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Review

Application of mechanochemical synthesis of advanced materials

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Abstract: An overview is given of recent development of mechanochemical processes for the preparation of advanced ceramics. Some fundamental mechanical effects are firstly compared and discussed. Several important application fields are listed as follow, stemming from oxide materials, non-oxide materials, and composite materials to nano-structured materials.

Key words: mechanochemical; advanced materials; composite materials; nano scale

1 Introduction

Mechanochemical reaction is a process that a strong mechanical force proceeds materials destruction and causes a formation of a different structure. Mechanochemical method has been widely used in synthesis of advanced materials, covered almost all aspects of material science [1-3]. Mechanochemical process is a simple, environmental, low-cost technology. Interests in this field tend to rise continuously, and the number of related papers increases annually [4-6]. Even though the mechanisms of mechanochemical process are not completely clear.

In this review, we give some discussion of the mechanical effects during grinding, especially a new proposal of the mechanical effects of extrusion. Some important preparation works of advanced materials via mechanochemical process are summarized to demonstrate their application capability in the future.

Planetary ball mill is a typical machine in current use of mechanochemical process. The planetary ball mill performs grinding by continually revolving the large plate and rotating the containers concurrently. Both the plate revolution (centrifugal) speed and container rotation (planetary) speed are independently adjustable (Fig. 1). During grinding process, collision of balls plays an important role of energy transferring from balls to raw materials. After accepting mechanical energy from balls, the particles of raw materials rupture. So the particle size decreases, and specific surface and surface energy increase. These mechanical effects caused by collision can initiate significant structural changes and even chemical reactions in materials, which was defined as

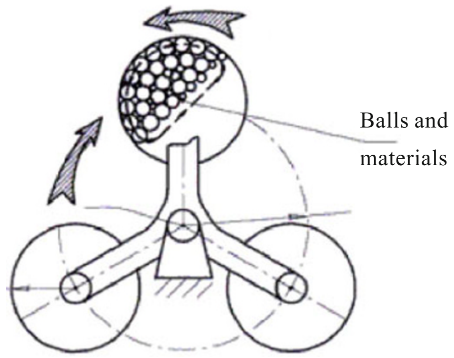

Fig. 1 A schematic diagram of the planetary ball mill

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mechanochemical reactions [7,8].

1 Mechanisms of mechanochemical processes

Mechanochemical reaction may be employed in synthesis of materials, and replace the solid state reaction at high temperature. However, there are two drawbacks of planetary ball mill. Firstly, most of direct collision of balls or between balls and chamber are useless to act the raw material and cause the loss of energy. Secondly, the collision at exact moment just induces short-lived activation of raw materials, and probability of chemical reaction is very low. So the low efficiency of planetary ball mill results in time-consuming (several days), energy-consuming and low productivity.

In order to extend the acting time of mechanical effects, a new mechanical effect should be selected. Some new grinding machines were designed to change the mechanical effects [9,10]. The new mechanical effect of these new machines is shearing force instead of collision. We also develop a new machine called screw grinding machine (Fig. 2). When the screw in the center rotates, powders of raw materials are compressed by the screw again the chamber wall, and extrusion is acted on particles. So most of mechanical energy are transferred to raw materials. Compared to collision, extrusion can act on particles and activate raw materials for a long time. So mechanochemical reaction drived by extrusion can be much more efficient and time-saving (several hours). In addition, the products can be easily collected from grinding machine.

