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Research Article

Making Marble Powder Waste Profitable by Using Nano-TiO_2 Surface Modification for Air Quality Improvement Applications

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We report a brand new recycling route of waste marble powder, by means of surface modification with homemade nano-TiO_2 particles to produce low cost coating materials for the application in air quality improvement. The as-prepared nano-TiO_2 in anatase phase exhibits excellent photocatalytic characteristic, reflected by the high degradation rate of over 95% of methylene blue within 6 hours of UV irradiation. The prepared coating consisting of nano-TiO_2 clad marble powder was tested by monitoring the decomposition rate of formaldehyde gas. A high degradation efficiency of about 95% within 9 hours of illumination is achieved, demonstrating a promising potential for removing the harmful and toxic organic pollutants in air while applying this coating in buildings both interiorly and exteriorly.

1. Introduction

Stones, especially marble, are commonly utilized in buildings and for decoration. However, a tremendous amount of marble powder waste will be produced while cutting and polishing these high numbers of marble raw materials. The micrometer- or submicrometer-sized marble powder is prone to drift into air, polluting the atmosphere by increasing the particulate matter content in air. Additionally, the marble powder can be easily inhaled by local workers and residents, causing serious lung diseases. Recently, awareness of such issue has been raised by the local environment departments of the stone product manufacturing sites, as well as researchers who focus on the recycling applications [1–3].

Nowadays the reuse of the waste marble powder concentrates upon incorporating the waste marble into the traditional construction materials, such as cement and concrete, to tailor their mechanical properties [3–7]. For instance, Aliabdo et al. found a 9% improvement in the compressive strength of cement when 10% marble powder was added to it [4]. It was also found that a 16% enhancement in the tensile strength was observed when 10% of the sand in the concrete was replaced with marble powder [5]. In addition, Bilgin et al. reported a linear increase in the hardness of the bricks with the content of incorporated marble powder [6].

However, few studies report on the recycling of the marble powder by combining nanomaterials or utilizing nanotechnologies. In this paper, a completely new way to reuse the waste marble powder was introduced, transforming the waste into functional coating with the help of nanomaterials. The milled and screened waste marble powder in micrometer size was clad with homemade highly dispersive nanometer-sized TiO_2 particles and was finally made into a new type of environmentally friendly and low price paint. Owing to the surface modification with the photocatalytic nanomaterial, the paint can decompose harmful and toxic pollutants in air, such as formaldehyde, benzene, volatile organic compounds (VOCs), and nitric oxides (NO_x) and sulfur oxides (SO_x) from vehicle exhaust [8–10], improving the air quality of human living environment both interiorly and exteriorly. In addition, the effectiveness of the degradation of hazardous organics by the novel coating materials based on the waste marble powder was studied and characterized in this work. Such coating holds a great potential for large-scale applications in buildings.

2. Materials and Methods

2.1. Coating Fabrication. Chemically pure (98% purity) titanium butoxide (TBT) purchased from Aladdin was mixed with ethanol with a massive ratio of 1 : 8 in a 150 ml reaction kettle. Then the reaction kettle was placed into an oven, maintaining a temperature of 160°C and a reaction duration of 12 hours. Then the reaction product was filtered, washed, and dried, producing highly dispersive TiO_2 nanoparticles, as described in [3, 11, 12]. 3 g of the prepared nano-TiO_2 was added to 40 g ethanol and then was sufficiently dispersed by using the ultrasonic bath for about 30 minutes.

The waste marble powder was milled by using a ball grinder and 1~5 mm zirconium balls as the milling media. Then the marble powder of large size was reduced into micrometer or submicrometer size, followed by screening with different meshes. 7 g of the milled and screened marble powder was added to 50 ml ethanol and stirred on a stirrer at a speed of 700 revolutions per minute (rpm). During the stirring, 50 ml of the as-prepared nano-TiO_2 dispersion was incorporated into the marble powder dispersion through a constant pressure hopper, at a rate of 5 drops per second. Then the mixture was continuously stirred for another 5 hours. Finally, a novel low cost paint based on the waste marble powder was fabricated.

