World Journal of Nano Science and Engineering, 2013, 3, 87-92
http://dx.doi.org/10.4236/wjnse.2013.33012 Published Online September 2013 (http://www.scirp.org/journal/wjnse)

Comparison of Acidic and Polymeric Agents in Synthesis of TiO_2 Nanoparticles via a Modified Sol-Gel Method

Masoud Karimipour
Department of Physics, Vali-E-Asr University of Rafsanjan, Rafsanjan, Iran
Email: masoud.karimipour@gmail.com

Received July 11, 2013; revised August 15, 2013; accepted August 21, 2013

ABSTRACT

TiO_2 nano particles were synthesized in Rutile and Anatase phases by sol-gel method using two kind of complex agents, acidic (Citric Acid) and organic complex agent (acetyl acetone) at 400˚C, 500˚C, 650˚C sintering temperatures. The structural analysis by XRD diffraction confirmed phase formation of titanium oxide. Particles sizes were determined by using Scherrer formula. TEM was employed to confirm nano particles formation. The size of nano particles as well as Phase formation can be controlled by the type of complex agent and sintering temperature. Acetyl Acetone causes a more crystalline structure and more uniformity of size distribution in 400˚C sintering temperatures. Moreover, it results in obtaining single phase TiO_2 nanoparticles at 400˚C and 650˚C sintering temperature. On the other hand, at high sintering temperature, the particles obtained from polymeric agent tend to agglomerate larger in size than the acidic product.

Keywords: Sol-Gel Method; Photo Catalyst; Rutile; Anatase; Complex Agent

1. Introduction

Titanium dioxide which is known as Titania occurs in four forms: Rutile (Eg = 3.0 eV), Anatase (Eg = 3.2 eV), Brookite (Eg = 2.96 eV) and TiO_2-*β*. Brookite and Anatase phases are rare and have more photocatalytic activity than Rutile phase [1]. TiO_2 is desirable due to its inertness, stability, and low cost [2]. It is also self regenerating and recyclable. Its redox potential of the H_2O/*OH couple (−2.8 eV) lies within the band gap. However, its large band gap (Eg = 3.2 eV) only allows the UV absorption of the solar spectrum. Titania nano particles are highly considered for the technological and industrial applications because of its photo catalytic activities [3], such as self-cleaning [4], anti bacterial [5], fog proofing [6]; and also, as a new source of energy saving in dye sensitized solar cells [7-9]. Titania nano particles are prepared by many techniques such as sol-gel [10], hydrothermal [11] and co-precipitation processes [12]. But, there are still many ongoing researches [13] to develop new features and simplification of nanoparticles synthesis within a desired size distribution. In this study, we used a simple Pechini sol-gel process [14,15] with two different complex agents in order to study the role of polymeric and non-polymeric agents in phase purity and size formation.

2. Experimental Details

The titanium oxide nano particles have been prepared by Sol-gel process in two steps. Titanium isopropoxide (TTIP) was used as precursor. Acetyl acetone (AcAc: $CH_3COCH_2COCH_3$) and acetic acid ($HOC(COOH)(CH_2COOH)_2$) were used as both complex and polymer agent and finally absolute ethanol as solvent. In first step, starting solution was prepared with diluting 0.1 M TTIP by 40 cc absolute ethanol with the same volume ratio and then mixed with 0.1 M AcAc (Citric Acid) and stirred with magnet for 1 hr in 40˚C to establish initial sol. This sol was red (yellow)-color and pH = 6.5 (3.0). For gaining transparent sol witch has nano particles of Titania as complex compounds, the sol was refluxed in oil bath at 130˚C for 4 h. After this step, sol was orange(yellow-green)-color and pH = 8.4(6.0). In the next step, we used oil bath to heat the sol, indirectly at T = 80˚C for 36 hrs until forming gel. The gel firstly was dried up by direct heating on hot plate at 120˚C for 2hrs and then for final drying, the gel was heated at 150˚C for 30 minutes. The titanium oxide nano particles cannot be obtained unless the dried gel calcinated at 400, 500, 650˚C for 1 hr. the weight of powders measured before and after calcinations that the results have come in **Tables 1** and **2**.

