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Effects of deep eutectic solvents in preparation of nanoparticles TiO_2

M. Aghazadeh[1], F. Aghazadeh[2]*

[1] *Department of Physics, Karaj Branch, Islamic Azad University, Karaj, Iran*
[2] *Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran*

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ABSTRACT: Deep eutectic solvents (DESs) have always been attractive to scientists due to their wide range of applications, a great interest in diverse fields including nanotechnology due to their unique properties as new green solvents. It used large-scale for chemical and electrochemical synthesis nanomaterial. DESs have had also active role in improving the size and morphology of nanomaterial during synthesis stage. This paper reports on chemical methods using for decrease size and purification of commercial TiO_2 powders by deep eutectic solvents (DESs). This method was based on the dissolution of TiO_2 powders in a deep eutectic solvent (DES), followed by precipitation of TiO_2 nanostructures from the DES upon introduction of antisolvent. Under appropriate conditions, the ethanol and water content of the antisolvent and the injection time of the TiO_2 containing DES, the morphology of the resulting TiO_2 nanostructures can be readily controlled. The present method can be readily extended to produce versatile nanostructures of other functional materials. We also studied morphology of TiO_2 nanoparticles. Size of TiO_2 particles were conformed ~60 nm.

Keywords: *Antisolvent, Dioxide Titanium nanoparticles; Natural deep eutectic solvents; Purification; Size control*

INTRODUCTION

It is well known that TiO_2 occurs in nature in three distinct crystallographic phases: anatase, rutile, and brookite (Vorontsov, *et al.*, 2001). While anatase TiO_2 are the most widely used photo catalysts for oxidative decomposition of organic compounds and an excellent photo catalyst for photodecomposition and solar-energy conversion due to its high photo activity (Li, *et al.*, 2009, Li, 2010). It has the advantages of both cheapness and nontoxicity, in addition to its excellent functionality and long-term Stability. The configurations of titanium oxide researched and reported have mainly been powders or films based on materials (Li, *et al.*, 2002). A notable problem connected with these traditional preparations is that the growth of TiO_2 nanocrystallites takes a long time. Therefore it is highly desirable to find some new ways that are capable of overcoming the above problems to prepare crystal structure TiO_2 (Qiu and Kalita, 2006). The applications for TiO_2 are also strongly dependent on the crystalline structure and morphology (Li, *et al.*, 2009). Thus, it is very important to develop synthetic methods in which the crystalline form (Zhang, *et al.*, 2001). It is also important that the

(*) Corresponding Author-e-mail: maryam.aghazadeh@kiau.ac.ir & aghazadeh_ch@yahoo.com

TiO_2 sizes and shapes be controlled. We report here a facile green antisolvent approach, which involves only biocompatible chemicals and mild processing conditions, to produce TiO_2 nanostructures with controllable morphology. The method uses commercial TiO_2 powders as the raw material, a biocompatible room temperature ionic liquid as the solvent, and ethanol/water mixtures as the antisolvent. Room temperature ionic liquids, possessing many advantageous characteristics, including high polarity, high ionic conductivity, negligible vapor pressure, good thermal stability, and wide liquid windows, are considered a new class of green solvents and may replace the role played by often hazardous organic solvents in many applications (Stathatos, *et al.*, 1997, Vorontsov, 2001). They have been used extensively in the preparation of nanostructured inorganic materials (Ma, *et al.*, 2010), deep eutectic solvents (DES), this can be prepared by simply mixing quaternary ammonium salts with proton donors, are a new class of 130 °C ionic solvents and are cheap and environmentally friendly (Abbott, *et al.*, 2003). For example, urea, with a melting point of 133 °C and choline chloride with a melting point of 302 °C, can be simply mixed in a 2 to 1 molar ratio to form a DES (denoted as UCC) with a reported melting point of only 12 °C, much lower than those of the two constituents. Both constituents of the UCC are cheap and commonly found in bio-organisms and therefore environmentally benign. Besides, one key characteristic of the UCC is that it is a good solvent for many metal oxides, such as CuO, NiO and especially ZnO (Li & Ho Row, 2016, Abbott, *et al.*, 2005). The solvent property of the UCC toward TiO_2 will be lost when the solution is mixed with water or ethanol, an antisolvent showing no solvation ability toward TiO_2. This would result in the nucleation and growth of TiO_2 to lead to the formation of TiO_2 nanostructures. In this work, the antisolvent concept was applied to fabricate nanostructures of TiO_2, including twin-cones and nanorods, with controllable crystallographic phases. This is the first example of using DES as a solvent in an antisolvent process for preparation of functional nanomaterial and a brand new addition to the ever expanding application scope of room temperature ionic liquids. Therefore, naturally eutectic solvents "greenness" is often used more than other solvents due to their self-destructive degradability, compatibility and stability (Abbott, *et al.*, 2005).

