

# Preparation of $\text{TiO}_2/\text{CaCO}_3$ Composites by Adsorption Phase Nanoreactor Technique

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**Abstract**—The Study on Preparation of  $\text{TiO}_2/\text{CaCO}_3$  Composites by absorption phase nanoreactor technique. The nanosized  $\text{CaCO}_3\text{-TiO}_2\cdot n\text{H}_2\text{O}$  composite was prepared by absorption phase nanoreactor technique. Solvent replacement experiment provided direct evidence that there was a water-rich adsorption layer on the surface of calcium carbonate, in the layer,  $\text{TiO}_2$  nanoparticles were prepared and then laid over surface of calcium carbonate. The characteristics of this composite including the chemical composition, superficial crystal structure, morphology, size, and the linkage of the composite particles are fully measured by EDS, XRD, TEM, FT-IR and XPS. All the results reveal that amorphous  $\text{TiO}_2$  has been coated on the surface of  $\text{CaCO}_3$  and there exist chemical bonds between them.  $\text{TiO}_2$  has been in situ prepared on the surface of calcium carbonate,  $\text{TiO}_2$  coating decreases with the increase of reaction temperature,  $\text{TiO}_2$  and  $\text{CaCO}_3$  are not simply mixed together but connected by some chemical bonds.

**Keywords**—adsorption layer; nanoreactor;  $\text{TiO}_2/\text{CaCO}_3$  composite; characteristic; chemical bond.

## I. INTRODUCTION

Nanoreactor is a reaction technology [1,2], for preparation of nanoparticles, which provides a relatively simple method to adjust the size of particles distributed by restricting the growth of crystal nucleus in a narrow space [3]. Microemulsions and inverse microemulsions [4] are typical cases. Methods using interlaminar construction and pore space of celit, montmorillonite as nanoscale reactors extend this idea [5, 6].

Dékány and his co-workers [7, 8] presented a technology of nanophase reactor to prepare nanoparticles

on support surface.

## II. MATERIALS

Both Tetra-*n*-butyl Titanate (TNB) and anhydrous ethanol, provided by the Beijing chemical and industry factory, were of analytical grade. Water was distilled water.  $\text{CaCO}_3$  was self-made, whose size was about 70nm, according to the particle distribution analysis (by a Malvern Zetasizer 3000HSA)

### A. The preparation of $\text{TiO}_2/\text{CaCO}_3$ composites

$\text{TiO}_2/\text{CaCO}_3$  composites were prepared by adsorption phase nanoreactor technique. Put 1g hydrophilic  $\text{CaCO}_3$  into a vessel, then added a little water and 20ml anhydrous ethanol, ultrasonic for half an hour. Because of hydrophilicity and strong adsorptive capacity of nano-sized  $\text{CaCO}_3$ , water-rich adsorption layer formed gradually on support surface and the concentration of water in ethanol decreased slowly. After the adsorption equilibrium was reached (12h, according to adsorption experiment), tetrabutyl titanate dissolved in ethanol was added. The molecule of tetrabutyl titanate diffused to the support surface and reacted with water in adsorption layer.  $\text{TiO}_2$  particles were formed in hydroxylation and condensation reaction on adsorption layer. After the reaction completed (5 h), the product was processed through several centrifugation–redispersion–washing cycles and dried at 75–100 °C for 24 hours.

### B. characterization of $\text{TiO}_2/\text{CaCO}_3$ composite

The size and morphology of the products were valued by transmission electron microscopy (TEM), which was carried out using a Hitach 8100IV at 100kv. The morphology of the samples was obtained by

Scanning Electron Microscope (SEM, Philips XL Series, XL30) equipped with EDS (Kevex Sigma TM Quasar, USA) to measure the elements samples containing. FT-IR was recorded by an Ominic system 2000 employing a KBr pellet method. The powder structure and phase transformation of the composites were characterized by X-ray diffractometry (XRD Rigaku, employing Cu K $\alpha$  radiation). X-ray photoelectron spectra are recorded on a Vacuum Generator ESCALABMKP photoelectron spectrometer using Al K $\alpha$  radiation from the Al anode source. Binding energies (EB) are referenced to the C1s energy at 284.6 eV. Experimental peaks are deconvoluted by Gaussian–Lorentzian mixture peak-fitting software provided by VG Scientific.

### III. RESULTS AND DISCUSSION

#### A. Adsorption experiment

Adsorption is not a fast step. In order to know when the adsorption equilibrium was obtained, we centrifuged the reaction system to separate upper clear solution from lower CaCO<sub>3</sub> after different adsorption time, and then added tetrabutyl titanate into the upper clear solution. In the experiment white deposition appeared immediately in the clear solution after 1h of adsorption time and the solution changed little after 8~9h of adsorption time, so we infer that the adsorption equilibrium was obtained after 8~9h of adsorption time. Therefore, we set 12h as standard adsorption time.

#### B. Solution replacement experiment

This experiment was designed to prove that water-rich adsorption layer forms on surface of calcium carbonate and that reaction takes place in adsorption layer. After adsorption equilibrium was reached, reaction system was centrifuged to separate upper clear solution from lower CaCO<sub>3</sub>, tetrabutyl titanate was added into upper clear solution and the solution changed little and remained clear. In contrast experiment white deposition appeared immediately while tetrabutyl titanate was added into ethanol dissolved in the same amount of water. This suggests that the water in reaction system is mainly adsorbed by CaCO<sub>3</sub> and the rest water in ethanol can not let tetrabutyl titanate hydrolyze. So, it is impossible that tetrabutyl titanate hydrolyzes to form TiO<sub>2</sub> in bulk and

that the formed TiO<sub>2</sub> is adsorbed by CaCO<sub>3</sub> in consequent treatment. The lower CaCO<sub>3</sub> separated from original adsorption system was mixed with 20 ml fresh absolute ethanol to form a new reaction system. The same amount of solution of tetrabutyl titanate dissolved in ethanol was added in the new system. After the reaction finished, the sample was gained by several centrifugation–redispersion–washing cycles and Fig .1 shows its sample TEM. Contrasting with TEM of blank sample, there were many black points on CaCO<sub>3</sub> surface and the blackness of CaCO<sub>3</sub> was deeper than that in blank sample. So, we can preliminarily judge the appearance of nano TiO<sub>2</sub> on support surface. As the water in upper clear solution was eliminated after changing the solution, there was little water in the fresh ethanol and the only source of water reacting with tetrabutyl titanate was the adsorption layer. So, the existence of water-rich layer on support surface was proved. Integrating the two experimental proof, the adsorption existed and tetrabutyl titanate could not hydrolyzed to form TiO<sub>2</sub> in the upper clear solution, TiO<sub>2</sub> was gained only by the reaction of tetrabutyl titanate with water in the adsorption layer. Therefore, we can determine that the adsorption layer was the place where the reaction occurred and TiO<sub>2</sub> particles formed.

#### C. Influence of temperature

Comparing TEM of samples at 0°C and room temperature (about 20 °C), the sample at room temperature had more black points with diameter from 5 to 25 nm, whereas the sample at 0 °C had large area of black region and fewer black points. The sample at 80 °C had few black points and lighter black region, even more parts of the region manifested the feature of blank sample. The major difference between the samples at 0°C and those at room temperature is on the morphologies of TiO<sub>2</sub>. At 0°C, TiO<sub>2</sub> is inclined to form a homogeneous film on calcium carbonate and at room temperature to form condensed particles. The great loss of TiO<sub>2</sub> at higher temperature may be caused by three factors:

The adsorption of water on calcium carbonate was restrained. The adsorption of CaCO<sub>3</sub> included physical and chemical adsorptions. The increase of temperature can let molecular motion acute, and physical adsorption is

restricted. Chemical adsorption is exothermal, so it can be restricted with the increase of temperature.

The hydrolyzation of tetrabutyl titanate was exothermal reaction, and the reaction was restrained with the increase of temperature

A large amount of tetrabutyl titanate hydrolyzed to intermediate products that did not condense further to generate TiO<sub>2</sub> particles at high temperature. After centrifugation, these intermediate products were washed out with solution. Under the influence of three factors, the amount of TiO<sub>2</sub> on support surface decreased sharply at 80 °C. Which factor is dominant in this experiment needs a further study.

#### D. Morphologies of TiO<sub>2</sub>

TEM analysis provides visual evidence of the morphology, size and structure of the particles. Detailed TEM observation shows that blackness increases more on the edge of support particle and on the steep surface. This indicates that TiO<sub>2</sub> in these regions formed as thin film. In all samples, TiO<sub>2</sub> exists in two states: one is individual particle whose size range is in several nanometers; and the other is the evenly distributed film of TiO<sub>2</sub> on support surface, and that the film is made of a large number of tiny particles or molecules of TiO<sub>2</sub> integrated with CaCO<sub>3</sub> directly is difficult to be distinguished by TEM at present.

#### E. Identification of surface compounds

FT-IR, XRD, EDS and XPS were used to identify the compounds formed on the surface of calcium carbonate [9, 10]. In IR spectroscopy of the TiO<sub>2</sub>/CaCO<sub>3</sub> composites, there are three characteristic peaks (at ~1449, ~877, ~698 cm<sup>-1</sup>), belonging to the fundamental vibration bands for the CaCO<sub>3</sub> structure in the wave number range of 450~3800 cm<sup>-1</sup> compared with the IR spectroscopy of the CaCO<sub>3</sub>. In addition, there is the characteristic peak of TiO<sub>2</sub> at ~540 cm<sup>-1</sup> in the IR spectroscopy of the TiO<sub>2</sub>/CaCO<sub>3</sub>. The XRD pattern of TiO<sub>2</sub>/CaCO<sub>3</sub> composite prepared at room temperature, it also shows the characteristic diffraction peak of calcite, but the intensity of calcite has greatly reduced, indicating that there is amorphous TiO<sub>2</sub> on the surface of CaCO<sub>3</sub>. In order to prove it, we put the TiO<sub>2</sub>/CaCO<sub>3</sub> composite in the dilute HCl (pH<1) for 48h, after being filtered and washed, the product was dried at 80°C and calcined at

700°C respectively, we could see that the TiO<sub>2</sub> in the TiO<sub>2</sub>/CaCO<sub>3</sub> composite was amorphous, while it turned into anatase after being calcined at 700 °C.