The X-ray diffractometer (D8 Advance Bruker), with

Table 1. Powder prepared by sol-gel process using AcAc as complex and polymer agent.

Calcination temperature (˚C)	Weight **before** calcination (gr)	Weight **after** calcination (gr)	Powder colours	Remain powder (%)
400	10.644	4.706	gray	44.20
500	10.644	4.681	white	43.98
650	10.644	4.677	Light yellow	43.83

Table 2. Powder prepared by sol-gel process using citric acid as complex and polymer agent.

Calcination temperature (˚C)	Weight **before** calcination (gr)	Weight **after** calcination (gr)	Powder colours	Remain powder (%)
400	8.04	3.210	black	39.9
500	8.04	2.289	gray	28.47
650	8.04	2.258	white	28.08

Cu-K$_\alpha$ radiation of wavelength 1.5405 Å (operated at 25 kV, 20 mA) was employed for structural studies. TEM was employed for nano particles size analysis. The Uv-Vis spectra were prepared by spectrophotometer (Agilent 8453) for determining band gap of nano particles.

3. Results and Discussion

Structural characterization: the XRD patterns of titanium oxide nano particles (**Figures 1** and **2**) show Rutile and Anatase phases formation. The (101)-plane for Anatase and (110)-plane for Rutile are the main diffraction planes seen in the figures. the mean crystalline size of nanoparticles is estimated using scherrer formula, and Anatase/Rutile phase ratio also is determined using Equation (1) [11] in which, x_A is the Anatase phase contribution in the powder, I_R and I_A are the intensity of the highest peaks of Rutile and Anatase in XRD patterns, respectively.

$$x_A = \left[1 + 1.26\left(I_R / I_A\right)\right]^{-1} \quad (1)$$

Figure 1(a) show phase formation of Anatase and small crystalline size (**Table 3**) in lowest sintering temperature, which may due to using organo-metalic precursor and organic complex agent, it allows Ti-O bonds formation and postpones the condensation process rather than hydrolysis [12]. Comparison of **Tables 3** and **4** shows that in the sintering temperature at which both Anatase and Rutile phases coexist, AcAc case results in a uniform crystalline growth process other than Citric Acid one. The observation of mixed Anatase and Rutile phases at 500˚C (**Figure 1(b)**) and Rutile phase at 650˚C (**Figure 1(c)**) indicates phase transition of Anatase to Rutile. Moreover, application of AcAc as complex agent results in obtaining single phase TiO_2 nanoparticles in 400˚C and 600˚C sintering temperatures. Actually powders did not show any crystalline phase below 400˚C sintering temperature. thus, comparing citric acid and AcAc chemical formula one can be said that the lower the amount of carbon existing in the dried powders, the lower the sintering temperature at which phase formation occurs.

Table 3. Nano crystalline size of calcined powders prepared by AcAc as complex agent.

Sintering temp. (˚C)	$D(101)_A$ (nm)	$D(110)_R$ (nm)	$X_{A/R}$ (%)
400	9	-	-
500	30	35	67
650	-	52	-

A: Anatase phase, R: Rutile hase.

Table 4. Nano crystalline size of calcined powders prepared by citric acid as complex agent.

Sintering temp. (˚C)	$D(101)_A$ (nm)	$D(110)_R$ (nm)	$X_{A/R}$(%)
400	-	-	-
500	12	46	62
650	60	50	28

A: Anatase phase, R: Rutile hase.

TEM images (**Figures 3** and **4**) show that with increasing of sintering temperature, agglomeration of nano particles has been occurred. Acetyl Acetone causes a more crystalline structure and more uniformity of size distribution in 400˚C sintering temperatures. On the other hand, in highest sintering temperature, the particles obtained from polymeric agent tends to agglomerate larger in size than the acidic one.