In the recent years, scaling optical and electronic properties of nanomaterial, which become strongly size dependents, focused attention on the preparation of nanoparticle semi-conductors (Tomkiiewicz, 2000). TiO_2 is the promising material as semiconductor having high photochemical stability and low cost. Well-dispersed Titania nanoparticles with very fine sizes are promising in many applications such as pigments, adsorbents and catalytic supports (Ramakrishna and Gosh, 2003, Rahman, *et al.*, 1999). In almost all of these cases, when the particle size is reduced greatly, especially to several nanometer scales, due to the large surface-to-volume ratio, some novel optical properties can be expected (Sahni, *et al.*, 2007). It is not surprising; therefore, that much research has been focused upon the reduction of particle size. It was usually found that different routes often produce different results (Li, *et al.*, 2002, KolenKO, *et al.*, 2004, Zhao, et al, 2007). So it is necessary for us to investigate in detail the methods which may have important effect upon the particle size.

MATERIALS AND METHODS

Preparation of TiO_2 Containing DES

For the preparation of TiO_2 nanoparticles using by wet chemical methods, all chemicals were used without further purification. First prepared by mixing 69 g of urea and 81 g of choline chloride in a molar ratio of 2 to 1. An amount of 0.3 g of TiO_2 powders (uses commercial TiO_2 powders as the raw material) was then added to the UCC. These UCC solutions were kept in an oven at 70-100 °C for 1-3 hour until all TiO_2 powders dissolved and to complete the process.

Preparation of TiO_2 in Antisolvent

Ethanol (Merck, 99.8%) and deionized water were mixed in different volume percent water and ethanol and used as the antisolvent for TiO_2. For the growth of TiO_2, whole of TiO_2-containing DES was injected into 100-250 mL of antisolvent in 5 s in a water bath maintained at 70-120 °C, followed by vigorous stirring for 1-3 hour. The resultant white suspending solid was

collected by centrifugation at 5000 rpm for 30 min and washed with different volume percent mixing of water and ethanol to remove remaining DES and impurities. The product was then dispersed in ethanol for later use. In this work, antisolvents of three different ethanol contents (0, 50 and 90 vol%) were employed for the growth of TiO_2. Besides, experiments with three different times of the TiO_2-containing DES (1-3 h) were conducted and compared to investigate the obtained with antisolvents of different ethanol contents.

Characterizations

The morphology and size of TiO_2 of the products were examined with a transmission electron microscope (TEM); model ZEISS, EM 10C-100KV. The crystallographic structures and distinct crystallographic phases of the samples were investigated with X-ray diffractometer (XRD) 1730 PW – Phillips with CuKα radiation in the range of 9.8-80o (λ= 1. 54 A°).

RESULTS AND DISCUSSION

The structures and dimensions of the as-prepared products were first investigated with TEM and XRD. Fig. 1 shows the TEM images and Figs. 2, 3 XRD patterns of the TiO_2 samples obtained with antisolvents of different ethanol contents. Further structural characterizations were carried out using TEM. These three TiO_2 samples were shown in Fig. $S_{1a\text{-}c}$. In Fig. S_{1a}, if examined closely, a slit can also be identified at the middle of the elliptically shaped particle, indicating that structure is products obtained with the fast injection practice. TEM images of TiO_2 nanostructures prepared with the antisolvent of (S_{1a}) pure water, (S_{1b}) 50% ethanol and 50% water, and (S_{1c}) pure ethanol. Clear spherical and non-homogeneous structures can be seen in the Fig. $S_{1a,b}$ a having diameter ~71-76 nm. We can see in the Fig. S_{1c} no clear spherical structures in the TEM image. Nanoparticles obtained in this case are adhering to one another. Agglomeration of nanoparticles is more in this case than the former one. As can be seen from the TEM image that the average particle size is ~60 nm. The corresponding XRD patterns are shown in (Fig. 3). Injection time of TiO_2-containing DES 5 s (Paiva, *et al.*, 2014, Rogers & Seddon, 2005). Pure water and 50% ethanol antisolvents were enhanced and suppressed, respectively, as com-

