



Geopolymer-supported photocatalytic TiO₂ film: Preparation and characterization



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HIGHLIGHTS

- TiO₂ films are chemically coated onto porous geopolymer substrates.
- A modified sol-gel dip coating method is used to relieve cracking and improve morphology of TiO₂ films.
- TiO₂ film prepared under proper processing conditions exhibits good photocatalytic efficiency.

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ABSTRACT

The article reports preparation and characteristics of TiO₂ films deposited on geopolymer substrates via sol-gel dip coating process. Serious cracking takes place within TiO₂ film derived from sol precursor with butyl titanate as titanium source and prepared by traditional dip-coating process on geopolymer substrates. It is found that the incorporation of 6% Polyvinylpyrrolidone, and the application of vacuum impregnation before withdrawing relieve cracking significantly, and the resulting TiO₂ film exhibits mesoporous morphology. The TiO₂ film annealed at 600 °C is mainly composed of anatase phase, and exhibits highest photocatalytic activity evaluated by degrading methylene blue. Multilayer dip-coating promotes photocatalytic activity of the obtained TiO₂ film in some extent, but decreases in photocatalytic efficiency and homogeneity are observed when the number of coating layers is over 3.

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1. Introduction

A variety of construction and building materials including window glass (soda-lime glass) [1,2], ceramic [3,4], cement-based materials [5,6], and bricks [7] have been used for support (or substrate) to immobilized TiO₂ for environmental applications such as air purification, self-cleaning. In the case of cementitious materials, nano-TiO₂ is usually immobilized in the form of either powder or slurry. However, the combination of TiO₂ and cementitious materials in such physical manners (TiO₂ powder blending, or TiO₂ slurry infiltrating) suffers from some problems including low photocatalytic efficiency, weak wear-resistance and possible corrosion of the cement-based supports [3,8,9]. Coating TiO₂ films onto supports via sol-gel process is an efficient approach to promote photocatalytic efficiency and improve wear-resistance of the TiO₂ film [10,11]. Sol-gel process involves annealing treatment of the amorphous precursor to induce crystallization. TiO₂ exists as three different polymorphs: anatase, rutile and brookite, among which

anatase possesses highest photocatalytic activity [12]. The annealing temperature to stabilize anatase phase, varies between 400 °C and 800 °C, depending on starting materials and processing conditions. Therefore, cementitious materials are not suitable supports for coating TiO₂ film through sol-gel process because of decomposition of hydration products (C-S-H gel, portlandite, ettringite and AFm phases).

Geopolymers exhibit much better thermal stability than cementitious materials [13–16] due to their inorganic framework or ceramic-like nature. In our previous study [17], thermal stability of geopolymers synthesized with fly ash, metakaolin as aluminosilicate sources was investigated in order to verify the feasibility of using geopolymers as supports for TiO₂ film coating via sol-gel process. It was found that geopolymers synthesized with appropriate fly ash content exhibit good thermal stability and can be used as substrate to support TiO₂ film via sol-gel process, thus make it possible to be applied on the surface of building or wall in form of tiles to diminish pollution such as CO, NO_x and volatile organic compounds (VOC's).

Cracking is commonly observed within films prepared through sol-gel process under certain conditions, and the factors affecting

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formation of cracks include compositions of the precursor, drying rate, film thickness, annealing temperatures [18,19] as well as the difference in coefficients of thermal expansion (CTE) between the film and the substrate [2]. The article reports the preparation of TiO₂ films on geopolymer substrates by sol-gel method; effects of precursor sol modification and processing conditions on morphology and photocatalytic efficiency of the TiO₂ films were investigated in the study.

2. Experimental

2.1. Materials

Class F fly ash and metakaolin were used as raw aluminosilicate sources in this study. Their chemical and phase compositions are shown in Table 1, XRD pattern and particle size distribution of the used materials were reported in our published article [17].

D-grade potassium silicate (15.5 wt% K₂O, 24.0 wt% SiO₂, 60.5 wt% H₂O) and laboratory grade potassium hydroxide (KOH, flakes with 95% purity) were used as the alkali sources in the study because geopolymer prepared using K-containing activators was reported to have better high-temperature resistant properties than those synthesized using Na-containing activators [20,21].

The substances used for TiO₂ film coating were analytical pure butyl titanate (Ti(C₄H₉O)₄, 99% purity), ethyl alcohol (C₂H₅OH, 99.8% purity), and diethanolamine (NH(CH₂CH₂OH)₂, 99% purity). These substances were used as titanium source, solvent and hydrolysis inhibitor respectively. Polyvinylpyrrolidone (PVP, K30, Mw = 58,000) was also used to modify the titania sol.

Methylene blue (MB, C₁₆H₁₈ClN₃S) dye was used for evaluating of photocatalytic activity of obtained TiO₂ films.

2.2. Preparation

2.2.1. Geopolymer substrate synthesis

Alkali-silicate activator with a modulus (molar ratio of SiO₂ to K₂O) of 1.0 was prepared by dissolving potassium hydroxide and adding extra deionized water in appropriate potassium silicate solution. The proportion of alkali-silicate activator was as follows: 100 g potassium silicate solution + 26.4 g KOH + 4.1 g H₂O (alkali concentration = 5.8 mol/kg). Obtained solution was stored for a minimum of 24 h prior to use.