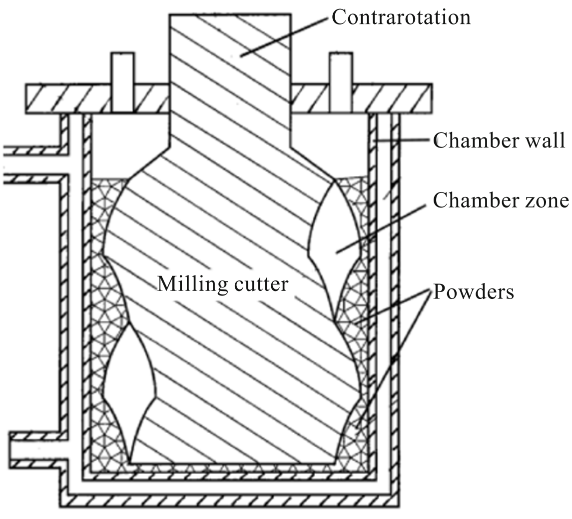

Fig. 2 A schematic diagram of the screw grinder

2 Synthesis of oxide materials

Early and major research works of mechanochemical synthesis are conducted at oxide materials. Stojanovic ever reviewed the research works of the formation of perovskite structure of BT, PT, PZT, PZN, PMN and LM ceramic materials by mechanochemical synthesis [11]. Zhang *et al*. synthesized a series of ABO_4-type oxide, and studied the relation between mechanochemical reactivity and the crystal structure in detail [12]. We also published some papers that reported the synthesis of complex oxide materials. Figure 3 is a typical SEM image of lead magnesiumniobate prepared by mechanochemical reaction. We found that high grind power can reduce the synthesis time, improve the purity of products and decrease the particle size [13] (Fig. 4).

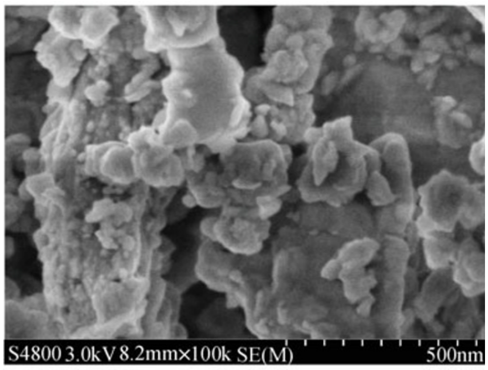

Fig. 3 SEM image of PMN prepared by mechanochemical reaction

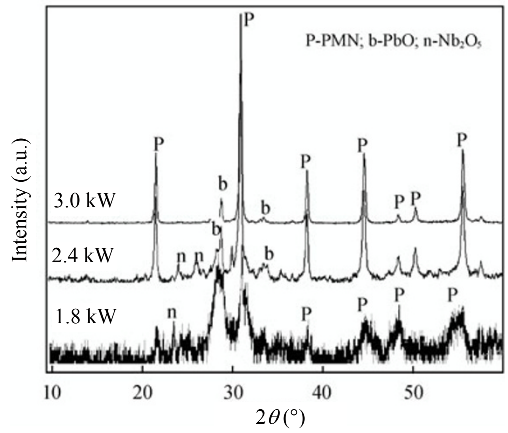

Fig. 4 Effect of grinding power on phase composition of product

We also successfully obtained Super Fine $LiMn_2O_4$ by a rapid mechanochemical process at low temperature [14] (Fig. 5).

From above research work, it was confirmed that mechanochemical process can be widely used in the synthesis of many important oxide ceramics.

3 Synthesis of non-oxide materials

When mechanochemical reaction is conducted at air atmosphere, oxide materials are usually synthesized. If the mechanochemical device can be gas tight and filled with inert gas, non-oxide materials can be prepared. Some non-oxide materials, such as ZrB_2, WC, AlN, etc. are successfully obtained via mechanochemical reactions at argon or nitrogen atmosphere [15-18].

ZrB_2 were produced by by magnesiothermic reduction, reaction (1), via mechano- chemical process at argon atmosphere [16].

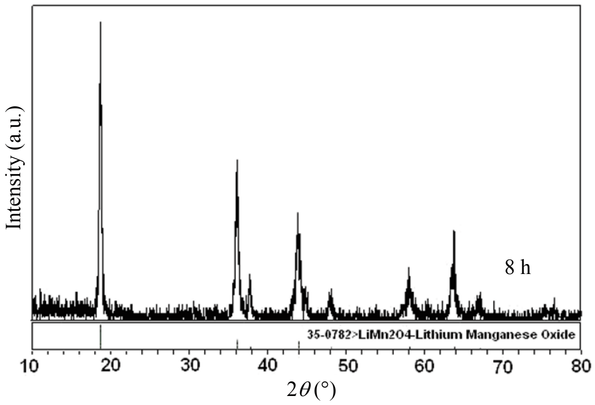

Fig. 5 XRD patterns of $LiMn_2O_4$ powders grinded under 3.0 kW after 8 h grinding