Optical characterization: Using Uv-Vis spectra and Tauc formula, The optical absorption edge was analyzed by the following relationship [16], $\alpha h\nu = A\ (h\nu - E_g)^m$ where A is a constant, m value is respectively 1/2 and 2

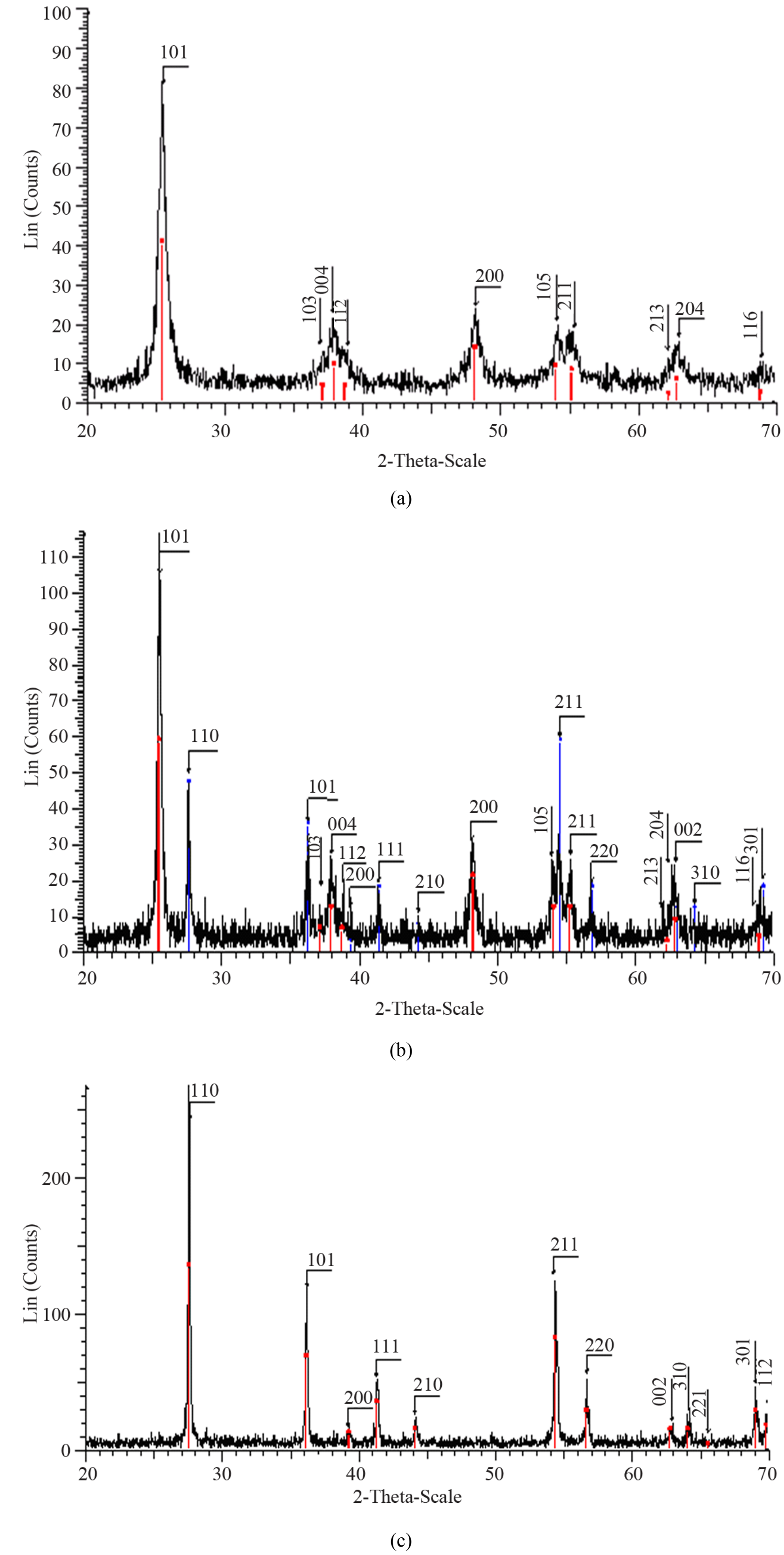


Figure 1. XRD pattern of nano powder prepared by AcAc as complex agent, calcined at (a) T = 400˚C, (b) T = 500˚C, (101) red-peak and (110) blue-peak implies to Anatase and Rutile phases, respectively, and (c) T = 650˚C.