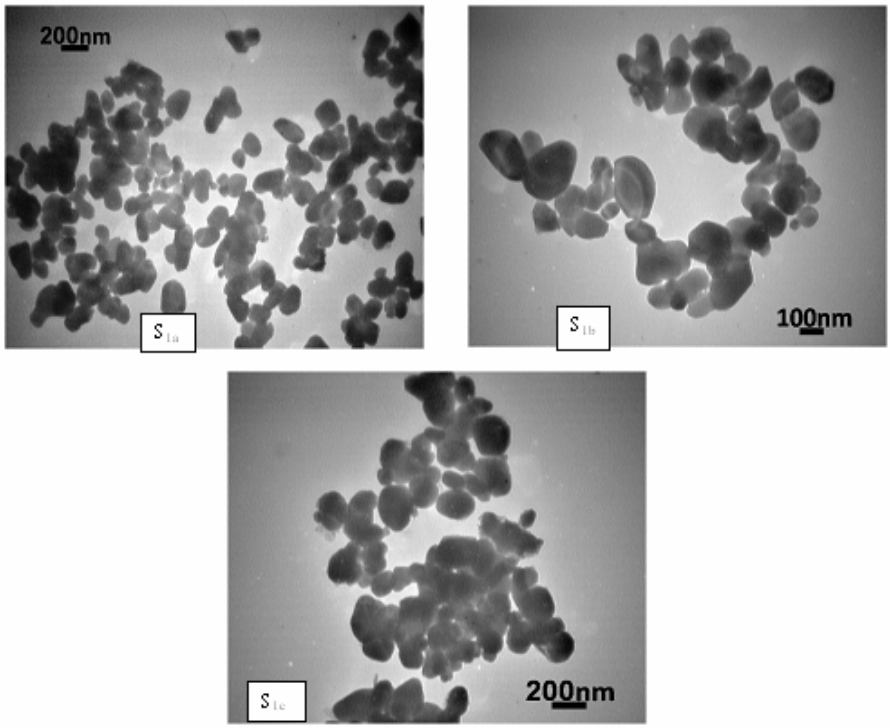

Fig. 1. TEM images of the TiO_2 nanostructure prepared with the antisolvent of (S1a) pure water, (S_{1b}) 50% ethanol and 50% water, and (S_{1c}) pure ethanol. Injection time of TiO_2-containing DES 5 s.

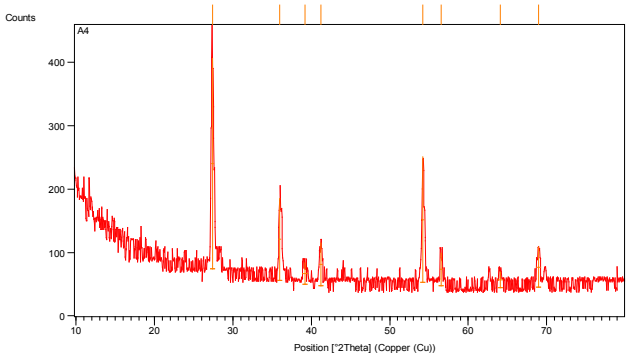

Fig. 2. XRD pattern of samples S_{1a}, S_{1b}, XRD two examples are similar.

pared with their relative intensities shown in the standard reference pattern. Fig. S_{1c} confirmed that sample S_{1a} and S_{1b} consists of round shaped particles, with an average size of 60nm. TiO_2 nanoparticles with similar morphology (round shaped) were also reported by (Vijayalakshmi & Rajendran, 2012).

The phase purity and crystal structure of the synthesized TiO_2 nanoparticles were investigated by powder X-ray diffraction (XRD), as shown in Figs. 2, 3. As it could be observed, the samples are well crystalline but the structure and phase same in three samples, depending on the reaction conditions. In samples S_{1a}, here the reaction time decrease from 3 hours, the phase purity improves drastically, showing peaks attributed to the tetragonal TiO_2 rutile phase. Fig. S_{1c} shows that the X-ray diffraction (XRD) patterns of the powder samples were prepared with the antisolvent of pure ethanol. The XRD patterns of dried sample at 100 ºC were largely regular.

