ORGANIC SOLVENTS IN THE SYNTHESIS OF INORGANIC NANOMATERIALS: THE CASE OF ETHANOL AND $Ti(OBu)_4$

Chorshanbiyev Abdimajit Anvar o‘g‘li
Samarqand state university named after Sharof Rashidov
Tursunov Firdavsi Hamzaevich
Samarqand state university named after Sharof Rashidov
E-mail: firdavsazi@yahoo.com

Abstract: In this paper, we consider the effect of ethanol on the synthesis of titanium dioxide (TiO_2) nanoparticles by the sol-gel method. Titanium tetrabutoxide (TBT) was used as a precursor; its hydrolysis was carried out in an ethanol medium with controlled addition of water. It is shown that ethanol slows down the hydrolysis rate, promotes the formation of a stable sol, and prevents particle aggregation. The structural and phase analysis confirms that the use of ethanol contributes to the production of homogeneous anatase nanoparticles with a high degree of dispersion. The results emphasize the importance of solvent selection in the sol-gel synthesis of oxide nanomaterials.

Keywords: TiO_2, titanium tetrabutoxide, ethanol, sol-gel synthesis, hydrolysis, nanoparticles, anatase, condensation.

Annotatsiya: Ushbu maqolada biz etanolning titan dioksidi (TiO_2) nanozarrachalarini zol-gel usuli bilan sinteziga ta’sirini ko‘rib chiqamiz. Prekursor sifatida titan tetrabutoksid (TBT) ishlatilgan va uning gidrolizi nazorat ostida suv qo‘shilishi bilan etanol muhitida amalga oshirildi. Etanol gidroliz tezligini sekinlashtiradi, barqaror eritma hosil bo‘lishiga yordam beradi va zarrachalar agregatsiyasini oldini oladi. Strukturaviy va fazaviy tahlil etanoldan foydalanish yuqori darajadagi dispersiyaga ega bir hil anataz nanozarrachalarini sintez qilishiga yordam berishini tasdiqlaydi. Olingan natijalar oksidli nanomateriallarning zol-gel sintezida erituvchi tanlash muhimligini ta’kidlaydi.

Kalit so‘zlar: TiO_2, titan tetrabutoksid, etanol, sol-gel sintezi, gidroliz, nanozarrachalar, anataz, kondensatsiya.

Аннотация: В данной работе рассматривается влияние этанола на синтез наночастиц диоксида титана (TiO_2) золь-гель методом. В качестве прекурсора использовался тетрабутоксид титана (ТБТ), гидролиз которого проводился в среде этанола с контролируемым добавлением воды. Показано, что этанол замедляет скорость гидролиза, способствует образованию устойчивого золя и препятствует агрегации частиц. Структурно-фазовый анализ подтверждает, что использование этанола способствует получению однородных наночастиц анатаза с высокой степенью дисперсности. Полученные результаты подчеркивают важность выбора растворителя при золь-гель синтезе оксидных наноматериалов.

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Ключевые слова: TiO_2, тетрабутоксид титана, этанол, золь-гель синтез, гидролиз, наночастицы, анатаз, конденсация.

Introduction

In recent decades, oxide nanomaterials in particular TiO_2 have attracted considerable attention from the scientific community due to their unique physicochemical properties. TiO_2 nanoparticles are widely used in photocatalysis, solar energy, sensorics, biomedicine and protective coatings due to their high chemical stability, biocompatibility and photocatalytic activity. To achieve high efficiency in these areas, it is necessary to ensure strict control over the morphology, size and crystal structure of nanoparticles. One of the most versatile and controllable methods for obtaining TiO_2 nanoparticles is sol-gel synthesis.

The sol-gel method is based on the hydrolysis and subsequent polycondensation of precursors, usually metal alkoxides such as titanium tetraisopropoxide (TTIP). These reactions produce a colloidal system (sol) in the solution, which subsequently transforms into a gel and can be thermally treated to produce metal oxide nanoparticles. One of the key factors determining the efficiency of this method and the characteristics of the resulting nanostructures is the choice of solvent, in particular the role played by ethanol during the hydrolysis and polycondensation of the precursor.

Ethanol performs several important functions in the sol-gel process. First, it serves as a solvent for TTIP, reducing its reactivity by diluting and stabilizing the precursor molecules. Second, ethanol affects the polarity of the reaction medium, which allows controlling the activity of water and, accordingly, the rate of hydrolysis. In the absence of ethanol, TTIP hydrolysis proceeds too quickly, which leads to the formation of uneven, aggregated or amorphous particles. Thanks to ethanol, the reaction becomes more controllable, which contributes to the formation of a stable sol with a uniform size distribution. In addition, ethanol can partially participate in ligand exchange reactions, replacing isopropoxy groups in the titanium complex, thereby additionally regulating the kinetics of the process. Ethanol also affects the final morphology of the particles. For example, changing the ethanol to water ratio allows you to control the size of nanoparticles, the density of the gel and the porosity of the final material. Thus, the choice of concentration and ratios of ethanol with other components plays a critical role in the development of TiO_2-based functional materials.