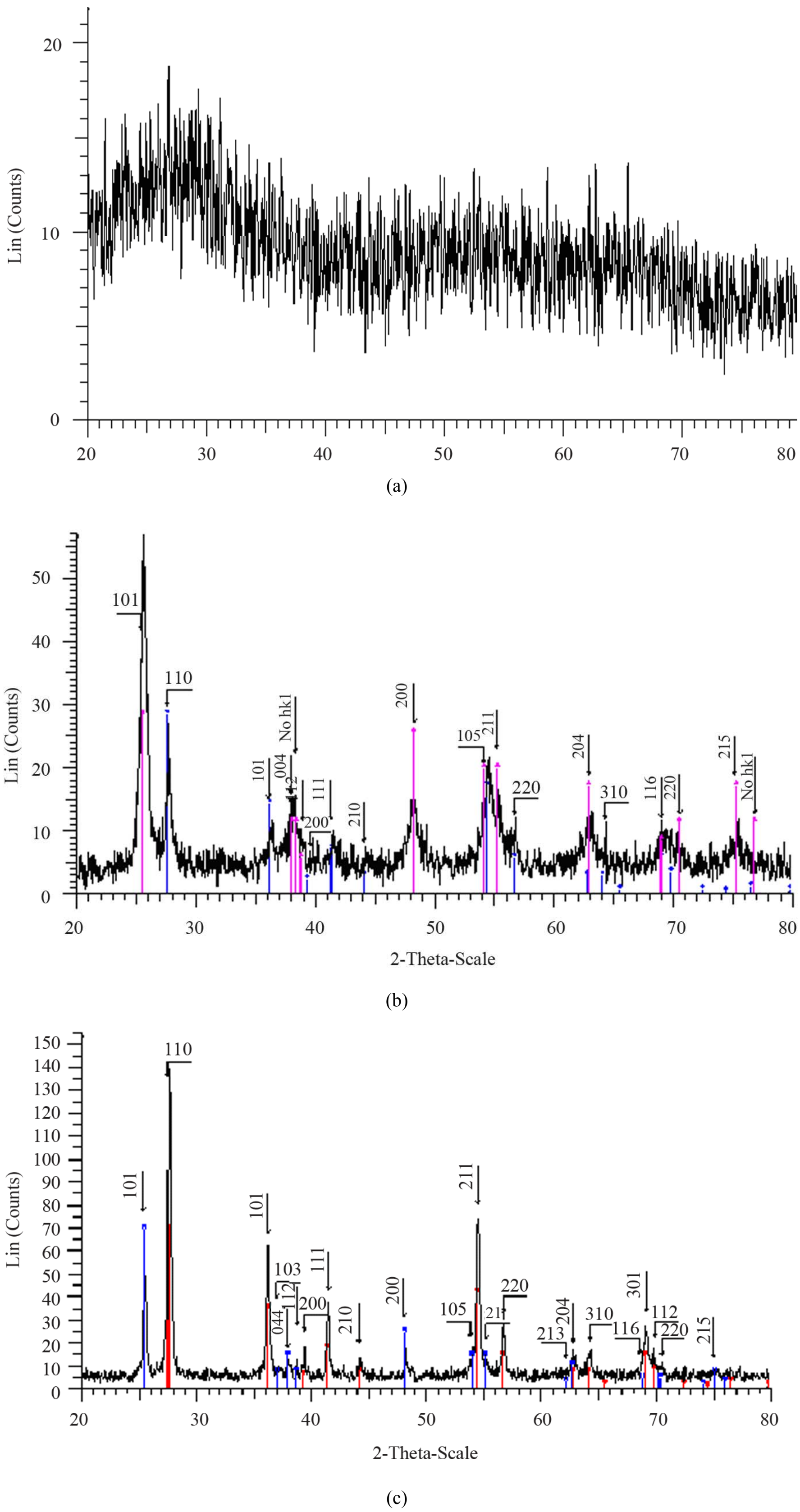