According to our previous study [17], the mixture of 95% fly ash and 5% metakaolin (by mass) was used as raw aluminosilicate source for synthesizing geopolymer, considering the thermal stability, strength at ambient temperature and possible efflorescence associated with very high fly ash content [22]. Geopolymer pastes were prepared by mixing the mixture of fly ash and metakaolin for 2 min, then adding alkaline activator solution (solution to binder ratio = 0.50) and mixing for another 10 min. Geopolymer paste was cast into Φ50 mm × 5 mm PVC molds which were placed on a smooth glass plate to obtain slice substrate. The cast fresh specimens were vibrated until no visible bubble released, covered with plastic films and stored in a climate chamber (20 °C, 90% RH) for curing. Geopolymers gain their strength quickly and the increase in strength beyond 48 h is not very significant [13]. According to our previous research [17], the compressive strength of geopolymer synthesized with 100% FA can reach a relatively high level at 14 days. So, in this study specimens were demolded after a period of 14 days of curing, then ultrasonically cleaned, rinsed using deionized water, acetone and finally vacuum dried for 7 days. All slices were then stored in desiccators until film coating. It should be noted that, the purpose of vacuum drying and storage is to remove free water to minimize damage caused by water immigration during the subsequent thermal treatment.

2.2.2. Sol preparation

A typical precursor sol composition was used according to the system of Ti(C₄H₉O)₄-C₂H₅OH-H₂O [23]. 20 ml of butyl titanate and 4.5 ml of diethanolamine were dissolved in 75 ml of ethyl alcohol. The mixture was homogenized with mag-

netic stirring for 1 h, and then 3 ml of de-ionized water and 15 ml of ethyl alcohol were added drop-wise into the former solution while stirring. The sol was stirred for another 1 h. The incorporation of diethanolamine was to form a complex through the reaction between butyl titanate and diethanolamine, so as to increase the stability of TiO₂ sol [18]. In some cases, a certain amount of PVP was also added and dissolved along with diethanolamine for the purpose of sol modification. All obtained sols were aged for 24 h before the use, allowing equilibrium between hydrolysis reaction and polycondensation of butyl titanate. However, prolonged aging time may lead to excessive volatilization of ethyl alcohol and gelation.

2.2.2.1. Films coating. The slices were dip-coated with a withdrawing speed of 10 mm/s on a DNS-100 electronic universal testing machine under a displacement control mode. In the case of applying vacuum impregnation, prepared sol was placed in a beaker, then the geopolymer slice was dipped in the sol. The beaker is subsequently placed in a desiccator which was connected to a vacuum pumper. Prior to withdrawing, the substrate was vacuum impregnated with the sol in the desiccator until no visible air bubbles came out from the porous substrate. Dip-coated samples were dried in an oven at 50 °C for 30 min, then cooled down to ambient temperature. The above-mentioned operations were repeated for multi-layer films coating. After drying, dip-coated slices were annealed at 500 °C, 600 °C, 700 °C, 800 °C respectively at a speed of 5 °C/min and maintained at the target temperatures for 1 h.

2.3. Film characterization

Crystallographic properties of the films were investigated with grazing incidence X-ray diffraction (GIXRD, X'Pert PRO, PANalytical B.V.). The diffractometer using the Cu Kα radiation was operated at 40 kV, 40 mA with an incident beam angle of 0.3°, 2-theta ranging from 20° to 60°.

Sol films after drying were observed with an optical microscope (Ge-5, Aigo). The surface morphology of the resulting TiO₂ films were observed using a scanning electron microscope (SEM, Quanta FEG 250, FEI) under the secondary electron (SE) mode.

2.4. Photocatalytic activity evaluation

The test method for evaluating photocatalytic activity is based on Chinese Standard GB/T 23762-2009. Methylene blue powder was dissolved in deionized water at 10 mg L⁻¹ concentration. For a more precise evaluation of photocatalytic efficiency, one side of coated geopolymer slices was polished with SiC paper (1200# Struers) to remove the coated film prior to MB decomposition measurement. A geopolymer slice was placed in a thermostatic cup with the dip-coated side upwards, and then 200 ml of the solution was added. The thermostatic cup was connected to a thermostatic water bath which was set at 20 °C. The thermostatic cup was placed on a mechanical shaker at 20 rpm in an UV chamber with 4 UV lamps (LP Hg lamps, 8 watts, main light emission at 254 nm) with an overall irradiance of 2.5 mW/cm². Fig. 1 schematically shows the device of decomposition of methylene blue. The UV irradiance was monitored regularly using an UV meter (ZDZ-1, Shanghai Jiading).

4 ml MB solution was collected every 60 min, and analyzed using an UV-vis spectrophotometer (756PC, Shanghai Hengping). In order to maintain the volume of the solution in the thermostatic cup, the samples were placed back after each measurement. The spectrophotometer was calibrated with solutions of MB at 1 mg/L, 3 mg/L, 5 mg/L, 7 mg/L, and 10 mg/L concentrations respectively. Curves of wavelength-absorbance as shown in Fig. 2(a) indicate that the maximum absorbance of MB occurs at 655 nm. Fig. 2(b) shows the calibration curve of the spectrophotometer.

In order to correct the possible decomposition of MB under UV light in absence of any photocatalyst, the concentration of 200 ml of MB solution (10 mg/L) was measured under identical testing conditions. A dip-coated geopolymer slice was immersed into 200 ml of MB solution (10 mg/L), then the sample and the solution were stored in a black box, the concentration of MB was also measured every 60 min to evaluate the absorption of MB by the geopolymer substrate.

Table 1
Chemical and phase compositions of raw materials (%).

	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	Others	L.O. ^a
Fly ash	29.8	53.2	2.8	6.1	0.87	0.55	0.34	1.84	4.5
Metakaolin	45.3	51.1	0.26	0.65	0.25	0.14	0.17	1.43	0.7
	Mullite	Quartz	Hematite		Anhydrite		XRD amorphous		
Fly ash	25.9	9.0	1.9		1.9		61.3		
Metakaolin							~100		

^a Loss on ignition.

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