2.2. Characterizations and Tests. The crystal structures of the materials were characterized by X-ray diffraction (XRD) using a Rigaku Smartlab 9 kW X-ray diffractometer, equipped with a Cu-$K_{\alpha 1}$ radiation source (λ = 1.5406 Å). Scanning electron microscopy (SEM) was employed to investigate the microstructure of the materials, using a JEOL 6490 microscope at an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) images of the as-prepared titanium dioxide were recorded through a JEM-2100F field emission scanning transmission electron microscope equipped with an Oxford INCA x-sight EDS Si(Li) detector at an acceleration voltage of 200 kV. The absorbance variation and degradation of methylene blue solution by the as-prepared nano-TiO_2 were carried out by using a Shimadzu UV-1800 spectrophotometer, and the tests followed the standard ISO 10678:2010.

3. Results and Discussion

Figure 1 shows the XRD θ-2θ diffraction patterns of the waste marble powder, highly dispersive nano-TiO_2 prepared by our research group, and the titanium dioxide coated marble powder, respectively. The upper curve shows the marble powder diffraction peaks, which match well with JCPDS data of rhombohedral structured $CaCO_3$ (Card Number 02-0623), indicating that the waste marble powder mainly consists of $CaCO_3$. According to JCPDS Card Number 01-0562, the middle curve suggests the as-prepared titanium dioxide is in the form of anatase crystal structure, which possesses highly efficient photocatalytic property [13–16]. The lattice constants are obtained as a = 3.73 Å, b = 3.73 Å, and c = 9.37 Å, respectively. Nano-TiO_2 in anatase phase, belonging to the wide band gap semiconductor materials [17–19], is extensively applied to the photocatalysis field, also because of its inexpensive, abundant, and nontoxic constituent elements [14, 20, 21]. It is obviously seen that the lower spectrum is a superposition of the upper and middle ones, implying the micrometer- or submicrometer-sized marble powder surface is sufficiently modified with the nano-TiO_2. The TiO_2 clad marble powder then could decompose the harmful and toxic organic pollutants due to its strong photocatalytic property under sunlight illumination [13–16].

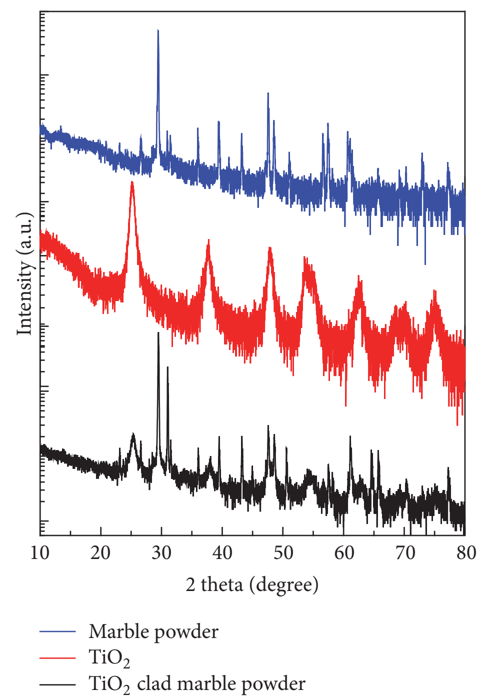
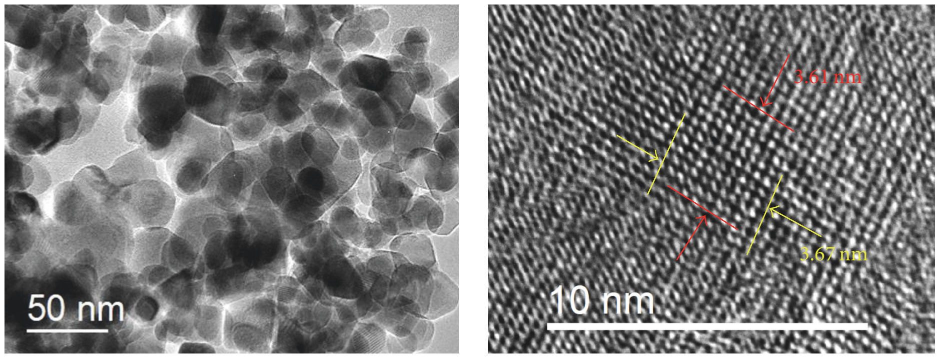


FIGURE 1: XRD spectra of marble powder (upper), as-prepared TiO_2 (middle), and TiO_2 clad marble powder (lower).

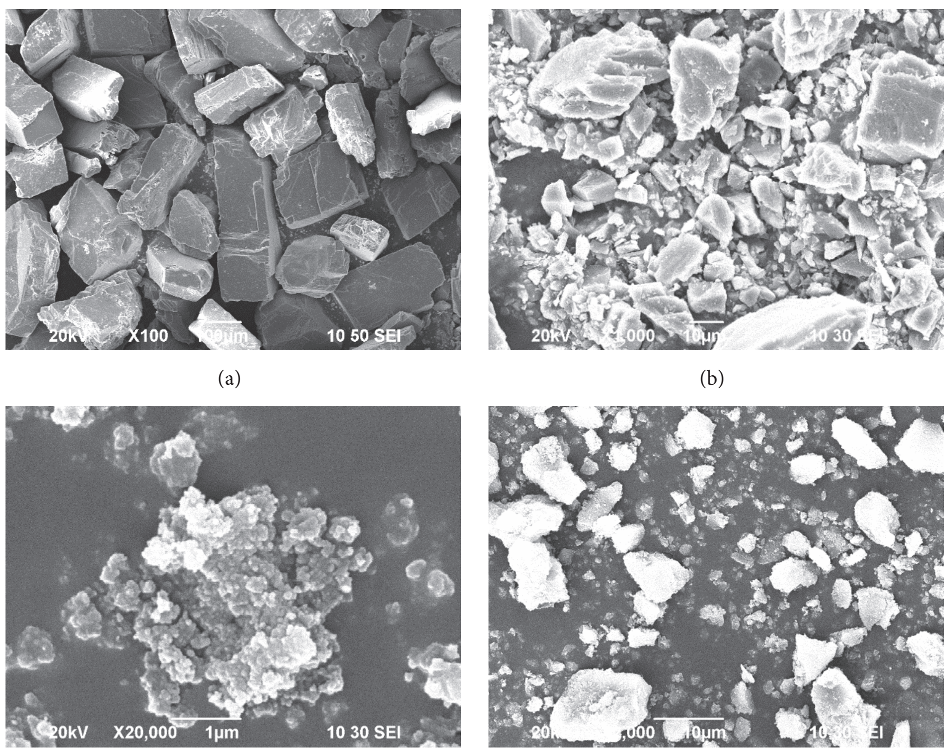
TEM images reveal the microstructure of the as-prepared highly dispersive nano-TiO_2, as illustrated in Figure 2. It is observed that the as-prepared TiO_2 crystal size is in the scale of several tens of nanometers, as shown in Figure 2(a). In addition, Figure 2(b) indicates that the lattice constant of nano-TiO_2 is 3.64 Å on average in the (001) plane, in reasonable agreement with the parameters deduced from the above XRD data. These data confirm the anatase crystal structure of the as-prepared nano-TiO_2 particles.

Corresponding to Figure 1, the microstructures and morphologies of the marble powder, nano-TiO_2, and TiO_2 clad marble powder were also examined by using a JEOL 6490 scanning electron microscope, which is equipped with an energy dispersive spectroscopy detector (EDS), as shown in Figure 3. The waste marble powder was milled or screened, producing micrometer-sized powder, as shown in Figures 3(a) and 3(b). The elements and their content in the marble



(a) (b)

Figure 2: TEM images of the as-prepared nano-TiO_2: (a) bright field image and (b) high resolution image.



(a) (b)

(c) (d)

Figure 3: SEM images of marble powder (a, b), nano-TiO_2 (c), and TiO_2 clad marble powder (d).

powder were examined by using EDS. As listed in Table 1, carbon, oxygen, and calcium elements were detected with an atomic ratio of around 18 : 54 : 25, confirming that the waste marble powder consists predominantly of $CaCO_3$. It should be noted that the appearance of gold in the testing originates from the gold-coating on the sample surface to facilitate the SEM characterization. Figure 3(c) shows the morphology of the as-prepared TiO_2, while the TiO_2 clad marble powder is displayed in Figure 3(d). It is confirmed by EDS that the nano-TiO_2 particles are connected to and entirely coated on the micrometer-sized marble powder surface, making an efficient cladding and rough surface to play the full role of the photocatalytic function.

