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Considering the effect of a ligand as new complexing agent in the characteristics of TiO_2 nanoparticles

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ABSTRACT

The effect of a Schiff-base ligand N,N′-bis[(Z)-(2-nitrophenyl)methylidene]propane-1,3-diamine; (Salpn(NO2)2)) on the size and optical properties and the effect of time in preparation of TiO_2 nanoparticles in a two-step sol–gel method were investigated. Different amounts of Schiff-base ligand were applied and the as-prepared products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectrum, Electron Dispersive X-ray spectroscopy (EDX) and ultraviolet–visible (UV–Vis).

1. Introduction

TiO_2 nanoparticles are widely utilized as photocatalysts, ceramic materials, fillers, coatings, pigments, cosmetics, etc. For these purposes, it is strongly desirable that the TiO_2 nanoparticles to be uniform and completely controlled in size, shape, and crystal structure. (See Scheme 1.)

A broad diversity of procedures has been developed for the preparation of TiO_2 nanoparticles, until now. Sol–gel [1,2], reverse micelle [3], sonochemical [4], microwave [5] and hydrothermal [6] are some examples of chemical routes for synthesis of well-define TiO_2 nanoparticles. Two-step sol–gel procedure is a similar adopted method of conventional "gel–sol" method, developed by Sugimoto [7–10].

A complexing agent assisted sol–gel procedure utilizing an organic ligand as a modulator can tailor the crystal structure and optical properties of thin films such as TiO_2 [11,12]. Surely, not each molecule is an equally good ligand. Fundamentally, ligands that accomplish the task of adsorbent and stabilizer have a functional head group and one or more hydrocarbon large groups, and both elements perform a role in the control of nucleation and growth [13–21].

In this research, TiO_2 nanoparticles were prepared utilizing organic Schiff-base ligand as complexing agents by a two step sol–gel procedure. The intension of this research is investigating the role of Schiff-base ligand on the size of the TiO_2 nanoparticles. As regards, to our knowledge there is not any report on the effect of this organic Schiff-base ligand on the size and properties of TiO_2 nanoparticles.

2. Experimental

2.1. Materials and characterization

Titanium(IV) ethoxide, and triethanolamine(TEOA) used in our experiments were purchased from Merck. For characterization of the products X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Optical analyses were performed using a V-670 UV–VIS-NIR Spectrophotometer (Jasco).

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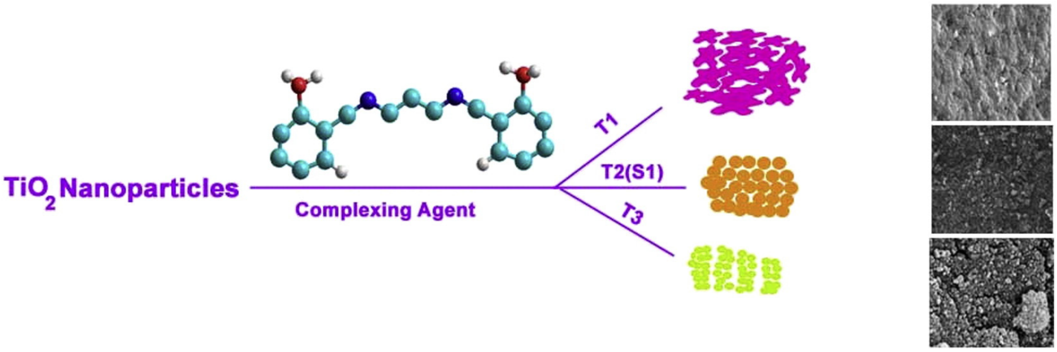

Scheme 1. Effect of different times on morphology of TiO_2 nanoparticles.

2.2. Preparation of N,N′-bis[(Z)-(2-nitrophenyl)methylidene]propane-1,3-diamine; salpn(NO2)2 [22]

The symmetrical Schiff-base ligand, N,N′-bis[(Z)-(2-nitrophenyl)methylidene]propane-1,3-diamine, C17H16N4O4 (Salpn-$NO_2)_2$, was prepared according to previously published methods, by refluxing 0.05 mol of 2-nitrobenzaldehyde (Merck-Schuchard, purified by distillation) and 0.025 mol of propylenediamine (Aldrich Chemie, 99%, purified by distillation) in 30 ml of dried ethanol, for 30 min and cooling the reaction mixture. The Schiff-base ligand was separated as yellow powder and was recrystallized twice from methanol (yield 90%). The compound was stable at room temperature and was characterized by FT-IR spectroscopy.