The Bravais lattice TiO_2 nanoparticles are as follows:

The values obtained from XRD for the crystals obtained by TiO_2 prove the tetragonal structure of the rutile phase. Structural tetragonal of the rutile phase

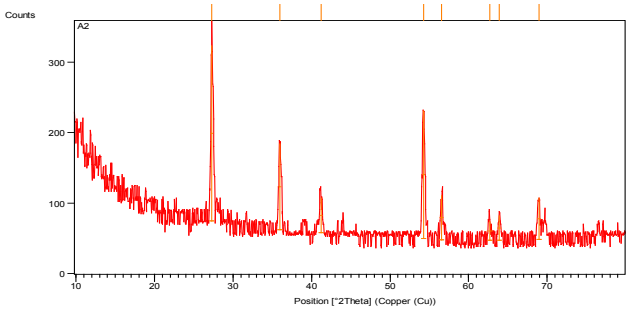

Fig. 3. XRD pattern of samples S_{1c}.

Table 1. Specification Bravais lattice for TiO_2 nanoparticle crystals in of samples S_{1a}, S_{1b}.

Specification of Brave	Value
a (Å)	4.6030
b (Å)	4.6030
c (Å)	2.9660
Calculated density (g/cm^3)	4.22
Volume of cell (10^6 pm^3)	62.84
Alpha (°)	90
Beta (°)	90
Gamma (°)	90

Table 2. Specification Bravais lattice for TiO_2 nanoparticle crystals in of samples S_{1c}.

Specification of Brave	Value
a (Å)	4.6017
b (Å)	4.6017
c (Å)	2.9647
Calculated density (g/cm^3)	4.23
Volume of cell (10^6 pm^3)	62.78
Alpha (°)	90
Beta (°)	90
Gamma (°)	90

with $a = b \neq c$ and $\alpha = \beta = \gamma = 90$ °. According to Tables 1 and 2, two Bravais lattices are few differences.

The TiO_2 nanoparticles synthesized by chemical method showed crystalline nature with 2θ peaks lying at 2θ =27.606 (110), 2θ =36.242 (101), 2θ =54.631 (211), 2θ =63.013 (002) and 2θ =70.126 (112). The preferred orientation corresponding to the plane (101), (110), (211) are observed in both the samples. All the peaks in the XRD patterns can be indexed as rutile phases of TiO_2 and the diffraction data were in good agreement with JCPDS files # 01-088-1173 and 01-076-0326 (Xu, *et al.*, 2008).

CONCLUSIONS

Chemical treatment of commercial TiO_2 powders as the raw material could generate TiO_2 nanoparticles and pure when the applied conditions are appropriate. The chemical preparation of TiO_2 nanoparticles

from amorphous and commercial TiO_2 powders was studied in the temperature 70-100 °C for 1-3 hour. In conclusion, we have developed an environmentally friendly antisolvent approach for preparation of TiO_2 nanostructures, including round shaped and rutile phase, with controllable size and phase. The method was based on the dissolution of TiO_2 in the UCC DES, followed by the precipitation of TiO_2 nanostructures upon the extraction of the DES using an antisolvent. Through suitably modulating the two key processing conditions, the ethanol content of the antisolvent and the injection time of the TiO_2 containing DES, the morphology of the resulting TiO_2 nanostructures can be readily controlled. The presence of ethanol in the antisolvent formation pure product and thus decreased the size. The present study provides a new synthetic route to prepare nanostructures of TiO_2 without the use of environmentally harmful chemicals, such as long-carbon chain surfactants and capping reagents, or severe reaction conditions, such as high temperature and high vacuum. The present method can be readily extended to produce versatile nanostructures of other functional materials.

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AUTHOR (S) BIOSKETCHES

Maryam Aghazadeh, PhD Candidate, Instructor, Department of Physics, Karaj Branch, Islamic Azad University, Karaj, Iran, *E-mail: maryam.aghazadeh@kiau.ac.ir & aghazadeh_ch@yahoo.com*

Fatemeh Aghazadeh, PhD, Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran