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Influence of synthesis conditions on the properties of electrochemically synthesized $BaTiO_3$ nanoparticles

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Abstract

The continuous miniaturization of advanced electronic devices will require dielectric layers of multi-layer ceramic capacitors thinner than 500 nm in the near future. Therefore, fine barium titanate ($BaTiO_3$) nanoparticles smaller than 100 nm are eagerly desired. Here, we synthesized $BaTiO_3$ nanoparticles by using an electrochemical method with titanium electrodes in alkaline solution at a current of ≈ 3.25 A. Initially, the composition of the solvent was modified by using water or a water/methanol mixture (50:50 v/v). Methanol replacement with other compounds was subsequently tested. NaOH concentration in the electrolyte was also varied from 0.5 mol L^{-1} to 4.0 mol L^{-1}. Crystal structure of the $BaTiO_3$ was examined by using X-ray diffraction. Morphology and microstructure of the particles were studied by using scanning electron microscopy and transmission electron microscopy. Compared with conventional methods, the electrochemical synthesis enabled the production of small nanoparticles (grain sizes < 200 nm) at temperatures lower than 60 °C in a short synthesis time (2 h). The particles with highest crystallinity were obtained in 1.0 mol L^{-1} NaOH solution in a mixture of methanol/water (50% v/v).

Keywords: Nanoparticle synthesis; Anodic sparks; Crystal structure; Transmission electron microscopy; X-ray diffraction

1. Introduction

Nanometer-sized particles (with diameters smaller than 100 nm) have attracted considerable interest for a wide variety of applications, including electronics, ceramics and as catalysts, because of their unique or improved properties, which are mainly determined by their size, composition and structure [1].

Barium titanate ($BaTiO_3$) is of practical interest because of its attractive dielectric, ferroelectric, piezoelectric and electro-optical properties. It is also chemically and mechanically very stable, exhibits ferroelectric properties above room temperature and can be easily prepared and used in the form of ceramic samples [2].

$BaTiO_3$ has been synthesized by using different techniques depending on its cost and application [3]. In traditional synthesis methods of $BaTiO_3$, BaO or $BaCO_3$ reacted with TiO_2, which led to $BaTiO_3$ particles with huge size and irregular morphologies due to inherent problems such as the high reaction temperature and heterogeneous solid phase reactions, among others [4,5]. Chemical synthesis of ultrafine $BaTiO_3$ powders has been achieved by using different techniques, such as polymeric precursor [6], hydrothermal [7], sol–gel [8], sol–gel-hydrothermal [9] and other methods [10].

It was reported by Tao et al. that $BaTiO_3$ nanoparticles can be synthesized by using electrochemical route [1]. These used two titanium plates as anode and cathode in water or water/ethanol mixtures containing KOH and $Ba(OH)_2$ as electrolyte. Anodic sparks appeared which played an important role in $BaTiO_3$ synthesis. They also found that sizes of the obtained

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particles became uneven and larger when distilled water was used as solvent, whereas the electrolyte containing 60 vol% of ethanol was suitable to produce smaller particles. It was demonstrated that $BaTiO_3$ nanoparticles synthesized in this way were of cubic phase and the size of these nanoparticles can be controlled by varying composition of the electrolyte.

However, there are a number of parameters that could affect the properties of $BaTiO_3$ nanoparticles by using electrochemical method, such as the type of solvents and NaOH concentrations. Thus, in the present study, we investigated the effect of such variables. Titanium electrodes in alkaline solution were utilized with an applied current of ≈ 3.25 A. The electrolyte solution consisted of NaOH (at different concentrations) and $Ba(OH)_2$ (0.1 mol L^{-1}) dissolved in ultrapure water or water/methanol mixtures. Composition of the solvent was adjusted by using water containing isopropanol, ethanol or ethylene glycol in the same ratio (50% v/v). 0.1 mol L^{-1} urea solution was also studied.

2. Experimental

Two titanium plates were used as the anode and cathode. Surfaces of the electrodes (area $\sim 16\ cm^2$) were mechanically polished with 180- and 360-grid sandpapers, and were then washed in acetone to remove residues such as grease originated from handling. An ultrapure water (purified by a Milli-Q system) used for the electrolytic solutions was boiled for 30 min to remove CO_2. A thermostatic Pyrex® glass electrochemical cell with a capacity of 250 mL coupled to an ultrathermostatic bath (Nova Ética, Brazil) was used. NaOH (1.0 mol L^{-1}) and $Ba(OH)_2$ (0.1 mol L^{-1}) were the precursors used to constitute the electrolytic solution and 0.1 L of water containing the same volume of methanol was employed initially as solvent. A schematic diagram of the electrochemical cell used in the experiments is shown in Fig. 1. The Ti plates were fixed on an acrylic lid and two-thirds of their length was immersed in the electrolyte, with a separation distance of 20 mm.