$$ZrO_2 + B_2O_3 + 5Mg = ZrB_2 + 5MgO \quad (1)$$

After 30 h of uninterrupted milling, ZrB_2 were formed. Figure 6 confirmed the existence of MgO and ZrB_2 at the end of 30 h uninterrupted milling treatment. The peaks of as-received ZrB_2 were intense and narrow. It is obviously that ZrB_2 has fine crystal structure. Another experiment of sample containing 30% excess Mg and B_2O_3 were preceded for 40 h milling. Fine phase of ZrB_2 were also obtained besides impurity of Fe due to long time milling. However, increasing both milling time and excess amounts of Mg and B_2O_3, unreacted ZrO_2 still remained. An additional treatment of 1M HCl was induced to remove MgO and Fe. As can be seen from Fig. 6, MgO and Fe can be completely removed.

Typical SEM image of product of mechanochemical process was shown in Fig. 7. Porous agglomerates of ZrB_2 and MgO was displayed, and ultrafine particles about 0.5 μm were found.

Vanadium nitride (VN) can be produced by mechanochemical process at a pressurized N_2 atmosphere [17], which is also a reactant. AlN was form by a solid-gas reaction, reaction (2).

$$2V+N_2=2VN \quad (2)$$

The analysis of XRD patterns (Fig. 8) display a broadening of Vanadium peaks due to comminution and refinement of Vanadium particles from 0.5 to 1.5 h at the same time the peaks of VN appear. After 4 h of milling, VN are the main phase shown in XRD patterns, in which the peaks of Vanadium disappear. Up to 8 h, the intensities of VN peaks continually rise.

The dimension of Vanadium metal and Vanadium

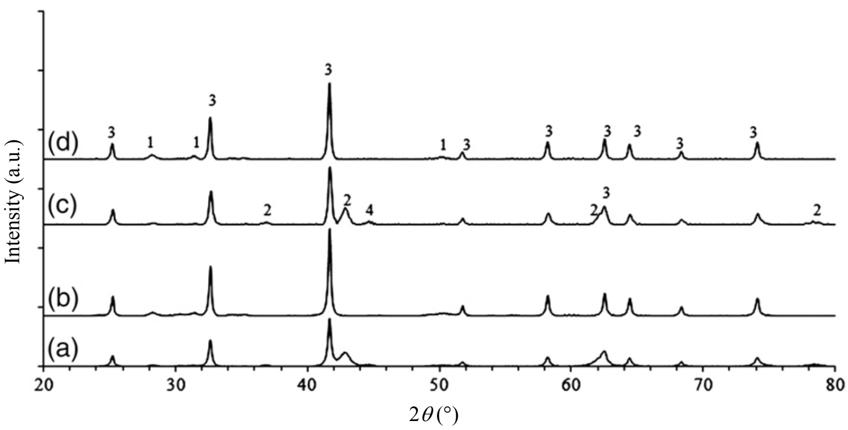

Fig. 6 XRD patterns of (a) sample containing 10% excess Mg and B_2O_3, ball milled for 30 h, (b) sample in (a) leached in 1 MHCl solution for 30 min, (c) sample containing 30% excess Mg and B_2O_3 ball milled for 40 h, (d) sample in (c) leached in 1 M HCl solution for 30 min, (1) ZrO_2, (2) MgO, (3) ZrB_2, (4) Fe

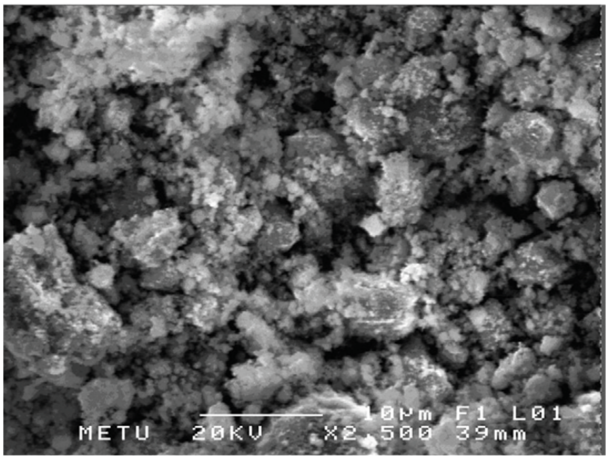

Fig. 7 SEM micrograph of sample containing 30% excess Mg and B_2O_3, ball milled for 40 h

