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A facile hydrothermal approach for construction of carbon coating on TiO₂ nanoparticles

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Abstract

Herein a facile hydrothermal approach is used to construct carbon coated TiO₂ nanoparticles employing dextrose as the source of carbon. The procedure is operated at a low temperature of 200 °C. Fourier infrared spectroscopy demonstrated the successful coating of carbon on TiO₂ nanoparticles. The phase composition of TiO₂ and carbon coated TiO₂ nanoparticles were studied using X-ray diffraction and the surface morphology was analyzed by scanning and transmission electron microscopy. The existence of carbon coating on TiO₂ nanoparticles was revealed by thermogravimetric analysis through different thermograms exhibited for TiO₂ and carbon coated TiO₂ nanoparticles. The reported method offers a simple and efficient approach for production of carbon coating TiO₂ nanoparticles.

Keywords

TiO₂; Carbon coating; Dextrose; Characterization

1. Introduction

The nanosized TiO₂ has continued to attract interests in both industry and academia due to unique properties [1] that has lead to its applications as photocatalysis [2,3], solar energy converters [4], interface in biomaterials [5], and sensors [6]. The construction industries also use nanostructured TiO₂ in composite with cement. The TiO₂ particle keeps the concrete white and through its photocatalytic properties can act as a catalyst for oxidizing organic grime impacting self cleaning ability to the coating [7].

Compared to polymer and silica shells, carbon shells exhibit much higher stability in various chemical and physical environments such as base or acid media, as well as high temperature and pressure [8]. This inherent advantage can be exploited to improve the unique properties of TiO₂ nanoparticles. Carbon coated TiO₂ have shown increase in photocatalytic activity [9], coating further adds to stabilizing the phase present and increases adsorptivity [10]. An increase in generation of hydrogen employing carbon coating of TiO₂ has also been reported [11-13].

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The methods available to coat TiO₂ with carbon includes pyrolysis of sucrose [14], solgel technique using alkoxide as precursors [15, 16], treatment of TiO₂ at very high temperature with various polymers under an inert atmosphere [10] etc. A single step synthesis approach for carbon coated TiO₂ has been reported by Hendrik et al [17]. However, most of these methods involved with elevated temperature, and consequently a high energy and operating conditions. In consideration of these technical issues, herein we report a low temperature hydrothermal method for preparation carbon coated TiO₂ nanoparticles using dextrose as source of carbon. This method is simple and offers stable carbon coating on TiO₂ nanoparticles.

2. Material and methods

All the reagents were of analytical grade and used without further purification. Titanium isopropoxide supplied by Aldrich was used as a starting material in the preparation of TiO₂ nanoparticles and the dextrose, obtained from EM Science was used as a source of carbon.

2.1. Preparation of TiO₂ nanoparticles

Titanium isopropoxide (4 mmol) was added to 15 ml isopropanol in a 500 ml round bottom flask equipped with a heater operated at 60-70° C was employed under vigorous stirring conditions. Slightly acidic water (150 ml) was then introduced to serve as the hydrolysis catalyst, which forms a turbid solution. The resulting mixture was stirred for 20 hr and transferred into a second flask for further heating at 105 °C for 12 hr for full precipitation to occur, the resulting white-yellow precipitate was isolated by filtration, washed with ethanol and dried at 100 °C for 5 hr. The TiO₂ nanopowder thus obtained was subjected to sintering process at 350 °C for 3 hr.

2.2. Carbon coating on TiO₂ nanoparticles

The TiO₂ nanoparticles were coated with carbon according to the procedure reported earlier with slight modifications [18]. The detailed procedure is as follows, TiO₂ (0.05g) nanopowder, dextrose (4g) and poly(ethylene glycol) (0.5g, Mw=10,000) were dispersed in distilled water (20 ml) by sonication for 1 hr. The resulting mixture was then stirred at room temperature for 1hr and transferred to a teflon lined stainless-steel autoclave (40 ml capacity) and subjected to heating at 200 °C for 12 hr. Then the product thus obtained was separated by centrifugation, subsequently washed with water and ethanol, and dried at 60 °C for 6 hr.

2.3. Characterization

FTIR spectra were recorded using Smiths ChemID diamond attenuated total reflection (DATR) spectrometer and thermogravimetric analysis (TGA) was performed using a Perkin Elmer Diamond TG/DTA instrument at a heating rate of 10 C/min. Powder X-ray diffraction (XRD) patterns were recorded on Scintag X-ray diffractometer (PAD X), equipped with Cu K α photon source (45kV, 40mA) at a scanning rate of 3 degrees/min. Scanning electron microscopy (SEM) measurements were carried out using JEOL JXA-8900 microscope and Transmission electron microscopy (TEM) images were obtained with a JEOL 2010 microscope.