Concentrations of NaOH were 0.5 mol L^{-1}, 1.0 mol L^{-1}, 2.0 mol L^{-1}, 3.0 mol L^{-1}, and 4.0 mol L^{-1}.

The electrochemical synthesis was performed by using a DC power supply (ICEL PS – 5000, Manaus, Brazil) with a voltage of 65 V (maintained for 2 h) and current of about 3.25 A. Nanoparticles were synthesized in one step and the solution reaction was maintained at 60 °C. The reaction that forms $BaTiO_3$ can be expressed as follows [1]:

$$Ba^{2+} + Ti + 6OH^- \rightarrow BaTiO_{3\ (s)} + 3H_2O + 4e^- \quad (1)$$

The final product of electrolysis, $BaTiO_3$, was filtered and washed with nitric acid solution (0.1 mol L^{-1}) to remove unwanted $BaCO_3$. Later, the samples were placed in an oven and dried at 60 °C for 8 h. XRD patterns were taken by using a Rigaku Rotaflex RU-200B diffractometer operating with Cu Kα radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 40 mA. All scans were carried out at 2° min^{-1} for 2θ values between 20° and 80°. Morphological characterization was performed by using a scanning electron microscope (Shimadzu, model SS 550 Superscan). Scanning electron microscopy (SEM) images were acquired by applying an accelerating voltage of 15 kV and a current intensity of 30 μA. Transmission electron microscopy (TEM) investigations in order to determine morphology and average particle size of the $BaTiO_3$ nanoparticles were performed with a Jeol JEM 2100 HTP transmission electron microscope operating at 200 kV. The powders were ultrasonically suspended in water for 30 min, and the suspensions were deposited onto carbon-coated copper grids.

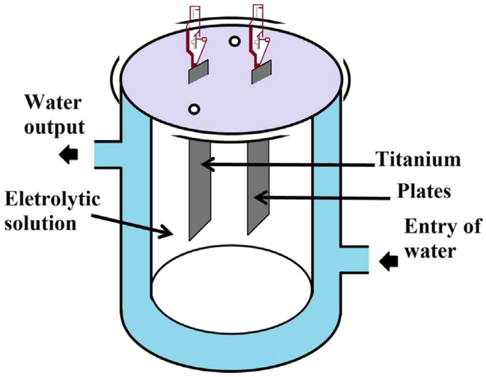

Fig. 1. Schematic diagram of the electrochemical cell setup.

3. Results and discussion

3.1. Formation of TiO_2 under electrochemical conditions

The current was maintained constant at 3.25 A. Anodic sparks, which appeared on electrode surface, indicated that electrical breakdown had occurred, accompanied by the destruction of the electrical insulating barrier layer [1] and by the oxidation of the Ti anode in the electrolytic cell. Since the reaction liberated energy, temperature of the electrolyte was controlled by an ultrathermostatic bath, thus avoiding boiling of the electrolyte. During the reaction, the appearance of sparks was diminished and they totally disappeared after 2 h of reaction, at which point the $BaTiO_3$ powder was observed as a white precipitate.

$BaTiO_3$ formation occurred with the dissolution of titanium oxides reacting with OH^-, preferably as $(TiO_3)^{2-}$ [10], followed by the reaction with Ba^{2+}. According to Tao et al. [1], anodic spark discharge played a key role and was responsible for the generation of TiO_2. Anodic oxidation proceeds according to the following two reactions [10]:

$$Ti \rightarrow Ti^{4+} + 4e^- \quad (2)$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (3)$$

Titanium oxides were dissolved due to the reaction with OH^- to form $(TiO_3)^{2-}$. The reaction can be expressed as follows [10]:

$$Ti + xH_2O \rightarrow [TiO_x]^{4-2x} + 2xOH^- + 4e^- \quad (4)$$

The latter ion reacted with Ba^{2+} in the solution to form $BaTiO_3$ [10].

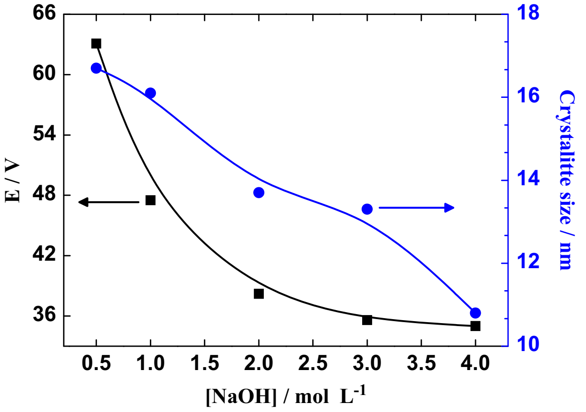

Fig. 2. Potential and crystallite size *versus* NaOH concentration.

3.2. Effect of electrolyte composition on the formation of the $BaTiO_3$ nanoparticles

Fig. 2 shows a plot of potential (V) and crystallite size as a function of the NaOH concentration (mol L^{-1}). Breakdown potential decreased when NaOH concentration was increased from 0.5 to 4.0 mol L^{-1}. As the content of alkalinity was increased, the conduction of electric current became easier and consequently lower applied potentials were needed for the reaction. The same trend was observed for crystallite size, where it could be seen that sparks were distributed more uniformly on the Ti surface with increased content of alkalinity, leading to a more uniform Ti detachment from the immersed area of the titanium plate. This improved distribution of Ti at the electrode/solution interface promoted a reduction in crystallite size. When, however, the concentration of NaOH was 0.5 mol L^{-1}, the migration of ions was impaired and the current reached a maximum value of only 0.25 A; therefore, little Ti detachment occurred and consequently less $BaTiO_3$ was formed, noting the formation of $BaCO_3$ instead, which will be discussed later.

Fig. 3 presents a plot of current and potential as a function of time. In Fig. 3a (2.0 mol L^{-1} NaOH) the potential was initially high, but decreased with reaction time probably due to the decrease in total surface area of the Ti electrode during anodizing by Ti dissolution. Similar behavior was seen for remaining NaOH concentrations studied, except for 0.5 mol L^{-1}. The results are shown in Fig. 3b where a constant potential could be seen during the entire electrolytic process probably because the Ti release was very slight.

Fig. 3a also shows that the applied current of 3.25 A remained almost constant during the reaction, suggesting that the highly alkaline environment of the electrolyte ensured the flow of current during the entire reaction. In Fig. 3b, the current steeply dropped in the first 10 min of the reaction from 3.25 A to 0.14 A and remained almost constant thereafter, with a small increase to 0.25 A. This current behavior occurred when NaOH concentrations were lower than 0.5 mol L^{-1}, which was due to the insufficient quantity of available OH^- ions, thus limiting the flow of current during the reaction.

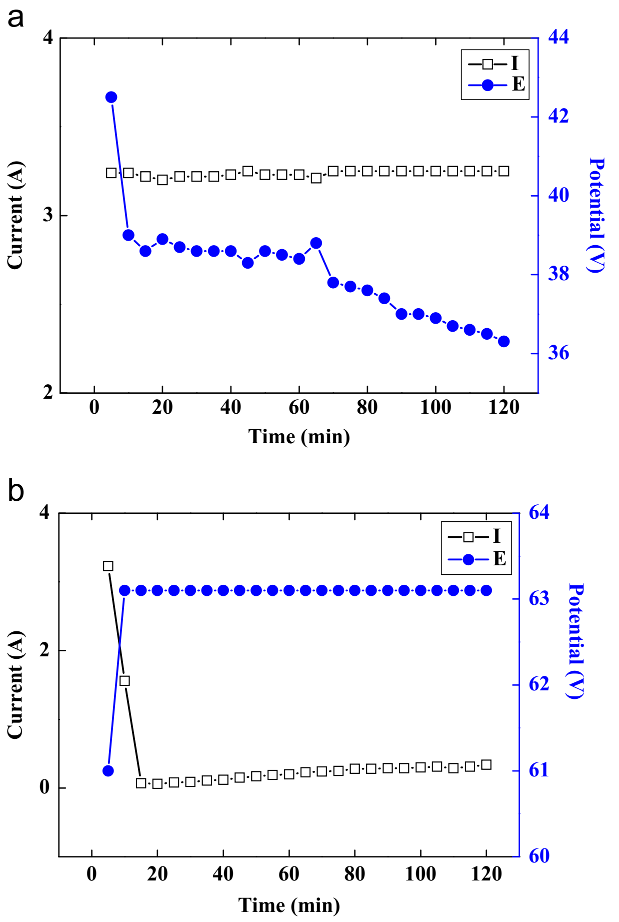

Fig. 3. Variations of current and breakdown potential during the reaction (2 h) for the synthesis of $BaTiO_3$ nanoparticles. Supporting electrolyte concentrations were 2.0 mol L^{-1} (**a**) and 0.5 mol L^{-1} (**b**).

A current of 3.25 A (Fig. 3a) was sufficient to promote the effective detachment of titanium from the electrode, as could be clearly seen from the sparks that occurred at the anode.

We also observed that a higher amount of $BaTiO_3$ nanoparticles were obtained with intermediate NaOH concentrations, *i.e.* 2.0 mol L^{-1} and 3.0 mol L^{-1} (Table 1).

3.3. Effect of solvent composition on formation of the $BaTiO_3$ nanoparticles

The effect of salt concentration was initially studied in a water/methanol (v/v 50:50) mixture. Later, it was evaluated using only water or using other alcohols (v/v 50:50) or compounds to replace methanol; they included isopropanol, ethanol, and ethylene glycol. In addition, an amide dissolved in water (urea) was also employed at a concentration of 0.1 mol L^{-1}.

Potential *versus* the type of solvent, depicted in Fig. 4, shows that for compositions containing only water and mixtures of water and methanol or ethanol, breakdown potentials were lower than 50 V. In contrast, for mixtures containing water and ethylene glycol or isopropanol, as well as for the urea solution, the potentials were high of that 60 V.

Table 1
Operating variables used and their influences on crystallite size and amount of $BaTiO_3$ synthesized.

Initial potential (V)	Final potential (V)	[NaOH] (mol L^{-1})	Initial current (I)	Final current (I)	Crystallite size (nm)	Mass (g)
63.1	63.1	0.5	0.14	0.25	16.7	0.020
47.6	38.8	1.0	3.25	3.25	16.1	2.741
38.2	37.6	2.0	3.25	3.25	13.7	3.036
35.6	33.7	3.0	3.25	3.25	13.3	2.902
35.0	34.1	4.0	3.25	3.25	10.8	1.889

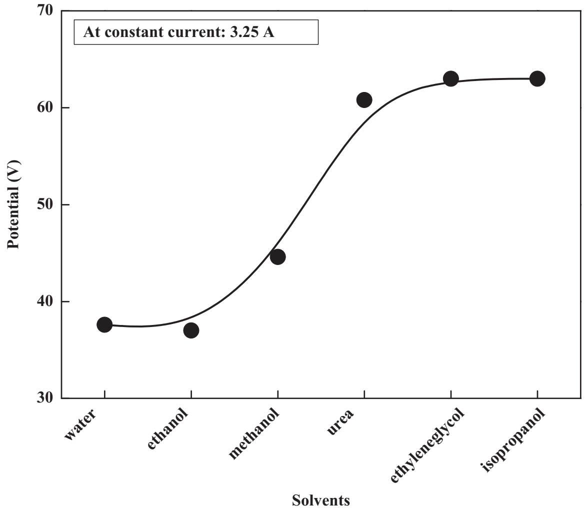

Fig. 4. Potential *versus* type of solvent employed in $BaTiO_3$ synthesis at an applied current of 3.25 A.

For urea, ethylene glycol, and isopropanol, insignificant anodizing of the anode was observed, because of the low current of 0.25 A, which increased the potential. For mixtures containing ethanol and methanol, a value of 3.25 A, necessary to promote the synthesis reaction, was reached. Consequently, the current flowed easily and the potential was lower than those for the other solvents. This decrease in potential is important, since it indicates a decrease in surface area of the electrode and suggests that titanium anodizing happened.

As will be shown hereafter, XRD analysis showed the preferential formation of $BaCO_3$ for solvents containing urea, ethylene glycol, and isopropanol, as expected; if detachment of Ti did not occur to a significant degree, $BaTiO_3$ could not be formed.

3.4. X-ray diffraction

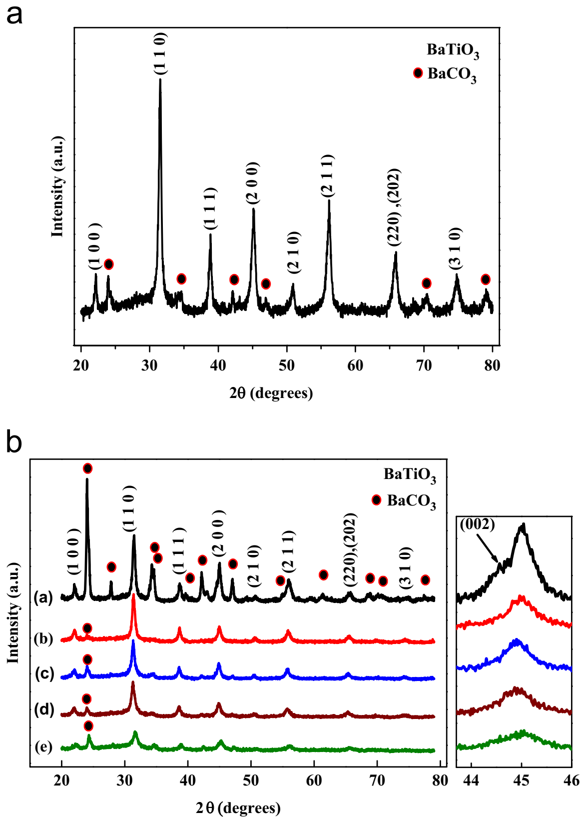

Fig. 5. XRD patterns of the samples prepared using NaOH (1 mol L^{-1}) and $Ba(OH)_2$ (0.1 mol L^{-1}) in ultrapure water as solvent (**a**) and using ultrapure water/methanol with different concentrations of NaOH in the electrolyte (**b**): (a) 0.5 mol L^{-1} (b) 1.0 mol L^{-1} (c) 2.0 mol L^{-1} (d) 3.0 mol L^{-1} and (e) 4.0 mol L^{-1}. Right: magnification of a region of Fig. 5**b**.

Fig. 5a shows XRD patterns of the samples prepared using only water as electrolyte. The presence of peaks related to $BaCO_3$ can be noted. Fig. 5b shows the high crystallinity of the nanoparticles produced at NaOH concentrations between 1.0 mol L^{-1} and 4.0 mol L^{-1} and the presence of considerable amounts of $BaCO_3$ at 0.5 mol L^{-1} NaOH could be seen.

Splitting of the (200) reflection at a lower angle signal indexed as (002) is an indication of tetragonal form of $BaTiO_3$ [11–14]. In cubic form, this peak is not split [14]. Moreover, the small grain size of nanoparticles can contribute to the overlapping of peaks leading. Ianculescu et al. [15] reported similar XRD results for $BaTiO_3$ synthesized by soft chemistry routes, such as a modified Pechini method and thermal decomposition of an oxalate precursor. The XRD patterns were indexed as single-phase $BaTiO_3$ perovskite. Although the almost symmetrical profile of the (200) peak at $2\theta = 45.3°$ seemed to indicate a "pseudocubic" structure, deconvolution and fitting techniques allowed to establish a tetragonal symmetry for the synthesized powders. Lu et al. [13] also synthesized tetragonal $BaTiO_3$ by using a hydrothermal method, where two overlapping peaks at 44.85° and 45.38° were observed.

Habib et al. [14] reported the synthesis of $BaTiO_3$ powders at 185 °C, where he achieved powders with crystallite size of 66 nm and high tetragonality by using a solvothermal route in an ethanol/water mixture. Tetragonal $BaTiO_3$ particles smaller than 100 nm in diameter have also been synthesized by using different methods [13,15–18]. In this study, we synthesized $BaTiO_3$ nanoparticles with sizes of 7–9 nm with a tetragonal structure at 60 °C for the first time.

Habib et al. [14] stated that the presence of ethanol was an important factor that facilitated the formation of tetragonal $BaTiO_3$, which was confirmed by Kown et al. [18]. Habib and colleagues also enforced what was proposed by Kown et al. [18] that OH^- played a vital role in the stabilization of tetragonal phase. However, it is difficult to show how OH^- contributed to this, as the reaction in alcoholic aqueous solutions is complex and there is currently limited information available regarding the kinetics and the underlying crystallization mechanism in these solutions.

Table 1 shows the operating variables used and their influences on crystallite size and the amount of $BaTiO_3$ synthesized. The crystallite sizes were in the range of 10.8 and 16.7 nm, indicating that the electrochemical method can produce nanoparticles with small crystallite sizes. The crystallite size of the $BaTiO_3$ nanoparticles was decreased as NaOH concentration was increased.

The latter behavior can be rationalized by considering that, at higher concentrations of supporting electrolyte (from 1.0 to 4.0 mol L^{-1}), the reaction became milder and the distribution of sparks on the electrode became more homogeneous. This improved distribution of sparks led to better Ti detachment and distribution at the electrode/solution interface, promoting a reduction in crystallite size.

Fig. 6a shows XRD patterns of the samples prepared with different solvent compositions. Crystalline $BaTiO_3$ can be synthesized when the electrolyte contained pure water (a), water/ethanol (b), or water/methanol (c).

Crystallite sizes of the samples synthesized with only water, water/ethanol, and water/methanol were 20.4 nm, 17.2 nm and 16.1 nm, respectively. Thus, the use of methanol in the solvent is more efficient in producing smaller nanoparticles.

In contrast, for the solvents containing 50 vol% of urea (a), water/ethylene glycol (b) and water/isopropanol (c), $BaTiO_3$ nanoparticles were not obtained. Instead, there was only $BaCO_3$ (Fig. 6b). In the XRD pattern of the samples obtained by using 50 vol% of urea, in addition to $BaCO_3$ (JCPDS No. 01-071-2394), peaks related to urea were also noted (JCPDS No. 01-072-1196) (Fig. 6b-(a)).

The XRD results observed in Fig. 6b can be attributed to the fact that these solvents participated negatively in current passage and prevented the dielectric rupture of Ti. Consequently, without any or with little release of Ti, the reaction of $BaTiO_3$ formation could not occur, and stable $BaCO_3$ was preferentially formed.

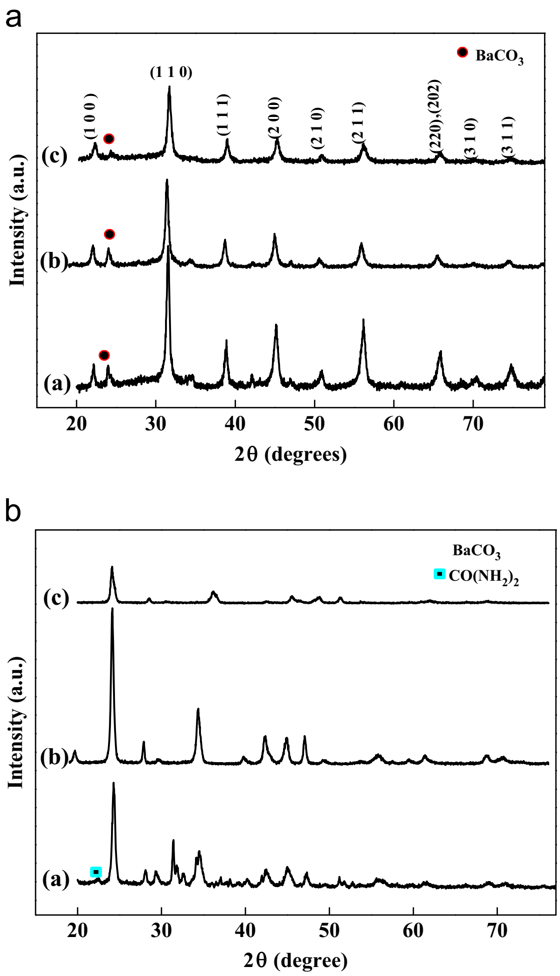

Fig. 6. XRD patterns of the samples prepared with different solvents (**a**): pure water (a), water/ethanol (b) or water/methanol (c), showing the formation of crystalline $BaTiO_3$ and (**b**): urea (a) ethylene glycol (b) and isopropanol (c).

3.5. SEM and TEM images

Fig. 7 shows SEM images of the samples synthesized using only water as solvent (Fig. 7a) and with different concentrations of NaOH in the electrolyte containing water/methanol (Fig. 7b–f). The presence of residual $BaCO_3$ in the sample prepared with only water as solvent was noted, as indicated by the arrow in Fig. 7a, which is in agreement with the XRD data. These nanoparticles (Fig. 7a) had areas with irregular sizes and were highly aggregated, indicating particles coalescence. Similar results have been reported by Ianculescu et al. [15]. Analogously, Tao et al. [1] found that when only distilled water was used as solvent, the size of the $BaTiO_3$ nanoparticles became uneven and large. They observed a decrease in nanoparticle size when an electrolyte containing 60 vol% of ethanol was used.

Fig. 7b shows micrographs of the $BaTiO_3$ samples synthesized using 0.5 mol L^{-1} NaOH. The presence of particles with different aggregations characterized the heterogeneity of the sample. It was also observed that the size of the particles was smaller and more homogeneous when methanol was used in the solvent and with a small amount of $BaCO_3$ (Fig. 7b–f). Similar behavior was reported by Chen et al. [19]. As shown in Table 1, the particle size decreased as the molarity of NaOH was increased in the supporting electrolyte.

The TEM micrographs of the $BaTiO_3$ nanoparticles synthesized using water/methanol as solvent and 3.0 mol L^{-1} NaOH as the supporting electrolyte (Fig. 8) show the agglomeration of the nanoparticles, probably because of the difficulty in dispersing this powder. Thus, it was difficult to estimate the average particle size by using TEM. Some particles of 7–9 nm

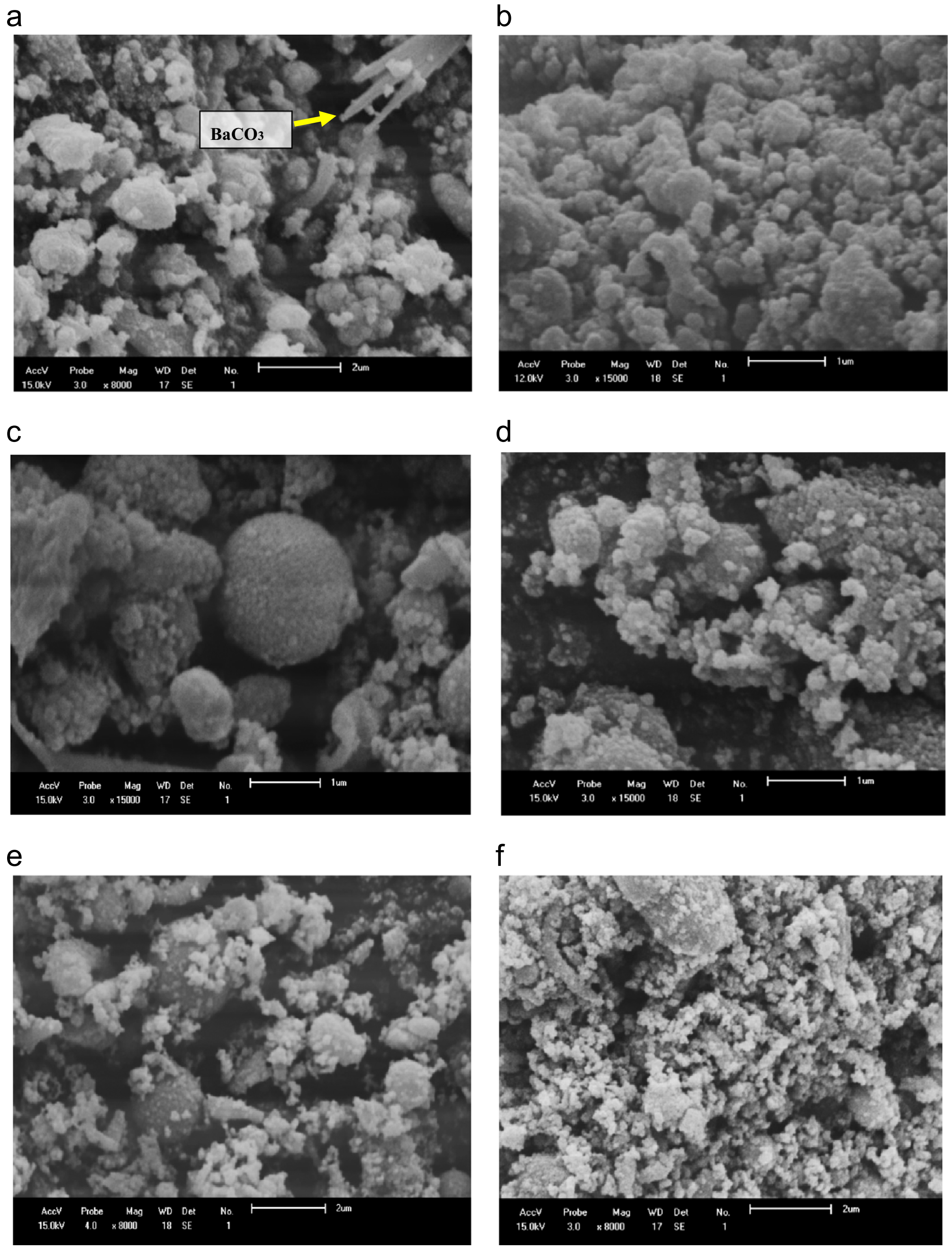

Fig. 7. SEM micrographs of $BaTiO_3$ synthesized using NaOH (1 mol L^{-1}) and $Ba(OH)_2$ (0.1 mol L^{-1}) in water as solvent to compose supporting electrolyte (**a**) and for solvents consisting of water/methanol with different concentrations of NaOH: 0.5 mol L^{-1} (**b**) 1.0 mol L^{-1} (**c**) 2.0 mol L^{-1} (**d**) 3.0 mol L^{-1} (**e**) and 4.0 mol L^{-1} (**f**).

can be observed in Fig. 8b as dark regions in images, along with one agglomerate of about 25 nm. Small particles (~13 nm) were also observed by Kobayashi et al. [20].

On the other hand, similar to what was observed by Suzuki et al. [21], clear lattice fringes in the TEM images revealed that the $BaTiO_3$ nanoparticles have high crystallinity (Fig. 4b).

4. Conclusions

The effects of composition of the electrolyte and concentration of NaOH on the formation of $BaTiO_3$ nanoparticles were studied. $BaTiO_3$ nanoparticles with different morphologies were successfully synthesized. The use of ethanol and methanol in the solvent produced nanoparticles with high crystallinity. It was clear that Ti released from the electrode surface was an important factor that was responsible for the final characteristics of the material. With high alkalinity (*i.e.* 4.0 mol L^{-1} NaOH), the sparks were distributed uniformly on the Ti surface, leading to more uniform Ti detachment from the immersed area of the titanium plate; consequently, the nanoparticles that were formed were homogeneous and smaller than those obtained at lower concentrations of NaOH in the electrolyte. When only water was used as solvent, the

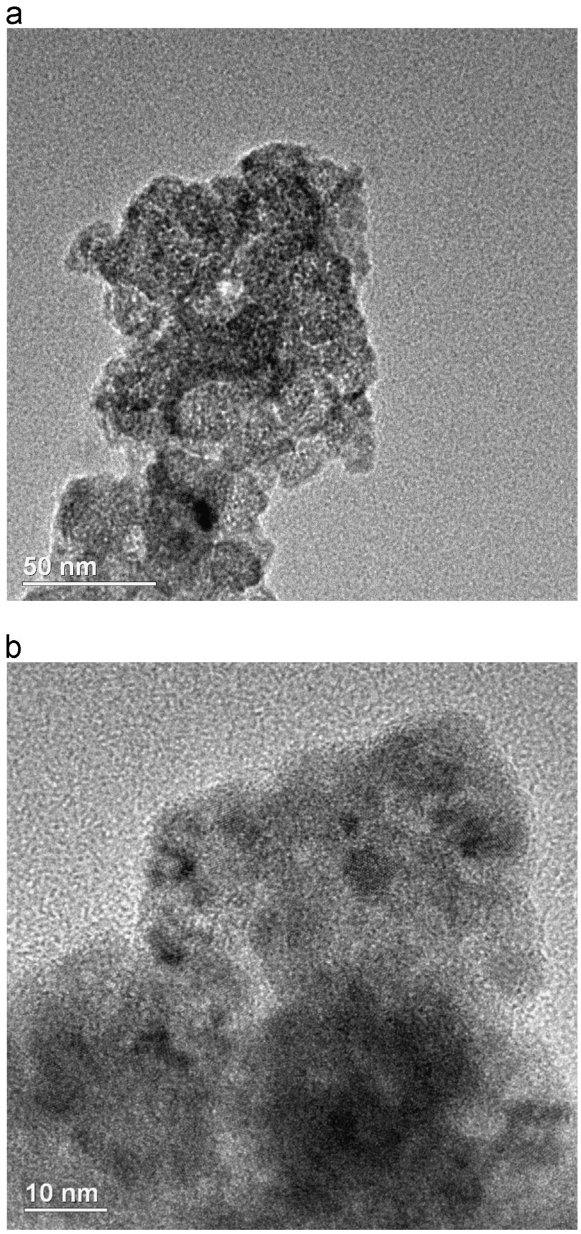

Fig. 8. TEM micrographs at different magnifications of the $BaTiO_3$ nanoparticles obtained by electrochemical synthesis using water/methanol as solvent containing $3.0\ mol\ L^{-1}$ NaOH and $0.1\ mol\ L^{-1}$ $Ba(OH)_2$ as supporting electrolyte.

nanoparticles aggregated and there was higher content of $BaCO_3$. This study demonstrated that it is possible to synthesize tetragonal $BaTiO_3$ spherical particles with sizes of 10.8–16.7 nm in tetragonal phase.

Acknowledgments

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