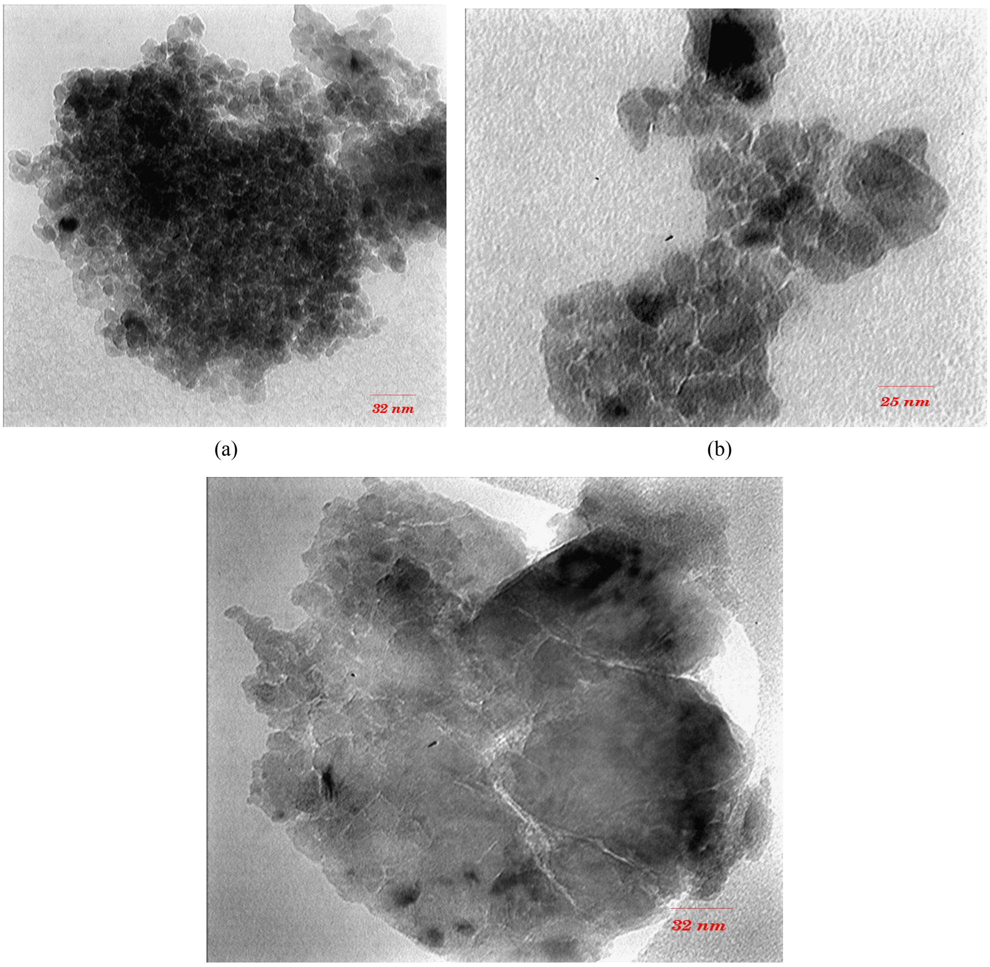