2.3. Preparationof TiO_2 nanoparticles

The standard procedure for the preparation of TiO_2 nanoparticles was conducted according to the literature [23–28]. Stock solution of Ti^{4+} (0.5 M) which is stable against hydrolysis at room temperature was prepared by mixing titanium(IV) ethoxide (TEO) and TEOA with a molar ratio of TEO:TEOA = 1:2, followed by the addition of distilled water. The final pH of solutions was 9.6 and was fixed at this pH by mixing with $HClO_4$ or NaOH solution after addition of complexing agents. Salpn$(NO_2)_2$ ligand with different ratios to the Ti^{4+} precursor (Table 1) was further added as complexing agents to each solution. The solution was placed in a Teflon-lined autoclave and aged at 100 °C for 24 h for gelation; then, the temperature was increased to 140 °C for 72 h to nucleate and grow TiO_2 nanocrystals. TiO_2 nanoparticles were prepared in the different times (Table 2). The resulting sol was washed with and centrifuged from NaOH (six times), HNO_3 (two times), and distilled water (four times) to remove residual organic compounds from the surface of the nanoparticles.

3. Results and discussion

The X-ray diffraction patterns of as-prepared product obtained from the two-step reaction have been shown in Fig. 1. Fig. 1a–c show the XRD patterns of samples S1, S0 and S1T0 which have been prepared in presence of both ligand and TEOA, in absence of ligand, and in absence of TEOA, respectively. All diffraction peaks can be well indexed to pure anatase structural titanium dioxide. All the peaks were labelled and can be indexed to JCPDS Card No. 76–1935, 04–0477, for sample S1, S0 and S1T0, respectively. The XRD patterns of samples show different line broadening. Generally, the crystalline domain size decreases with increasing line broadening. The line broadening of the peak of the (101) index is related to the size of the crystalline phase. The data for the full width at half maximum (FWHM) of the samples S1, S0 and S1T0 at $2\theta = 25.35$, 25.48, and 25.45 was estimated to be 0.4133, 0.2952, and 0.2362, respectively. The crystallite size diameter (D) of the TiO_2 products has been calculated by Debye–Scherrer equation, $D = 0.9\ k/\beta\cos\theta$. Calculated crystalline domain sizes have been found to be 21, 30, and 38 nm for the samples S1, S0 and S1T0, respectively. It can be concluded that the employed Schiff-base ligand has a significant influence on crystalline size of the product so that in the presence of only ligand (sample S1T0) the calculated crystalline domain size increased to 38 nm. It seems that applying both the ligand and TEOA (S1) has a different effect so that the particle size of S0 sample was smaller than S1T0. Preparation of TiO_2 nanoparticles with tuneable size is of great interest for different applications. Here, it has been shown that different conditions lead to different crystalline size from ca. 21–38.

Fig. 1d shows the XRD patterns of sample T1 prepared in time 2 days. All the peaks were labelled and can be indexed to JCPDS Card No. 71-1166, 88-1175, and 31-1827 show anatase, rutile, and impurities, respectively. The data for the full width at half maximum (FWHM) of sample T1 at $2\theta = 20.0148$ was estimated to be 0.1771 and the calculated crystalline domain size has been found to be 52 nm for sample T1.

FT-IR spectra have been demonstrated in Fig. 2a. Based on these spectra, Salpn$(NO_2)_2$ as a ligand has been synthesized successfully (Fig. 2a). The board peak on 3350 cm^{-1} was depended to OH, the sharp peak on 1642 cm^{-1} was pertained to C═N; the peaks that were placed on 1514 cm^{-1}, 1342 cm^{-1} are attributed to symmetric and asymmetric stretching vibration of O–N–O and the peak that occurred in 2850 cm^{-1} is the result of CH_2 in ligand structure.

The surface conditioning of as-prepared TiO_2 product was recorded using FT-IR spectrum in order to detect the residual organic compounds. Fig. 2b shows FT-IR spectrum of L1 sample. The absorption from 3000 to 3600 cm^{-1} can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1628 cm^{-1} is due to the bending vibration of water molecules. The broad band below 950 cm^{-1} in the FT-IR spectrum belongs to the

Table 1
Different samples prepared in various aspect ratios.

Sample abbreviation	Ti^{+4}:S	Ti^{+4}:TEOA
S1T0	1:1	1:0
S0	1:0	1:2
S0.5	1:0.5	1:2
S1	1:1	1:2
S3	1:3	1:2
S6	1:6	1:2

S: Schiff-base ligand.
T: TEOA.

Table 2
Different samples prepared in various times.

Sample abbreviation	Time, temperature	
T_1	12 h, 100 °C	36 h, 140 °C
T_2	24 h, 100 °C	72 h, 140 °C
T_3	30 h, 100 °C	90 h, 140 °C