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Nanostructural Properties of Cement – Matrix Composite

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ABSTRACT

Nanotechnology progress in concrete science offers the opportunity to enhance the understanding of the effects of nano-particles in concrete, to engineer its properties and to lower production and ecological cost of construction materials with the potential of improving concrete properties by modifying the structure of cement hydrates and controlling the delivery of admixtures. In the present work, Titanium dioxide (TiO_2) is added to cement, which can impart self-cleaning and smog-abating functionality to cement based materials. Different types of cement containing nano-sized titania (TiO_2) particles are prepared by sol gel method in an ambient media, which contained 2 - 10 wt% TiO_2 nano- particles and other usual materials in cement. After two months, contents are analyzed and studied for evaluation of stability using Atomic Force Microscopy (AFM) – tapping mode and X- Ray Diffraction (XRD) techniques. The objective of this research is to study the effect of the TiO_2 nanoparticles on the rate of hydration and dimensional stability during early stages of cement hydration.
KEY WORDS: Nanostructures, Cement, Nano-composite and sol– gel method.

1. INTRODUCTION

In general, any ordinary concrete usually consist several simple materials such as sand, coarse aggregates, admixtures and water. Although the precent of cement in this combination plays a main role, the scale of its size can change the concrete properties. Furthermore existence of nano- particles like titania nano – particles can allow concrete to be produced in a relatively different fluid form with complex chemistry and physical structure. This issue can make concrete to have a good potential to contribute to more stability and reliability and provide further insight into the nature of hydrated cement phases and their interaction with admixtures. These interactions offer the possibility of modifying cement reactions, creating new surface chemistries, developing new products for the concrete industry and allowing a more controlled and ecologically friendly manufacturing route to cement and concrete [1-7].

There are nano-sized air voids in the cement and the aggregate which may have significant effects on the nano-composite's mechanical properties [8-11]. Many researchers have studied the effects of nano- particles on mechanical and thermal properties of mortar cement and concrete by incorporating nano-materials into matrix composite. We have demonstrated a series of experiments to synthesis nanostructure cement with nano- anatase titania and zycosil materials. The obtained results show not only a homogeneous and stable structure of cement, but also the nano- structural properties could emerge a situation, quite different in the area of cement-matrix composites, because of its relative loose structure. Moreover, existence nano particles in cement can make much more rooms for improvement of cement composites by incorporating nano-materials into the cement-matrix. Researchers [12-16] have noted that the addition of fine TiO_2 – anantas phase nano- particles in cement can change the early hydration reaction of cement with potential implications relating to setting time, dimensional stability and strength development, which will be discussed in the next future.

However, the addition of fine TiO_2 – anantas phase nano- particles, found here, could also affect the dimensional stability of a cement mix by increasing shrinkage of the cementitious material [2]. We have tried to synthesis nano- scale cement and titana to find a suitable and optimize size, to modify the hydration reaction but not significantly affect the dimensional stability of the cement system. These issues as found in [2,3], cause changes to the mechanical properties of pavement concrete. It means the effects of nano- particles on the flexural, compressive and splitting tensile strengths of pavement concrete are so important. We found as researchers [2,3] found before, that the mechanical properties of pavement concrete will be increased with more nano-particles, whereas the mechnical properties of pavement concrete reduced with the increasing content of nano-particles. We have thus studied the effects of TiO_2 nano-particles amount on concrete and found the optimum amount of nano-TiO_2 into pavement concrete can be 8%. It is clear that it can affect on flexural and compressive strengths of pavement concrete.

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2. Experimental procedures and discussions

The synthesis procedures for producing nano – particles are similar, so we prefer to explain how for instance, TiO2 – anantas phase nano- particles is produced. The composition of the starting solution and the experimental conditions used for ternary powders are listed in table (1). Figure (1) illustrates the preparation procedures. The precursors: tetraethoxysilane (TEOS, Merk, ≥ 99), tetra isopropy ortho titanate (TIOT, Merk with ≥ 98), Cu(NO3)2.3H2O (applichem), acetic acid (Floka), HCl (Merk,36%), Ethanol (Merk≥ 98) and deionized water are used without further purification.