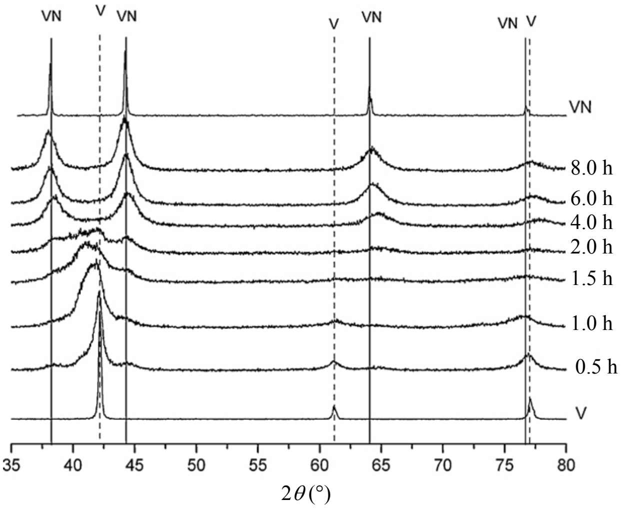

Fig. 8 X-ray diffraction patterns of vanadium ground from 0 to 8 h and the commercial VN for comparison

nitride cubic unit cell determined by XRD were enlarged while milling time was increased. The dimension of unit cell is sensitive to the nitridation level, which is obviously raised by prolonged milling time.

Morphology images (Fig. 9) of as-obtained VN ground under nitrogen atmosphere for 8 h by SEM exhibits agglomerated grains with size of 1-5 μm, and they are formed by nano-scale spherical particles.

4 Synthesis of composite materials

During mechanochemical process, homogenous dispersion and mixture of different components are its important functions. So mechanochemical process is very suitable for preparation of composite materials, and produces homogenous hybrid structure. Some synthesis of important composite materials was explored via mechanochemical process, for examples, some metal-oxide system [19-22].

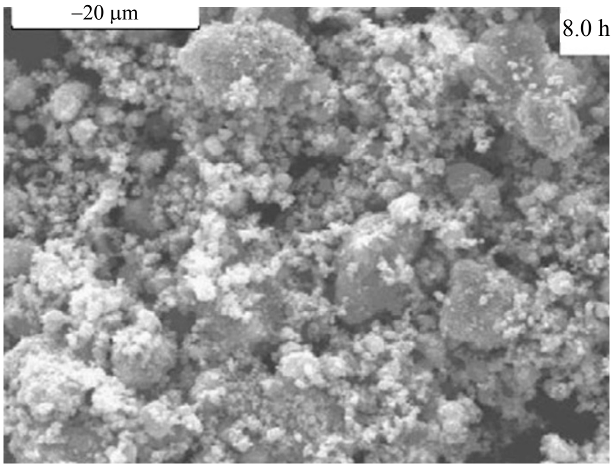

Fig. 9 Micrographs of vanadium ground under nitrogen atmosphere for 8 h

Al_2O_3 is an important reinforcement candidate in the intermetallic compounds (IMC). Alumina reinforced intermetallic is provided with several advantages of high strength, good wear resistance and improved fracture toughness. So it is a good attempt to fabricate Al_2O_3/IMC composite by mechanochemical process. The new high temperature structural materials, Ti_5Si_3-Al_2O_3, were prepared by mechano- chemical reaction from raw materials of TiO_2-Al-Si [23]. The mechanochemical reaction includes several steps:

$$3TiO_2 + 4Al = 2Al_2O_3 + 3Ti \qquad (3)$$

$$3Ti + 1.8Si = 0.6Ti_5Si_3 \qquad (4)$$

The XRD patterns (Fig. 10) of mixtures after different milling time confirm the formation of Ti_5Si_3. After the mixture was milled for 45h, the peaks of TiO_2-Al-Si starting materials disappeared and only peaks of Ti_5Si_3 could be found. In suit formed Al_2O_3 have very fine size with an amorphous structure, and cannot be found in XRD pattern. But in suit formed Al_2O_3 with fine size prompt a homogenous reinforced structure and enhance the properties of composites.