This work is aimed at a comprehensive study of the role of ethanol in the sol-gel synthesis of orthorhombic TiO_2 nanoparticles. It considers the mechanisms of interaction of ethanol with precursors, the effect on the kinetics of hydrolysis and condensation, as well as the structural characteristics of the resulting nanoparticles.

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Particular attention is paid to the optimization of synthesis parameters to obtain materials with desired properties.

RESULTS AND DISCUSSION

The aim of this study was to investigate the formation of TiO_2 during sol-gel synthesis using $Ti(OBu)_4$ in an ethanol medium. A series of experiments were conducted with varying component ratios, water addition rates, and heat treatment conditions. Particular attention was paid to the effect of ethanol on the kinetics of precursor hydrolysis and the morphology of the final nanoparticles. Hydrolysis of titanium tetrabutoxide is the first and key step in the formation of TiO_2 nanostructures. This reaction is a nucleophilic substitution of butoxy groups (–OBu) by hydroxyl groups to form intermediate compounds Ti–OH, which subsequently condense to form Ti–O–Ti bonds:

$$Ti(OBu)_4 + xH_2O \rightarrow Ti(OH)_x(OBu)_{4-x} + xBuOH$$

$$Ti–OH + HO–Ti \rightarrow Ti–O–Ti + H_2O$$

In the absence of ethanol, $Ti(OBu)_4$ hydrolysis occurs abruptly and uncontrollably: instantaneous turbidity of the solution and precipitation are observed, indicating rapid aggregation and the formation of uneven structures. This complicates the production of a stable sol and leads to the formation of amorphous or coarse-grained particles.

The role of ethanol in slowing down and stabilizing hydrolysis

Adding ethanol to the reaction system significantly changes the dynamics of the process. Ethanol performs the following functions:

- *Diluent:* reduces the concentration of active $Ti(OBu)_4$ centers and water, slowing down the reaction.
- *Polarity regulator of the medium:* reduces the dielectric constant, which reduces the availability of water for interaction with Ti centers.
- *Coordinating agent:* partial formation of weak Ti–OEt complexes is possible, contributing to the stabilization of intermediate products.
- Ligand exchange mediator: ethanol can participate in exchange reactions by displacing butoxy groups:

$$Ti(OBu)_4 + EtOH \rightleftharpoons Ti(OEt)(OBu)_3 + BuOH$$

Thus ethanol regulates both the rate of hydrolysis and the course of polycondensation.

Sol formation and stabilization

The $Ti(OBu)_4$ solution in ethanol is a transparent system stable when stored dry. With controlled addition of water (H_2O:$Ti(OBu)_4$ ratio = 0,8:1…3:1), gradual turbidity was observed, indicating the nucleation of colloidal particles. The sol

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appeared within 10–40 minutes, depending on the water addition rate and ethanol concentration.

The maximum stability of the sol was achieved with a $Ti(OBu)_4$:H_2O:EtOH ratio = 1:8:100. Under these conditions, the particles had a rhombic shape and a size of about 280-320 nm, according to dynamic light scattering (DLS). Increasing the water content above 3:1 led to partial aggregation and the formation of a loose gel.

Phase composition and morphology after annealing

After drying the sol at 50°C and subsequent annealing at 500°C for 2 hours, the resulting powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

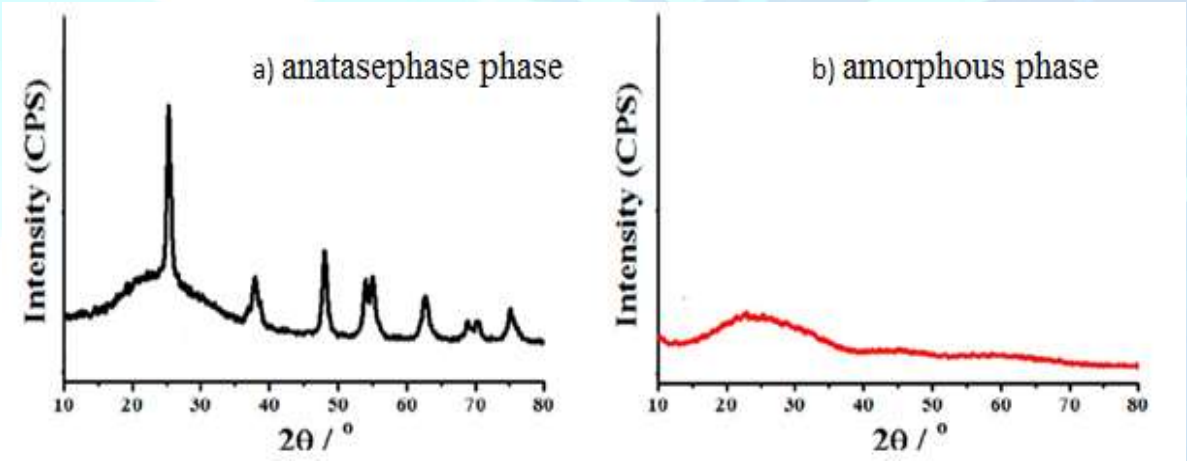


Figure-1. X-ray diffraction analyses of titanium dioxide nanoparticles.

