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Aqueous Solution of $VOSO_4 \bullet xH_2O$ in Solution Plasma Process

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Abstract: In this work, the goal was to synthesize vanadium containing nanoparticles with solution plasma process (SPP) method. The solution plasma was produced by discharging with a bipolar DC power supply and the system was applied to 0.25 M aqueous solution of $VOSO_4 \bullet xH_2O$ to prepare vanadium containing nanoparticles. The effects of different discharge times (0, 10, 20 and 30 minutes) and applied voltage (1500 V) during the synthesis were investigated. From all experiments same vanadium oxide compound(s)/mixture(s), named as "the product" and formulated as "V_xO_y", were obtained. The product was tried to be characterized by using FTIR, TGA, DTA, XRD and FESEM-EDX analysis results.

Keywords: Nanoparticle, nanocrystal, $VOSO_4.xH_2O$, solution plasma process

Çözelti Plazma Sürecinde $VOSO_4 \bullet xH_2O$'nun Sulu Çözeltisi

Öz: Bu çalışmanın amacı çözelti plazma yöntemiyle vanadyum içeren nanoparçacıklar sentezlemektir. Vanadyum içeren nanoparçacık elde etmek için, 0.25 M VOSO4•xH2O çözeltisinde DC güç kaynağından gelen elektriğin deşarjıyla üretilen plazma kullanılmıştır. Farklı deşarj sürelerinin (0, 10, 20 ve 30 dakika) ve uygulanan voltajın (1500 V) senteze etkisi incelenmiştir. Bütün deneylerden ürün olarak V_xO_y olarak formüllendirilen aynı vanadyum oksit bileşikleri/karışımları elde edilmiştir. Bu çalışmada elde edilen ürünler FTIR, TGA, DTA, XRD ve FESEM-EDX analiz sonuçları kullanılarak karakterize edilmeye çalışılmıştır.

Anahtar kelimeler: Nanoparçacık, nanokristal, $VOSO_4.xH_2O$, çözelti plazması işlemi

1. Introduction

The solution plasma process (SPP) has been gathered great attention for many applications like nanoparticle preparations, water purification, chemical degradation as well as sterilization [1]. The plasma in solution or SPP looks novel, useful, and simple technique to synthesize the metal nanoparticles [2-9]. Silver and gold nanoparticles were successfully prepared by using SPP without addition of any reducing reagents [6-9]. SPP was also used for the precise nanomaterial synthesis Pt, AuPt, Pd, PdAu, Ag, Au alloys, metal oxide nanoparticles, and nanosheets [10-19]. Because the non-equilibrium plasma may yield extremely accelerated reactions due to the reactive chemical species, radicals and UV radiation originated in the atmospheric pressure conditions [2-5]. In other words, SPP suggests many advantages by presence of active species like H, O, OH, and HO_2 radicals and radiation. During discharge SPP provides high energy electrons and UV radiation for chemical reactions [9,19-21]. Although there are many chemical synthetic methods, chemists are still looking for new synthetic methods for preparation of compounds in high yield. In this

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perspective SPP method might be superior to other conventional synthetic methods by having properties like easy of handling of chemicals, not necessary to control pressure and temperature, etc.

Vanadium oxides have much interest in the last three decades due to their potential use as secondary cathode materials for advanced lithium batteries and their important role in many catalytic applications [22-27]. Deep crystal chemistry of open framework oxide structures has been intensively filled with various vanadium oxide compounds. The variety of vanadium oxidation states and their redox properties have been revoked great interest in vanadium oxide structures [23-25]. The structures of these vanadium oxides are formed by coordination of vanadium (oxidation state change from V to III.) and oxides ions. The coordination geometries in the vanadium oxide compounds consist of tetrahedral, trigonal pyramidal, square pyramidal, octahedral and octahedral polyhedrons by sharing corner/edge/face of polyhedrons [22-24].