Figure 11 displays the typical SEM photos of composites at different milling times. After long time of milling, the mixture was uniform and homogenous. Finally after 45 h of milling, agglomerated structure

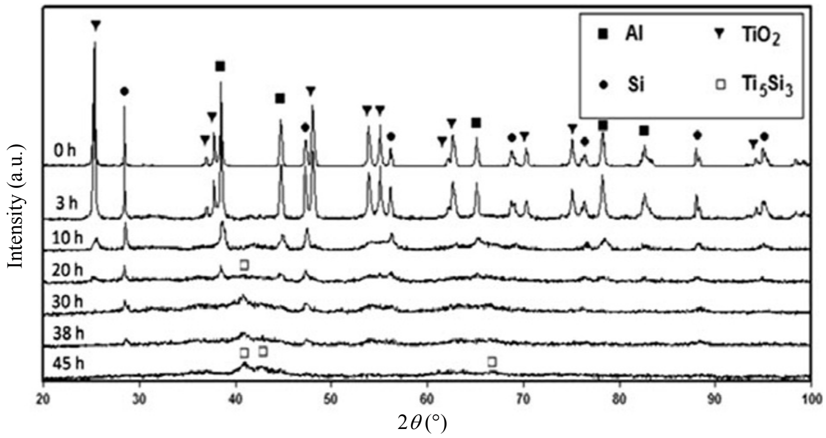

Fig. 10 XRD patterns of powder mixture as-received and after different milling times

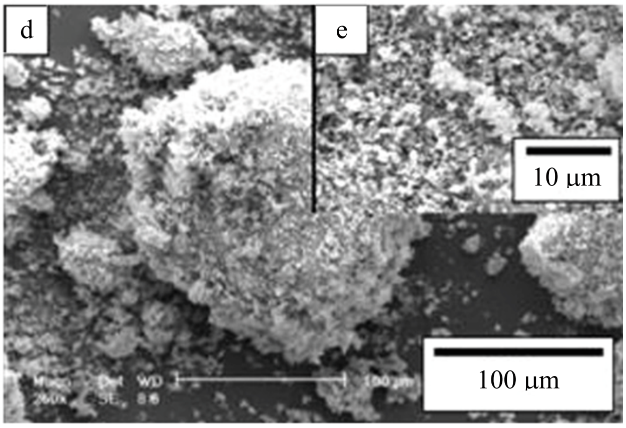

Fig. 11 Morphology of mechanically alloyed powders at different milling times: 20 h (d) and (e) 45 h

consisted of nano-scale particles were formed. It can be known that nano-scale hybrid can improve the properties of composite materials.

Other serial composite materials are oxide materials. Mechanochemical process can also be utilized in the preparation of these composite materials [24-26].

A mixed cathode materials of $LiMn_2O_4/LiCoO_2$ was designed as a novel core-shell structure by mechanical activation (MA) [24].

Figure 12 presents SEM images of spinel before and after coating. The coating process by mechanical activation (MA) causes the decreasing of particle size of $LiMn_2O_4$, and compare favorably with the traditional solution precipitation method (Fig. 12b). The as-received composite grains are round-shaped, uniform in size, and loose agglomerates. Reduction of particle size and surface electrolyte interface of core-shell enhance the electrochemical performance of composite materials.

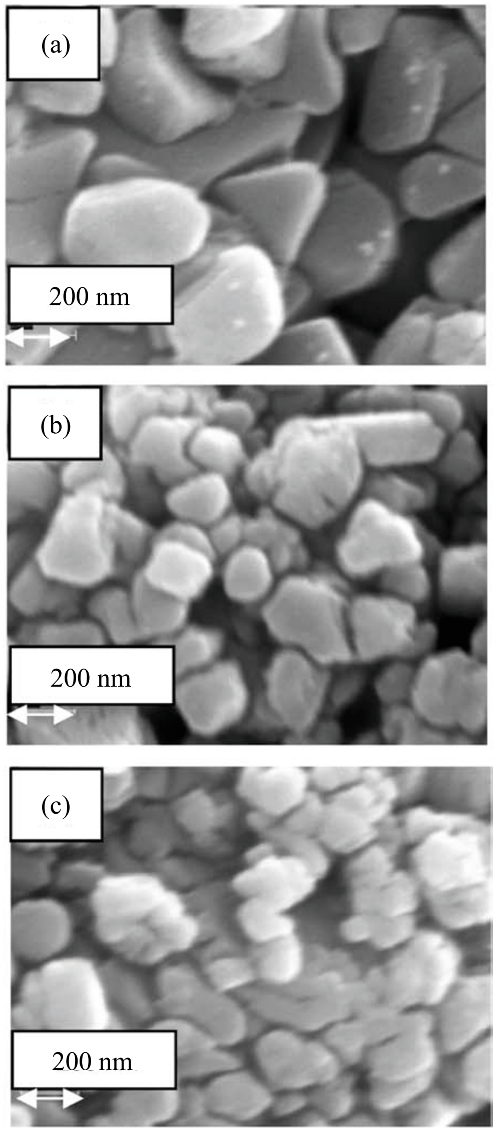

Fig. 12 SEM images of pristine (a) and coated $LiMn_2O_4$, (b) solution method, (c) MA method

5 Synthesis of nano-structured materials

The most attractive feature of mechanochemical method is that it is an easy synthesis process of nano-structure materials. This conclusion can be necessarily reached from above research works. From those SEM images, nano-scale particles are always observed. So mechanochemical process are often applied to produce nano-structured materials [27-30].

Hydroxyapatite (HAp) is important bio-materials. A novel mechanochemical approach was created to synthesize nanorods and nanogranules of HAp [31]. In this work, two reactions were employed.

$$6CaHPO_4+4Ca(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2+ 6H_2O \quad (5)$$

$$4CaCO_3+6CaHPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2+4H_2O+4CO_2 \quad (6)$$

XRD patterns of Fig. 13a reveal the formation of HAp in reaction (5). The XRD patterns confirmed that the product is HAp as expected besides impurity of $CaHPO_4$.

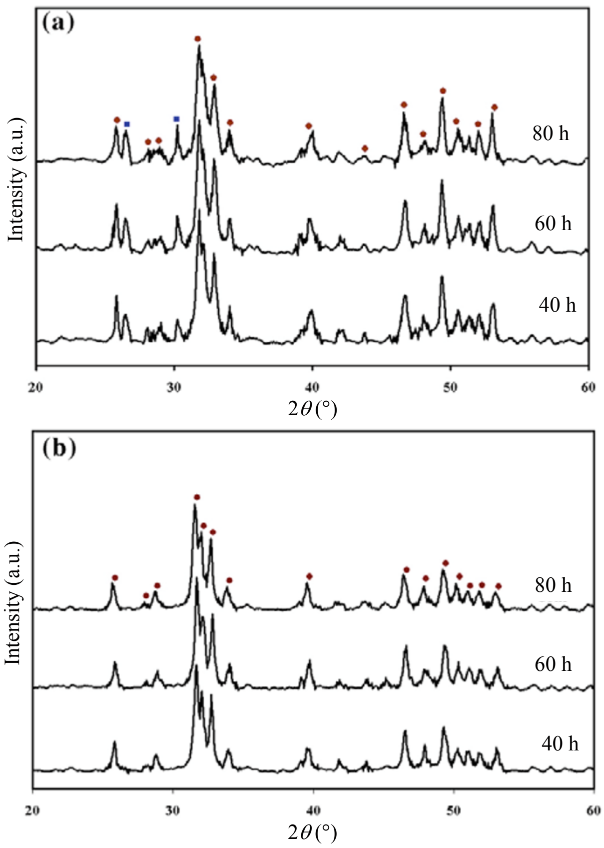

Fig. 13 XRD patterns of samples milled for 40, 60 and 80 h, reaction (5) (a) and reaction (6) (b). $CaHPO_4$ (■) and HAp(●)

In Fig. 13b after 40, 60 and 80 h of milling, the extra peaks of impurity are not observed and the only detected phase is HAp.