The starting point for the synthesis of a targeted system is a solution prepared by mixing precursors: (TEOS, deionized water, ethanol, HCl) and (TIOT, deionized water, ethanol, acetic acid for chelating the TIOT) separately at room temperature (RT) for 30 minutes.

Table 1. Composition of starting solutions and experimental conditions for ternary powders preparation.

Sol-Gel Method Step	Molar Ratio of Precursors	Stirring Time (h)	PH
	$TEOS/Cu(NO_3)_2 \cdot 3H_2O/TIOT = 1:2/1$		
Alkoxide Rout	$TEOS/EtOH/HCl/H_2O = 1:50/0.1/2$ $TIOT/EtOH/CH_3OOH/H_2O = 1:50/4/2$	0.5	3

Acetic acid acts an important role in hydrolysis because this mechanism decreases the rate of hydrolysis, meaning very fine particles of titanium hydroxide will be formed and suspended in solution. After then, two above solutions mixed vigorously at RT for 30 minutes. After 48 hours gelation is formed. Afterward, the gel is dried for about 24 hours at 50^0C temperature in air and calcined in three different temperatures (300 and 800^0C). Moreover, the effects of varied calcinations temperature are studied with as-prepared, 300 and 800^0C.

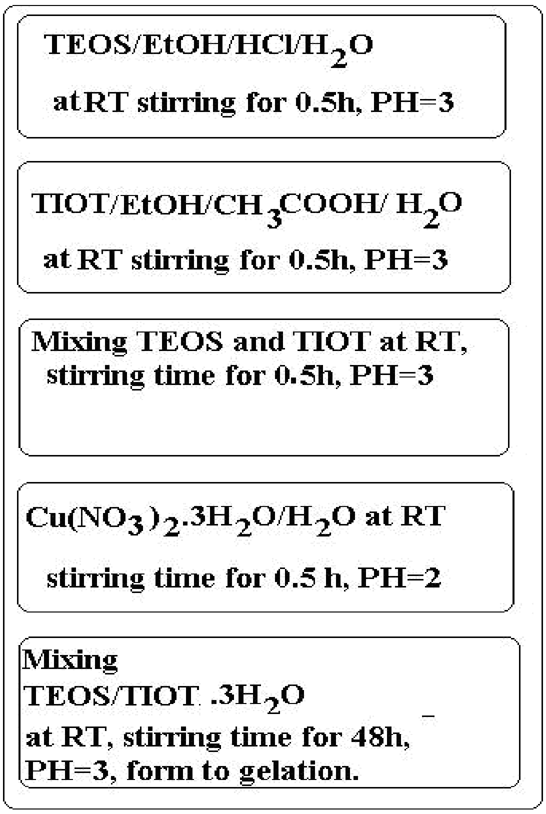


Figure 1. Schematic flow chart illustrating the steps in the synthesis pathway of TiO_2-SiO_2 nano-materials.

Figure (2). Cement with nano-particles (see Table 2).

From [2], Portland cement consists of five major compounds and a few minor compounds. The composition of a typical portland cement is listed by weight percentage in table 2.

Table 2. Composition of present cement with TiO_2 nano – particles. There are also chemical composition and weight percent.

Weight Percentage	Chemical Composition
48 %	Ca_3SiO_5
24 %	Ca_2SiO_4
10 %	$Ca_3Al_2O_6$
8 %	$Ca_4Al_2Fe_2O_{10}$
0- 8 %	$CaSO_4{\cdot}2H_2O$
2-10 %	TiO_2 - anatas

XRD technique is used for crystal phase identification and estimation of the crystallite size. XRD patterns are measured on a (GBC-MMA 007 (2000)) X-ray diffractometer. The diffractograms are recorded with (K_1 (α) (Cu), 1.54 Å, 0.02^o step size in where the speed is 10 deg/ min radiation over a 2θ range of 10°–80°. The XRD patterns of TiO_2- nano particles compose calcined at different temperatures shown in figure 3. The crystalline peaks corresponded to TiO_2 in the form of either highly pure anatase phase or mixed anatase–rutile, except the as – prepared nanostructure showing nearly amorphous phase. However, when the composite papered at above 300^{0}C, it shows a rutile phase as well. This point indicates that increase in anatase-to-rutile transformation of TiO_2 peak place when the calcination temperature is increased from 300 to 800^{0}C.

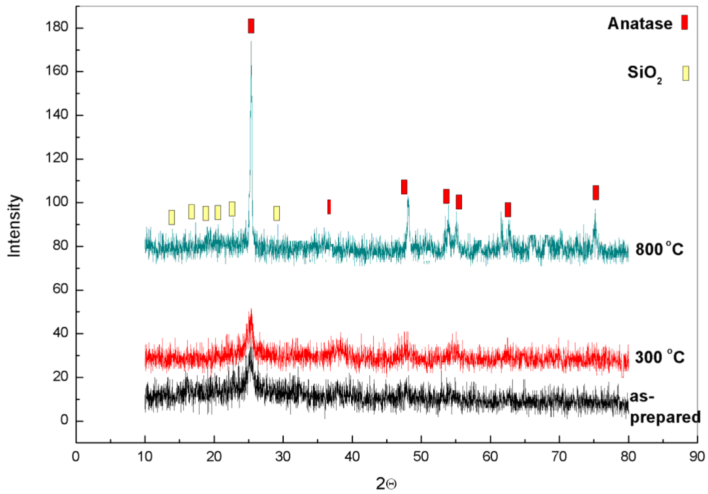
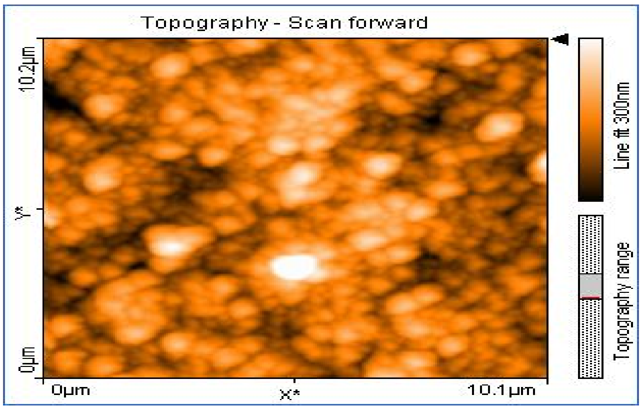
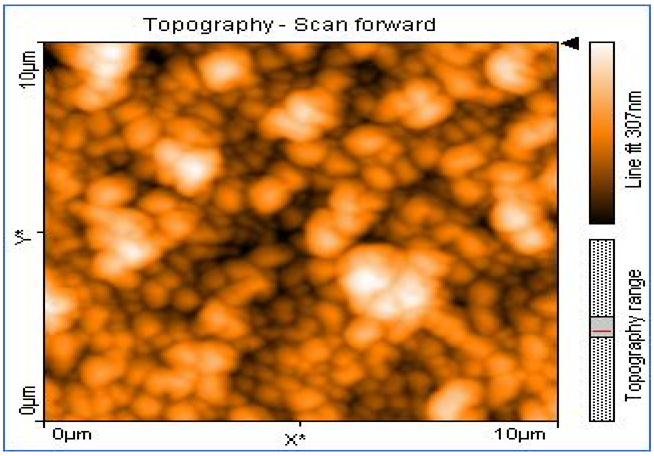


Figure 3. XRD patterns of TiO_2 -SiO_2 obtained from a) without hydrothermal treatment (as-prepared). b) calcined at 300^{0}C and d) calcined at 800^{0}C.

Figures 4 and 5 show AFM images, suggesting the crystalline structure of composites at higher (> 300^{0}C) temperature. They reveal mixtures of the anatase and the rutile phase. This also agrees with the results of XRD in figure 3. Anatase-type TiO_2 has been reported to be unstable at high temperature and its transformation temperatures are varied in a wide range, typically 300–800^{0}C [11].