Our works recently focused on reactions of vanadium compounds with organic ligands and we also tried to prepare vanadium containing nanomaterials in SPP conditions. In the present work, vanadium oxide compound(s)/mixtures "the product" in microcrystalline form were synthesized from $VOSO_4 \bullet 5H_2O$ aqueous solution by using one-step SPP method. Although we could have not reached the goal yet, SPP method still looks promising for vanadium related synthetic procedures. This work still demonstrates another merit of the SPP method for the preparation of vanadium containing crystalline/nanomaterials. It is worth that the other compounds of vanadium and their reactions with organic ligands in SPP conditions will be investigated.

2. Experimental

Materials. All chemicals used are in reagent grade and as received from the commercial sources (Fluka).

Methods. The SPP system reported by Watthanaphanit was modified and used for the experiments [28]. A 50 ml glassware was used as the plasma vessel. Two tungsten needle electrodes (diameter of 1 mm), covered by ceramic tubes, were fixed by the conical Teflon plugging. The distance gap between two electrodes was set to 0.3 mm. The bipolar-DC power supply (Pekuris MPP HV-04) was used for discharge production. The pulsed electric discharge was generated at fixed voltage (1.5 kV), pulse width (2.5 s) and frequency (15 kHz). During the experiment, no action was applied to minimize the increase of temperature.

The IR spectrum (KBr Pellet; 4000-400 cm^{-1}) was recorded on a Shimadzu brand IRAffinty-1S FTIR spectrophotometer. Thermogravimetric analysis was performed on Netzsch brand STA 449F3 model under air and inert gas atmosphere (argon) by heating (20°C/min) in the temperature range 25-1300°C. FESEM images were obtained by using Carl Zeiss brand Supra VP40 model instrument. XRD patterns with CuK_α radiation (λ=1.54056 Å) were obtained by using Bruker brand D8 Advance model instrument.

3. Results and Discussions

0,25 M aqueous $VOSO_4 \bullet xH_2O$ (x=5) solution was prepared and SPP experiments of the solution were done with the pulsed electric discharge generated at fixed voltage (1.5 kV), pulse width (2.5 s) and frequency (15 kHz) for 5, 10, 15, 20, 25 and 30 minutes without temperature control. Each experiment gave same dark greenish-black microcrystalline vanadium oxide products which was not able to be fully characterized. FTIR spectrum (Figure 1) and XRD pattern (Figure 2) of the products show that all the products were same compound or mixture. FTIR spectrums and XRD

patterns are different than commercial vanadium oxide compounds such as V_2O_5, VO_2, V_4O_7 and V_2O_3 [29-33]. The product also does not contain hydroxyl or sulfate groups.
The XRD patterns showed that vanadium oxide compound or mixture is in microcrystalline form. The strong peaks observed at 2θ angles of 25.780, 34.70, 47.250, 50.250 and 71.380 in the XRD patterns do not match the peaks of known vanadium oxide compounds.

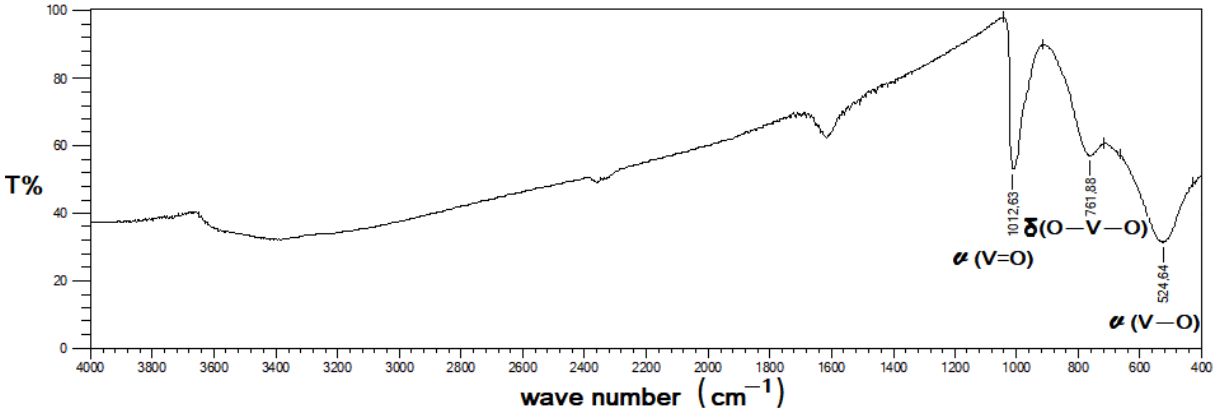

Figure 1. FTIR spectrum with vibration modes of the product.

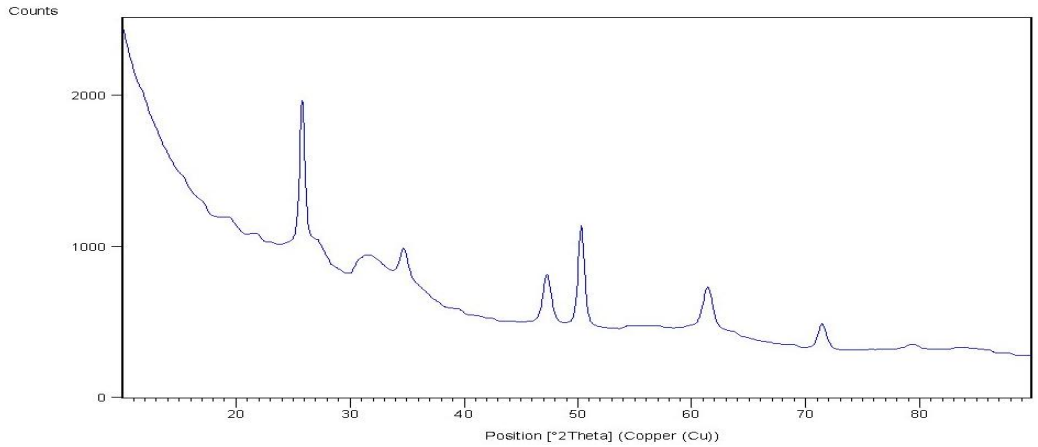

Figure 2. XRD pattern of the product.

TGA and DTA analysis between 25 and 1300°C were done in air and argon atmosphere to understand chemical composition and thermal behavior of the material (Figure 3).

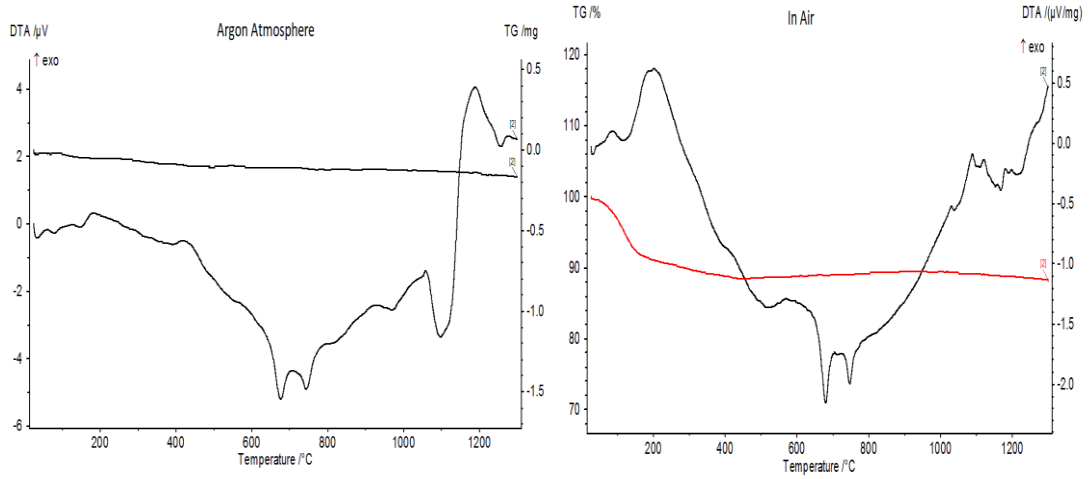

Figure 3. TG and DTA curves of the product in argon and air atmosphere.

In inert atmosphere no weight loss were observed. But in air about 10% weight loss were observed between 25 and 125^oC. If it is due to water molecules, it must be observed in argon atmosphere. So that we cannot say anything about this weight loss.

This weight loss may be due to humidity of sample container. If the mixture contains vanadium with low oxidation states (from +2 to +4), a weight increase in air atmosphere were expected between 375 and 650^oC [29-33]. But no weight increase in air atmosphere was observed and we could say that the products need more investigation in future. Also, the SPP method would be a novel method for preparation of vanadium oxide nanomaterials.

The FESEM image of the product is shown in Figure 4. Elemental analysis of the products by FESEM-EDX showed that the product was not a pure vanadium oxide compound. Elemental composition of the microcrystalline material varied between 59.22% and 75.93% for vanadium and between 23.34 and 40.72 for oxygen. So that it is formulated as V_xO_y. The image was obtained with 50.00 KX magnification and 200 nm strain. It can be said that from the FESEM image, the layers of vanadium oxide form a leaf-shaped pattern. It also is understood that the product contains layers (nano-sheets) with a thickness in nano-size rather than forming a nanoparticle.

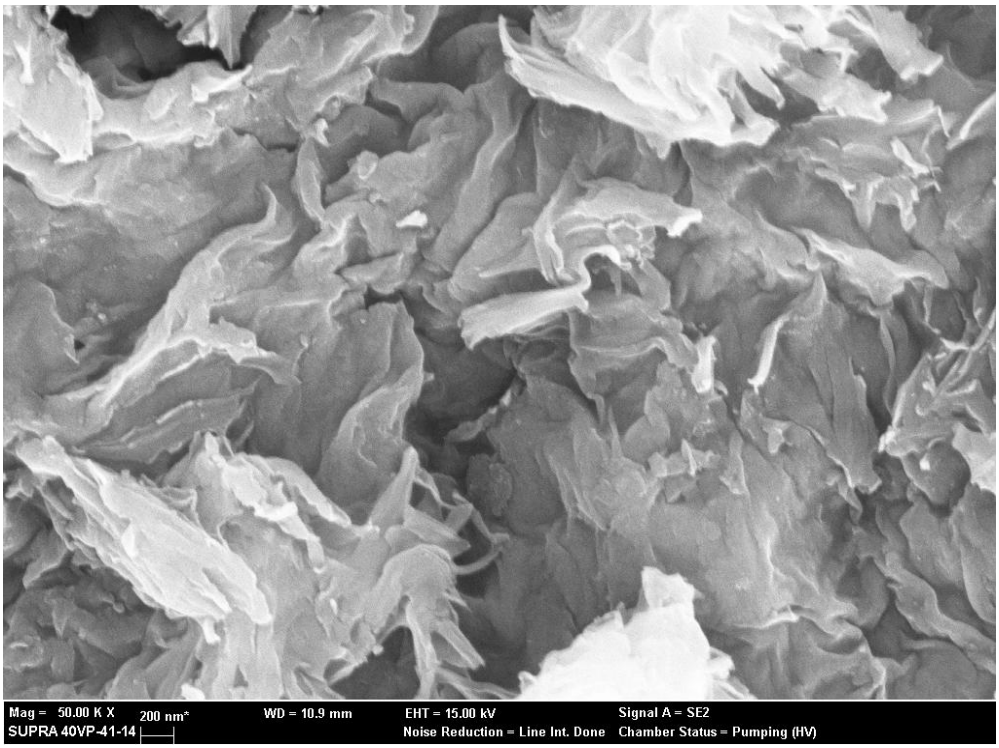

Figure 4. FESEM image of the product

4. Conclusions

A novel process was applied for preparation vanadium oxide compound(s) by SPP method. Analysis of the results did not give certain formula of the product. So that we were not able to fully characterize the product. The experimental results showed that the process described in this work is a suitable and effective approach to synthesis of vanadium oxide compounds. The SPP method may be optimized for the relevant chemical reactions of vanadium compounds with organic ligands. In future, this novel method should be more investigated and applied to the other chemical systems. Our ongoing works will contain effect of parameters such as pH, temperature, reagent types, concentration, time, voltage, pulse width in SPP method.

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