The different reaction routes of HAp preparation result in distinct morphology of products. Fig. 14 shows nanorods HAp from reaction (5) and nanospheres HAp from reaction (6).

A new attempt of utility of mechanochemical process in preparation of nano- structured materials is to synthesize nanosheets by mechanical cleavage process [32], which presents a novel approach to obtain the nanosheets starting from the layered compound.

Figure 15 exhibited the lighter and translucent nanosheets. The sizes of these nanosheets were in a range from 50 to 200 nm, which could be observed from the TEM image. The same mass-thickness contrast of nanosheets in TEM image meant that they had the uniform thickness.

6 Summary

Present research works have made great achievement

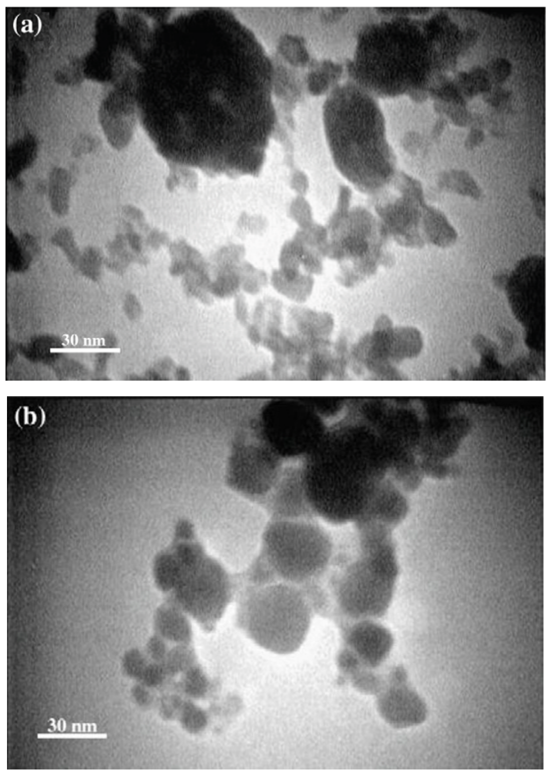

Fig. 14 Typical TEM micrograph of nanorods HAp for reaction (5) (a) and nanospheres HAp for reaction (6) (b) after 80 h milling time

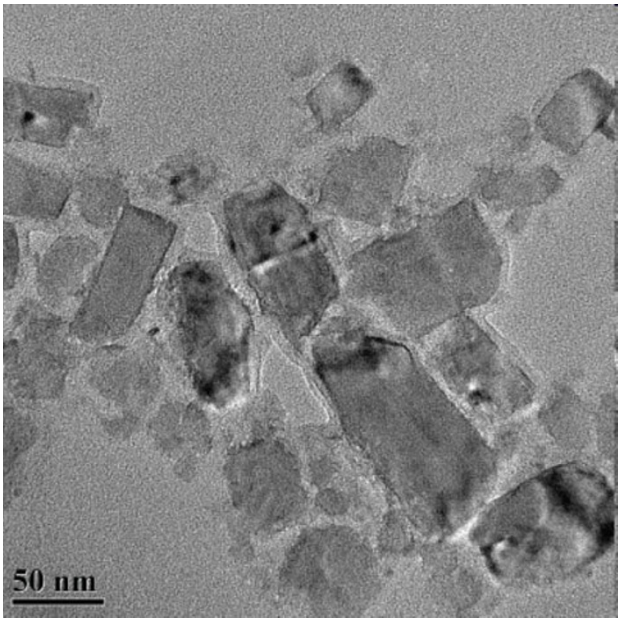

Fig. 15 Transmission electron microscopic image of Ti_5NbO_{14} nanosheet

in many aspects of material synthesis. However the most exciting fields are the preparation of nano-structure materials and nanocomposites. Mechanochemical process supplies a novel route to design nano-structure, which is also environment friendly, low-cost, controllable and Efficient.

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