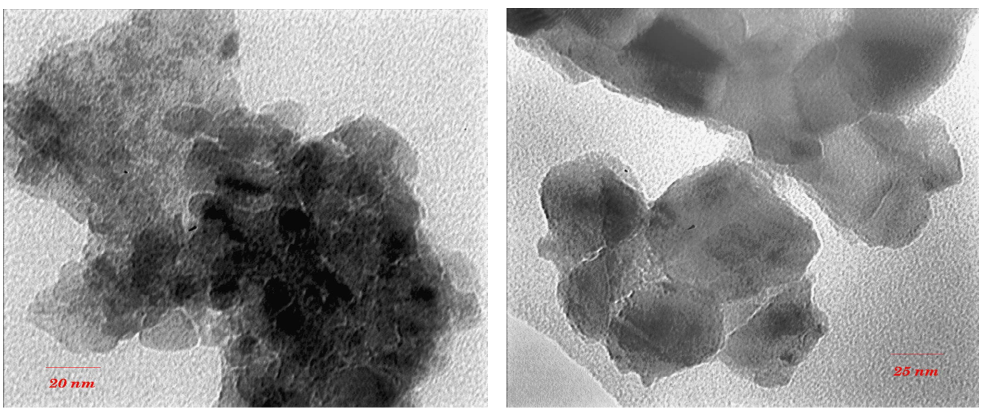
Figure 2. XRD pattern of nano powder prepared by citric acid as complex agent, calcined at (a) T = 400˚C, (b) T = 500˚C, (101) red-peak and (110) blue-peak implies to Anatase and Rutile phases, respectively, and (c) T = 650˚C.



(a) (b)

(c)

Figure 3. TEM images of nano powder prepared by AcAc as complex agent, calcined at (a) T = 400˚C, (b) 500˚C, (c) 650˚C.



(a) (b)

Figure 4. TEM images of nano powder prepared by citric acid as complex agent, calcined at (a) T = 500˚C, (b) 650˚C.

for direct and indirect transitions and E_g is the optical band gap. We estimated the direct energy band gap of nano particles. The optical results show that nano particles with smaller size which sintered at 500˚C have smaller band gap rather than nano particles which sintered at 650˚C (**Figure 5**). This may be due to existing of traps that lies within the band gap. Nano particles that have been sintered at 500˚C which contain two phases (Anatase and Rutile) have more traps rather than those who sintered at 650˚C.

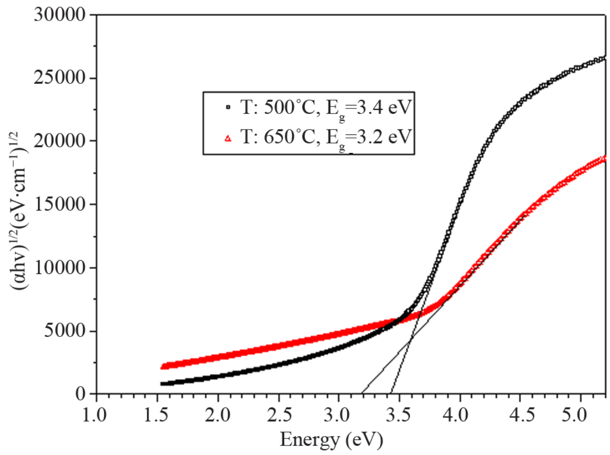


Figure 5. energy gap of nano particles prepared with solgel process and using AcAc complex agent (T: sintering temperature).

4. Conclusion

TiO_2 nanoparticles have been synthesized simply via complexing-polymerizing sol-gel method. The effect of polymer agent on size distribution of particles shows that AcAc is a proper candidate to synthesize particles in pure Anatase phase below 10 nm. Also, sintering at 650˚C shows pure Rutile phase with narrow size distribution about 100 nm. Moreover, application of Citric acid gives rise to a less agglomeration of particles after annealing at 650˚C which does not have pure phase.

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