3. Results and discussion

The FTIR spectra of TiO₂ nanoparticles and carbon coated TiO₂ nanoparticles are shown in Fig. 1. Both TiO₂ nanoparticles (Fig. 1a) and carbon coated TiO₂ nanoparticles (Fig. 1b) displayed weak and broad peaks identified to have the frequencies corresponding to bulk TiO₂ skeletal at 776 cm⁻¹ [19]. The bands at 1634 and 3274 cm⁻¹ were attributed to bending

and stretching vibrations of -OH, respectively. These bands are also evident in carbon coated TiO₂ nanoparticles (Fig. 1b). The presence of -OH bands in both spectra was owing to chemically and physically adsorbed H₂O on the surface of nanoparticles [20]. The spectrum of carbon coated TiO₂ nanoparticles displayed all the characteristics bands of TiO₂ in addition to bands at 1099 and 2914 cm⁻¹, these bands are attributed to Ti-O-C bonds and C-H stretching within the molecule, respectively. Appearance of these bands is indication of presence of carbon coating on TiO₂ nanoparticles.

X-ray diffraction patterns of TiO₂ nanoparticles and carbon coated TiO₂ nanoparticles are shown in Fig. 2. The diffraction peaks observed at 2θ values of 25.3°, 37.9°, 48.16°, 55.28° and 62.11° in Fig. 2a are assigned to (1 0 1), (0 0 4), (2 0 0), (2 1 1) and (2 1 3) reflections of anatase TiO₂, respectively (JCPDS file No. 21-1271). In addition to anatase phase, existence of minute quantity of brookite phase was also observed in TiO₂ nanoparticles, which is represented by a strong diffraction peak corresponding to (121) reflection, displayed at 2θ value of 30.8 (JCPDS file No. 29-1360). The pattern of carbon coated TiO₂ nanoparticles demonstrates its amorphous nature, in addition, it displayed the low intensity peaks corresponding to anatase TiO₂. The presence of carbon coating on TiO₂ nanoparticles might act like a mask, hence the reduction in the intensity of diffraction peaks was observed. In general, XRD analysis confirms the successful modification of TiO₂ nanoparticles through perfect coating of carbon.

The morphology of TiO₂ nanoparticles and carbon coated TiO₂ nanoparticles was examined with SEM and the images are shown in Fig. 3. Figs. 3(a) and (b) demonstrate the spherical nature of TiO₂ nanoparticles. The carbon coating on TiO₂ nanoparticles is clearly evident in Fig. 3(c) and (d). It is also observable that growth of carbon was along spherical axis of nanoparticles, thus preserving the integral shape of TiO₂ nanoparticles after coating of carbon also. Moreover there was a visible change was observed from whitish yellow to dark brown after coating of carbon on TiO₂ nanoparticles. The carbon coated TiO₂ nanoparticles has a rough surface, which resulted from the growth of carbon coating on TiO₂ nanoparticles [18]. These morphological phenomena were further supported by TEM images shown in Fig. 4. The average particle size estimated for TiO₂ nanoparticles and carbon coated TiO₂ nanoparticles were found to be in the range of 55-120 and 70-140 nm, respectively. Coating of carbon over TiO₂ nanoparticles was expected to lead an increase in the size of carbon coated TiO₂ nanoparticles, which was revealed in TEM images.

The TGA profiles of TiO₂ nanoparticles and carbon coated TiO₂ nanoparticles are shown in Fig. 5. A total weight loss of 8.6% was observed for TiO₂ nanoparticles (Fig. 5a) within a temperature range of 30-800 °C. This weight loss was ascribed to removal of physically adsorbed and chemically bound water and also removal of -OH groups exist on the surface of TiO₂ nanoparticles [21]. The thermal behavior of carbon coated TiO₂ nanoparticles was entirely different from that of TiO₂ nanoparticles (Fig. 5b), which demonstrates perfect coating of carbon over TiO₂ nanoparticles. The total weight loss exhibited for carbon coated TiO₂ nanoparticles was about 5%, the initial weight loss of 1.4% below 280 °C was attributed to loss of physically adsorbed water and release of chemically bound water. The consecutive weight loss observed in the temperature range of 280-580 °C (3.2%) was mainly due to combustion of carbon, coated on TiO₂ nanoparticles. The residual weight calculated for TiO₂ nanoparticles and carbon coated TiO₂ nanoparticles at 800 °C was 91.4% 95.2%, respectively. Overall, carbon coated TiO₂ nanoparticles showed improved thermal stability compared to TiO₂ nanoparticles, hence the carbon coating provided higher thermal stability to TiO₂ nanoparticles.

4. Conclusions

In conclusion, a facile and low temperature hydrothermal method for successful coating of carbon on TiO₂ nanoparticles has been demonstrated. This method can be extendable for the production of carbon coating on variety of semiconductor or metal nanoparticles. The ease of using dextrose as carbon source and low temperature procedure affords less cost production. Further studies on the catalytic activity of carbon coated TiO₂ nanoparticles are under way in our laboratory, those will be reported in due course.

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Fig. 1.
FTIR spectra of (a) TiO_2 nanoparticles and (b) carbon coated TiO_2 nanoparticles.

Fig. 2. Powder XRD patterns of (a) TiO₂ nanoparticles and (b) carbon coated TiO₂ nanoparticles.

Fig. 3.
SEM images of (a-b) TiO₂ nanoparticles and (c-d) carbon coated TiO₂ nanoparticles

Fig. 4.
TEM images of carbon coated TiO₂ nanoparticles.

Fig. 5. TGA profiles of (a) TiO_2 nanoparticles and (b) carbon coated TiO_2 nanoparticles.