To assess the degradation efficiency of hazardous organics by the prepared nano-TiO_2 by way of its photocatalytic activity, a methylene blue degradation test was carried out according to the standard of ISO 10678:2010 [22–25]. Firstly, 0.4 mg methylene blue powder was dissolved sufficiently into 100 ml deionized water, followed by adding 12.5 mg as-prepared TiO_2 nanoparticles into the solution. Then the mixture was stirred on the magnetic stirrer at a speed of 700 rpm for 30 minutes. Before each measurement of the absorbance between the wavelengths at 500 nm and 700 nm performed on the UV-visible spectrophotometer, the solution was illuminated under a UVA lamp with an irradiation wavelength of 365 nm for 1 hour. Then the degradation percentage

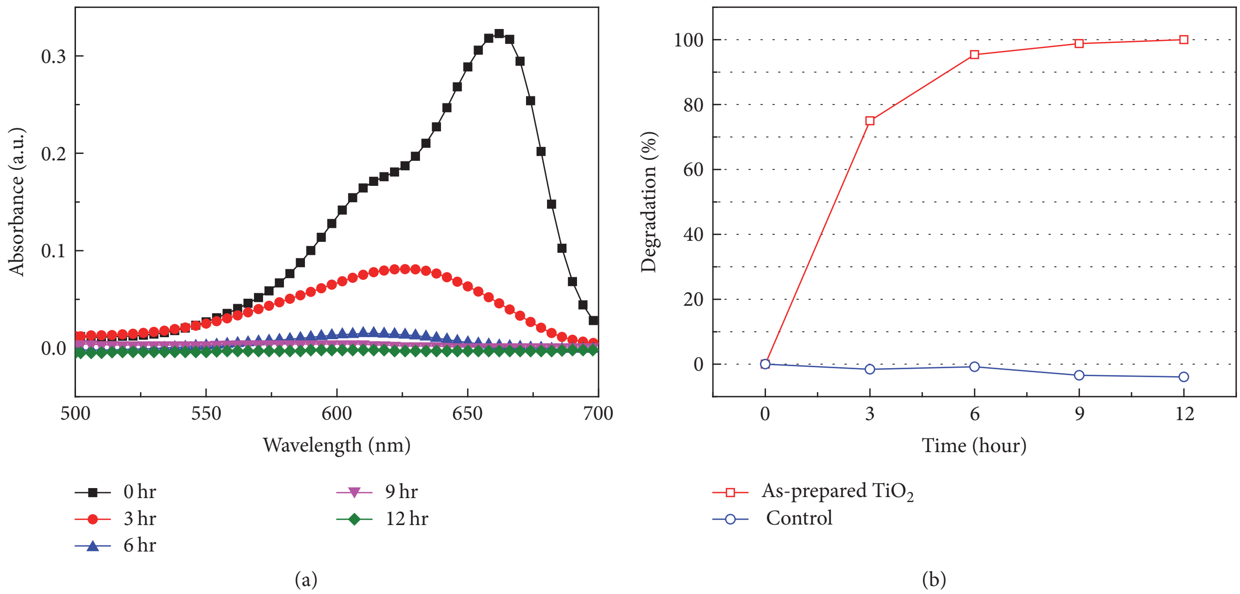


Figure 4: Methylene blue absorption as a function of wavelength at the varying durations (a) and the evaluated degradation efficiency with time (b).

Table 1: Elements and their content detected in the marble powder.

Element	Weight%	Atomic%
C	8.82	18.32
O	34.86	54.34
Ca	40.78	25.37
Au	15.54	1.97
Totals	100.00	

of methylene blue against the duration was derived from the absorbance variation [23]. The dependence of methylene blue absorbance on the wavelength at different duration is plotted in Figure 4(a). It is seen that the light absorption of methylene at wavelength of about 660 nm is significantly reduced to be negligible when the solution is irradiated under the UVA lamp for about 6 hours. As shown in Figure 4(b), the degradation efficiency reached 95.4% after 6-hour irradiation, and the figure was raised to 98.7% when the duration lasted 9 hours. This test shows a strong photocatalytic property of the as-prepared TiO_2 nanoparticles, demonstrating an effective and efficient approach to decompose the hazardous organics around human living environment.

The high performance nano-TiO_2 was then incorporated into the micrometer-sized marble powder and finally was made into a type of coating or paint. To evaluate the performances of this coating, a degradation experiment on formaldehyde gas was conducted, simulating the degradation of harmful and toxic gasses while applying this paint in human living environment. First, the paint was coated on three pieces of A5-sized glasses, of which two were vertically placed against the inside walls of a transparent acrylic box with a dimension of $360 \times 160 \times 160\,mm^3$ and the other one lying on the inside bottom of the box. Before testing, four drops of formaldehyde solution with a concentration of ~38.5% were put on a glass slide, which also lies on the inside bottom of the transparent acrylic box next to the lying A5 sized glass. At the same time, a formaldehyde detector with a Dart 2-FE5 sensor inside was placed on the lying A5 sized glass in the acrylic box. Finally the box was sealed by a transparent acrylic cover with a rubber ring. After the saturation of the evaporated formaldehyde in the box, a UV lamp of 20 Watt power (model number L6274Z) was placed on the box cover and turned on to provide UV illumination, and immediately the data was recorded. Figure 5 shows the variation of formaldehyde concentration with the irradiation duration. A reduction in the formaldehyde concentration is clearly monitored from $2.371\,mg/m^3$ to about $1.109\,mg/m^3$ after 3 hours of irradiation under the UV lamp, corresponding to a degradation rate of 53.2%. The degradation rate reached approximately 95% after 9 hours and the figure increased to about 98% after 12 hours of illumination. The experimental data show a high performance on the decomposition of formaldehyde harmful gas. This demonstrates that the novel coating holds great potential for applications in the interior and exterior walls of buildings, effectively decomposing the harmful and toxic pollutants in air and greatly improving the indoor and outdoor air quality.

4. Conclusions

The marble powder waste, originating from the stone product manufacturing, would bring severe problems associated with living environment and human health. To recycle the waste in an environmentally friendly and cost effective way and make the waste profitable, a new strategy of incorporating nanomaterials was introduced in this work. A novel coating or paint combining the micrometer-sized waste marble

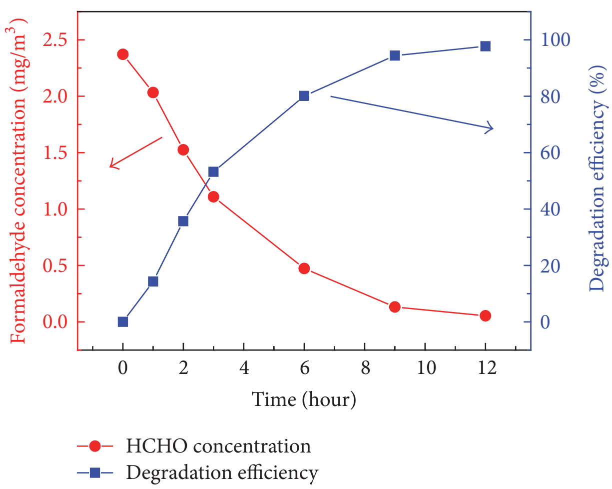


FIGURE 5: The variation of formaldehyde concentration and degradation rate with UV irradiation time.

powder and homemade nano-TiO_2 particles was prepared. The as-prepared nano-TiO_2 shows anatase crystal network and excellent photocatalytic performance, mirrored by the high degradation rate of methylene blue solution. A formaldehyde-decomposing test was conducted to simulate the degradation of hazardous organics in air while applying the coating on building surfaces. A high degradation efficiency of about 95% with 9 hours of UV irradiation is achieved, proving the effectiveness in air quality improvement. This novel coating made of waste marble powder and photocatalytic TiO_2 nanoparticles has great potential for applications in buildings for purifying the environmental atmosphere.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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