (Table S7). The main
reason for this was that Ca and K were greatly affected by crystalline bloom, while the
elements Fe, Al, and Si were affected less by this phenomenon.
In regard to this phenomenon, it would be better to select a brick located on a higher position in the wall. In comparison to the bricks close to the ground, capillary suction of the wall at a higher position is much smaller. Therefore, crystalline bloom at a higher position would be lighter, leading to a lesser impact on K and Ca. Meanwhile, if conditions permit, it is better to select the bricks inside a room of the ancient building for the measurements.

3.4 Correlation and linear regression analysis

In a previous study, several laboratory techniques, excluding ICP-OES, were used to perform cross-validation in order to assess the reliability of HH-XRF. Examples of such techniques are atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

For instance, certain researchers employed ICP-OES to perform cross-validation [21, 26, 27]. In 2009, Radu assessed the reliability of FPXRF using AAS [24], while certain other scholars employed ICP-MS [23, 26, 28–30] and ICP-AES [31–33] to conduct the comparison using FPXRF.

In the present study, ICP-OES was employed to conduct the cross-validation of Fe, Ca, K, Al, and Si. XRF analysis targets all the atoms present within the limits of critical penetration depth, irrespective of the mineral structure. Aqua-regia hot-plate dissolution prior to conducting the ICP-OES/MS analyses has been demonstrated to result in reduced recovery of elements, in certain cases, compared to the microwave extraction protocols incorporating hydrofluoric acid for the break-down of silicate
phases [23]. In this context, total microwave acid digestion, which is suitable for
organic-rich and silicate-containing media with proven recoveries approaching 100%,
was used in the present study to ensure maximum comparability between the
HH-XRF and ICP data.

In order to verify the reliability of the HH-XRF results in the present study,
correlation regression analysis was performed between the concentration values
measured using ICP-OES and those measured using HH-XRF (Fig. 3). In case of Fe,
Al, and Si elements, all the 20 bricks were used, while for K and Ca, 16 and 12 bricks
were used, respectively, after removing certain cases in which either the surface was
not uniform or the difference between the surface and the interior was huge.

In the case of Fe, Al, and Si, the coefficient of determination was greater than
0.85, implying that a Q3 quality level was achieved (Fig. 3a and 3c-3d). In the case of
K, a Q2 quality level was achieved (Fig. 3b). All these four elements fulfilled the
precision requirements for Q3 level (<10% RSD). In addition, for the inferential
statistics (gradient and intercept), all these four models fulfilled the requirements for a
Q2 quality level, i.e., the relationship \( y = mx \) or \( y = mx + c \) was accepted.

In the case of Ca, even after removing certain values as stated in 3.3.1 and 3.3.2,
the \( R^2 \) for this element reached only 0.61. Therefore, the reliability of HH-XRF for Ca
was not satisfactory (Fig. 3e).

In the case of Fe, K, Al, and Si, the value obtained using ICP-OES was used to
correct the value from the HH-XRF measurements. The equation used for this
correction was:
Sample corr = \frac{Sample_{meas} - c}{m}

where \(Sample_{corr}\) represented the corrected concentration of the investigated sample, \(Sample_{meas}\) denoted the raw concentration of the investigated sample, and \(c\) and \(m\) represented the intercept and the gradient of the linear model obtained from XRF and ICP-OES results, respectively.

After this correction, the corrected values were much closer to the values obtained using ICP-OES. When HH-XRF is used to perform the in-situ measurements of elements Fe, K, Al, and Si, a few bricks that have the same matrix as the target bricks should be selected to perform a preliminary experiment in order to conduct a correlation regression analysis between HH-XRF and ICP-OES, which would provide a cross-validation correction for the values that were measured in situ.
The correlation regression analysis for HH-XRF data and ICP-OES concentrations for elements: Fe, K, Al, Si, and Ca. The US EPA criteria were used to evaluate precision (Table 1). The solid red line is the fitted linear regression, the dashed black line is 1:1 ratio, the dashed blue line represents the 95% confidence limit.

### 4. Conclusion

It was concluded that HH-XRF is a reliable instrument for the in-situ determination of the main elements, with the exception of Ca. Owing to the complex conditions of bricks in situ and the characteristics of HH-XRF, a scientific method is necessary. The scientific suggestions for the application of HH-XRF in in-situ measurements provided in the present study are as follows: (1) The suggestions for measurement times are presented in Table 2. However, a suitable measurement time must depend on the target elements and samples. Preliminary tests must be performed to determine appropriate measurement times for the target elements to ensure measurement precision; (2) Selecting a sunny day, when it has not rained for the previous three days, is important. If it begins raining during the measurements, it is essential to halt the measurements and to compare the concentrations measured after the rain and prior to rain in order to ensure measurement accuracy; (3) In regard to the
surface conditions of the bricks, 10 points should be selected for the measurements, and a sickle should be employed for polishing the measurement point. The specific values should be removed. If for certain elements, the surface is not uniform, the brick should be discarded for those elements. In order to avoid the influence of factors such as crystalline bloom and acid rain, the brick located at a higher position in the wall should be selected. If conditions permit, it is better to select bricks from a room of the ancient building; (4) In case of elements Fe, K, Al, and Si, a few bricks should be used in a preliminary experiment that would allow a correlation regression analysis between HH-XRF and ICP-OES (or any other reliable laboratory method), as it would provide cross-validation corrections for the values measured in situ.

**List of abbreviations**

HH-XRF: Hand-Held X-ray fluorescence spectrometry;

ICP-OES: Inductively coupled plasma optical emission spectrometry;

RSD: Relative standard deviation;

DM: Direct measurement;

MPS: Measurement after polishing by sickle;

PCA: Principal components analysis;

AAS: Atomic absorption spectroscopy;

ICP-MS: Inductively coupled plasma mass spectrometry;

ICP-AES: Inductively coupled plasma atomic emission spectroscopy
Availability of data and materials

All data generated during this study are included in the article.

Competing interests

The author declares that they have no competing interests.

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Authors’ contributions

All the authors contributed to the current work. ZXC and LZ planned and conducted the experiments and collected the data. ZXC and LZ performed the analyses and wrote the article. JLX assisted in experiment 3-1. FH supervised the entire process and provided constructive advice. All authors read and approved the final manuscript.

Corresponding authors:

Correspondence to Zexuan Chen or Long Zhang or Feng Hou.

Co-first authors:

Zexuan Chen and Long Zhang

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None

**Author details**

1. Tianjin International Engineering Institute, Tianjin University, Tianjin 300072, People’s Republic of China.

2. School of Architecture, Tianjin University, Tianjin 300072, People’s Republic of China.

3. Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People’s Republic of China.

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