In order to know whether there are chemical bonds between CaCO<sub>3</sub> and TiO<sub>2</sub>, we took XPS test. We can see that the chemical shifts of the Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> components of the spin-orbit splitting appear at 458 eV and 463.7 eV respectively. According to the previous studies, the Ti 2p<sub>3/2</sub> binding energy of pure TiO<sub>2</sub> is 458.5 eV [23, 24]. The downward shift of Ti 2p<sub>3/2</sub> value of TiO<sub>2</sub>/CaCO<sub>3</sub> composites shows that there are chemical bonds between CaCO<sub>3</sub> and TiO<sub>2</sub>.

The C1s peaks the CaCO<sub>3</sub> and TiO<sub>2</sub>/CaCO<sub>3</sub> composites shown are at 289.6 eV and 290.1 eV respectively. (the peaks at about 284 eV is the contaminative carbon of the spectrometer). The upward shift of C1s value of TiO<sub>2</sub>/CaCO<sub>3</sub> composites shows that the chemical environment of the carbon element in the CaCO<sub>3</sub> has been changed.

The O1s XPS spectrum of the TiO<sub>2</sub>/CaCO<sub>3</sub> composites is showed. The fit of curve gives positions of these two peaks at 529.495 and 531.655 eV being ascribed to O1s for TiO<sub>2</sub> and O1s for CaCO<sub>3</sub> respectively. Compared with the O1s peak at 529.7 eV for TiO<sub>2</sub> and at 532.65 eV for CaCO<sub>3</sub>, a little shift is happened, which proves that the chemical environment of the oxygen element in the CaCO<sub>3</sub> and TiO<sub>2</sub> has been also changed compared with their pure compound. However, the peaks for Ca2p of TiO<sub>2</sub>/CaCO<sub>3</sub> composites have no shift compared with that of CaCO<sub>3</sub>. According to the above analysis, we can conclude that TiO<sub>2</sub> and CaCO<sub>3</sub> are not mixed together simply but there are some chemical bonds among Ti, O and C.

#### IV. CONCLUSIONS

A. TiO<sub>2</sub> has been in situ prepared on the surface of calcium carbonate and the experiment proves that the existence of adsorption layer and the reaction region in the adsorption layer.

B. TiO<sub>2</sub> coating decreases with the increase of reaction temperature. Limited hydrolyzation, changes in adsorption equilibrium and the loss of intermediate products are probable reasons.

C. TiO<sub>2</sub>/CaCO<sub>3</sub> composite has been successfully prepared. IR and XRD data show that TiO<sub>2</sub> in the

obtained composite is amorphous and XPS analysis shows that  $\text{TiO}_2$  and  $\text{CaCO}_3$  are not simply mixed

together but connected by some chemical bonds.

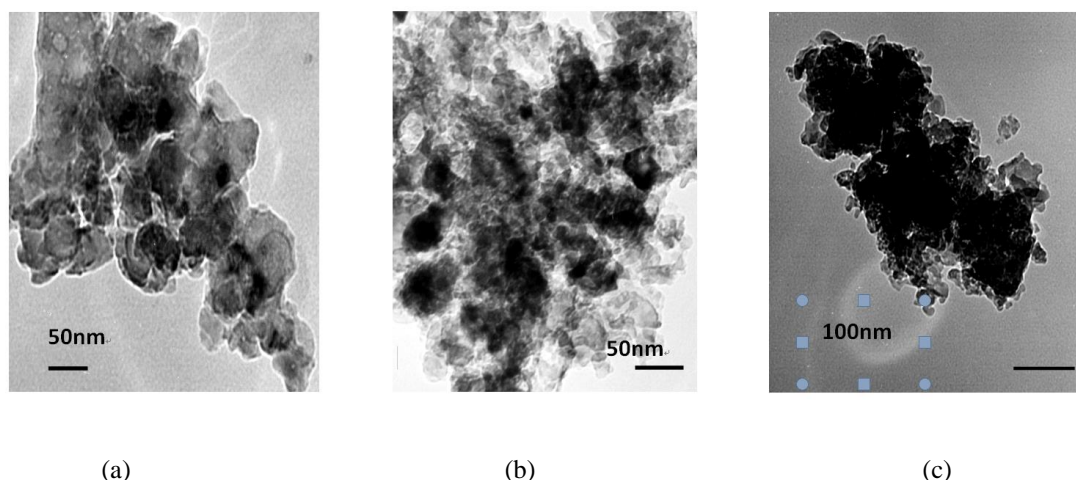


Figure 1 .TEM images of  $\text{TiO}_2/\text{CaCO}_3$  composites prepared at (a) room temperature and (b)  $0^\circ\text{C}$  (c)  $80^\circ\text{C}$

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