(a)



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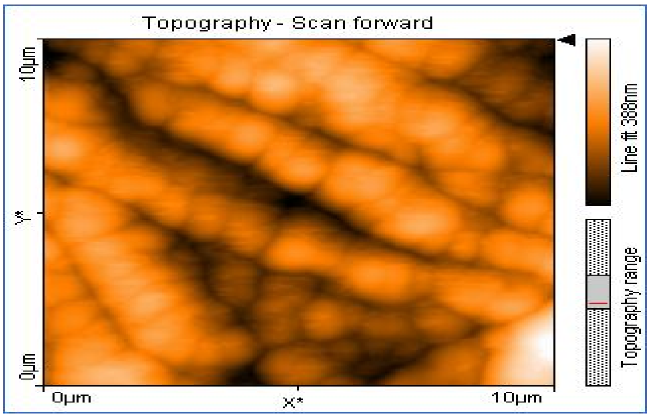

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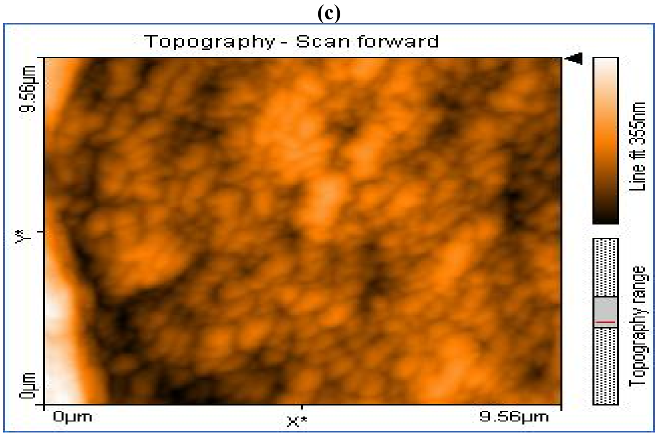
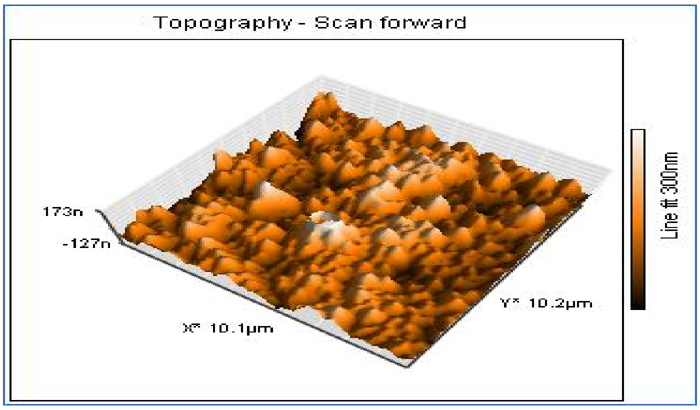
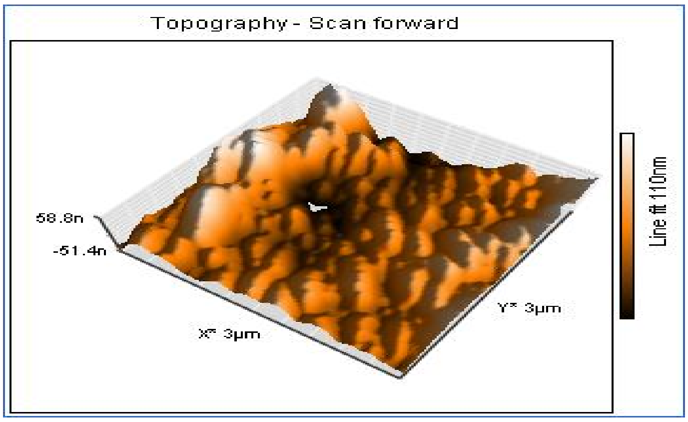