XRD diffraction patterns showed the appearance of characteristic peaks of anatase (Figure-1a) a thermodynamically metastable phase of TiO_2, typical for low-temperature synthesis conditions. In systems without ethanol, the presence of an amorphous phase (Figure-1b) and weak signs of a rutile structure were observed, which confirms the destructive effect of rapid hydrolysis.

In **Figure-2** TEM image confirmed the formation of rhombic particles with a length of 280–320 nm at high ethanol content and uniform distribution. In the absence of ethanol, the particle size increased to 800-1000 nm and a tendency to aggregation and shape deformation was observed. Thus, ethanol not only ensures uniform nucleation but also stabilizes the resulting TiO_2 cores, preventing adhesion and enlargement.

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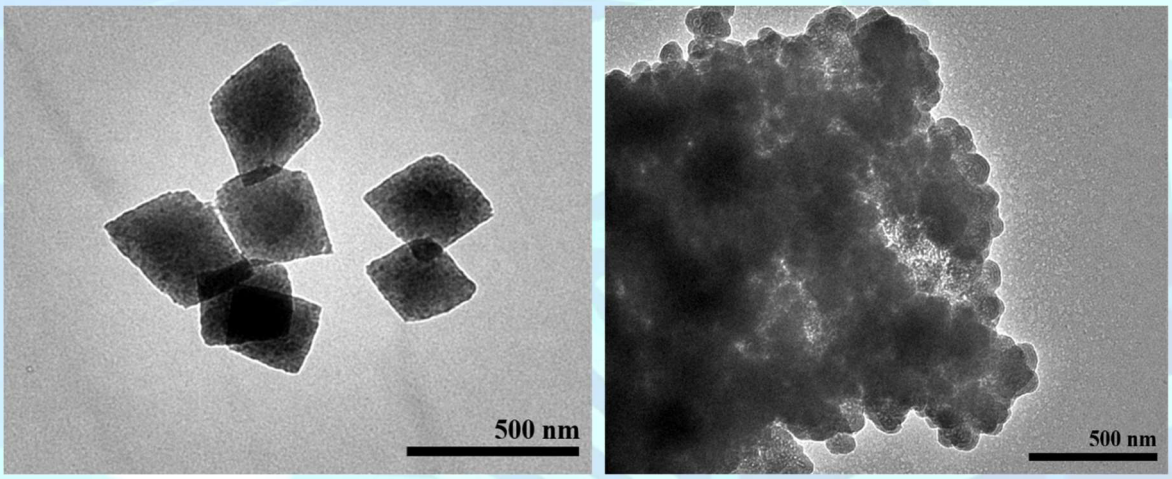


Figure-2. TEM images of TiO_2 nanoparticles: (a) rhombic particles; (b) aggregated particles.

In **Table-1** results indicate that ethanol is a key parameter to control the morphology and phase purity of TiO_2 nanoparticles.

Table-1

Influence of synthesis parameters on the properties of TiO_2

Parameter	Change	Effect on structure
Increase H_2O:Ti	Fast hydrolysis	Aggregation, large particles
Increase EtOH:Ti	Slow reaction	Smaller and more stable particles
Without ethanol	Sharp precipitate	Amorphous TiO_2, agglomerates

The proposed mechanism for the formation of TiO_2 nanoparticles includes the following stages:

1. Solubilization of the precursor in ethanol with possible ligand exchange (Ti–OBu → Ti–OEt).
2. Slow hydrolysis with the formation of Ti–OH groups in a dilute medium.
3. Condensation with the formation of Ti–O–Ti bonds and the formation of a sol.
4. Stabilization of particles due to the organic environment (residues of EtOH, BuOH) and spatial separation.

The introduction of ethanol shifts the hydrolysis equilibrium towards slow nucleation and promotes the formation of a thermodynamically more stable and uniform nanostructure.

CONCLUSIONS

Ethanol plays a key role in controlling the hydrolysis of titanium tetrabutoxide $Ti(OBu)_4$, acting as a diluent and coordinating agent. Its presence allows to slow down the rate of nucleophilic substitution and prevents abrupt aggregation of particles at the initial stage of the synthesis. Hydrolysis and subsequent condensation of $Ti(OH)_4$ lead to the formation of Ti–O–Ti bridges,

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which is confirmed by spectroscopic and microscopic methods. The presence of ethanol promotes the formation of the anatase phase of TiO_2 after annealing. The morphology and crystallinity of the final TiO_2 nanoparticles depend on the presence of ethanol: when it is used, the formation of spherical, less aggregated particles with a high degree of structural homogeneity is observed.

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