(d)

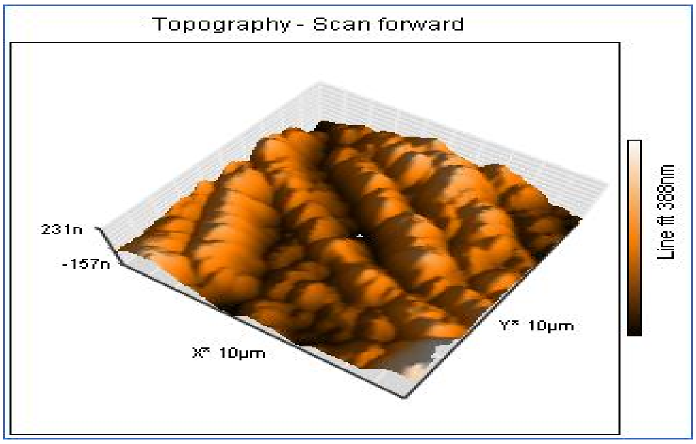
Figure 4. Two dimension AFM images of concrete fluid with (a) 2%, (b) 5%, (c) 8% and (d) 10% of TiO_2 nano-particles.



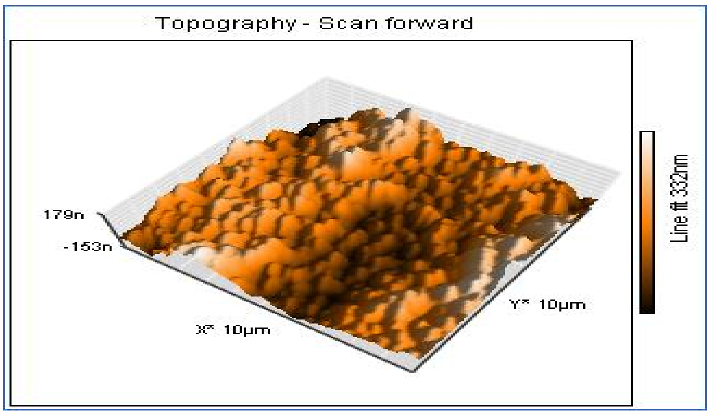
(a)



(b)



(c)



(d)

Figure 5. Three dimension AFM images of concrete fluid with (a) 2%, (b) 5%, (c) 8% and (d) 10% of TiO_2 nano-particles.

The suitable and desirable AFM images are revealed in figures 4(c) and 5(c) with 8% of TiO_2 nano- particles into composites. This point indicates that the desired characteristics of the concrete depend strongly on nano- particles amount. It is clear, the density of concrete can be determined by the density of the nano- aggregate as well as nano- particles. It may result in weak concrete with low wear resistance, while using hard aggregates (8% of TiO_2 nano-particles), the strong concrete with a high resistance to abrasion will be achieved. It is then separated into various sizes by passing the material through a series of screens with different size openings. When TiO_2 nano-particles and water are added to cement, each of the compounds undergoes hydration and contributes to the final concrete product. Only the calcium silicates contribute to strength.

By looking at AFM images and XRD patterns and noting to kind of compositions in table 2, we see producing calcium and hydroxide ions are continued until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize with TiO_2 nano- particles. This makes concrete more workable or fluid without adding excess cements. The strength of the concrete is related to the TiO_2 nano-particles to cement mass ratio and the curing conditions. A high water to cement mass ratio yields a low strength concrete due to the enhancement of porosities.

3. Conclusions

In the present work, Titanium dioxide (TiO_2) is added to cement, which can impart self-cleaning, and smog-abating functionality to cement based materials. It causes concrete to set, stiffen, and become hard and continues to harden (cure) and stronger for a long period of time. The obtained results for evaluation of stability found with using AFM – tapping mode and XRD techniques so that the TiO_2 nano-particles could prepare homogeneous hydrolysis of tetra isopropy ortho titanate via sol-gel route. It can be a promising candiadte for preparing photosensitive material with uniform nano particles as well.

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