# PREPARATION AND PROPERTIES OF NANOPARTICLES BY CHEMICAL REACTIONS WITH ASSISTANCE OF PHYSICS FACTORS

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***ABSTRACT:*** *Versatile chemical reactions with the help of physical factors such as microwaves, sonic radiations, laser, elevated temperature and pressure have successfully been used to prepared silicon (high surface area), iron oxide (in amorphous and crystalline state), silver, gold, iron-platinum, cobalt-platinum nanoparticles. The microwaves fostered the chemical reactions via homogeneous and fast heating processes; the sonic radiations from an ultrasonicator created ultra-fast cooling rates at high power or just played a role of mechanical waves at low power; laser provided energy nanoparticles from bulk plates; elevated temperature and pressure produced good environments for unique reactions. All those preparation methods are simple and inexpensive but they could produce nanoparticles with interesting properties.*

***Keywords:****nanoparticles,*

## 1. INTRODUTION

Nanoparticles may be the most studied nanomaterials because of the simplicity in the preparation process when compared to other types of nanomaterials such as nanotubes, nanowires,… Interesting properties of nanoparticles come from (i) the large surface areas and (ii) the size of particles is smaller than the critical length of a certain chemical and physical properties. Atoms on the surface have different properties (may come from the dangling bonds) from that of the atoms inside a material. Therefore large surface materials are good for catalysts, adsorbents,… When the particle size is smaller than the critical length of a property, the property changes suddenly. For example, if the size of metallic nanoparticles is much smaller than the wavelength of the electromagnetic waves, an interesting phenomenon called surface plasmon resonance will occur.

In contrast to many complicated and expensive physical routes such as melt-spinning [1-3], evaporation [4], sputtering [5], deformation [6], and solid state reactions [7], aqueous chemical techniques are simple and inexpensive for making nanoparticles [8, 9]. Coprecipitation [10] and sol-gel [11] methods are mostly used for this purpose. However, with the assistance of physical factors, the chemical reactions can be fostered. The physical factors applied in our studies are microwaves, ultrasonic waves, laser and elevated temperature and pressure. Resulting effects of the physical factors are unique reaction conditions of high temperature, high pressure, high heating rate and extremely cooling rate under which the reactions occur strongly. This article briefly presents the techniques we have used to obtain nanoparticles.

## 2. MICROWAVE HEATING

Microwave – an electromagnetic wave has been used as high frequency electric fields in chemical reactions. Mobile electric charges in the reaction solvent such as ions and polar molecules are forced to rotate under the electric fields and collide with each other and as the result create heat. It is believed that the first article on the use of microwave in chemical reactions is 1986 [12]. Since then, microwaves have widely been used in chemistry. We have used microwave to prepare $Zn_{1-x}Co_xO$ from precursors zinc acetate dehydrate and cobalt acetate tetrahydrate [13]. The microwave was from a commercial microwave oven (Sanyo 1200W, Model EM-D9553N) with the power of 300 W for 20 min. The successful incorporation of Co into ZnO was evidenced by X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) absorption, and micro-Raman scattering, which showed that Co is homogeneously incorporated into the Zn-site without changing the host wurtzite structure for Co doping up to 5 %. Similarly, $Ti_{1-x}V_xO_2$ has been produced by this technique with the precursor of Titanium (IV) isoproxide. XRD and Raman studies revealed that, two crystallite structures, anatase and rutile, coexist with V-doping higher than 5 %. The strong visible light absorption was found in the $TiO_2$ doped with 10 % V. V-doping and subsequent coexistence of both anatase and rutile phase are considered to be responsible for the enhanced absorption of visible light up to 800 nm [14]. Microwave could also produced amorphous iron oxide materials due to the fact that the fast and homogeneous heating by microwaves stimulated more simultaneous nucleation of iron oxide than heating with conventional methods. The amorphous state can change to crystalline state with the activation energy of 0.71 eV [15]. Combining magnetic study and thermal dynamics provides information of the crystallization process of the amorphous state.

## 3. ULTRASONIC RADIATIONS

The use of ultrasonic radiations in chemistry is also known as sonochemistry. The ultrasounds come from a high-intensity sonicator can make hot spots in the chemical solution with the temperature of 5000 K and the pressure of 1000 at. which results to the extremely high cooling rate of $10^9$ K/min [16]. This cooling rate is much higher than the cooling rate achieved from melt-spinning technique ($10^6$ K/min). We have used ultrasonic waves to prepared amorphous $Fe_{2-x}Cr_xO_3$ materials. It is proved that the presence of Cr enhanced the amorphous state, i.e., increased the activation energy of the amorphous materials and as the result, the presence of Cr slows down the ageing effect of the amorphous state when being used in practice [17].

The ultrasounds with low-intensity can simply played a role of mechanical waves to dislodge nanoparticles attaching on the surface of the cathode in an electrodeposition system (sonoel technique) [18]. We have applied this technique to prepared Co-Pt nanoparticles encapsulated in carbon cages. We proved that, contrast to many other earlier reports, the as-deposited Co-Pt nanoparticles were not in the fcc disordered phase. Instead, the as-prepared materials were heterogeneous mixture of Co-rich and Pt-rich nanoparticles [19]. Fe-Pt with strong hard magnetic properties has also been made by this technique [20]. Silver and gold nanoparticles obtained by sonoel are very biocompatible [21]. Especially, silver nanoparticles in a non-toxic solution have been prepared by this green method [22]. The particles were then loaded on activated carbon (made from agriculture residual such as bamboo and coconut husk) to obtain a material with highly adsorbed carbon possessing antibacterial properties.

For example, to make ZnS nanoparticles, we employed the electrolyte contained 0.1 M/L $ZnSO_4.7H_2O$, 0.1 M/L $Na_2S_2O_3.5H_2O$, the total volume 100 ml. The deposition process was conducted under $N_2$ gas at the temperature of 80 °C, the time of deposition was 120 min. The potential was 3 V and the current intensity was 10 mA. Figure 1 is the XRD patterns of the ZnS nanoparticles prepared by sonoelectrodeposition. Beside the diffraction peaks presenting for ZnS phase, there was the presence of Zn metal. The peaks for ZnS are very wide which suggested that the particles are extremely small. The size determined from Sherrer's formula was less than 2 nm. TEM images of this material supported the small size (Figure 2) in which the material was hallo tubes with very thin walls. XRD data in Figure 1 was the diffractions from the walls containing ZnS material. This type of structure can only be obtained by electrodeposition with the help of ultrasonic waves.

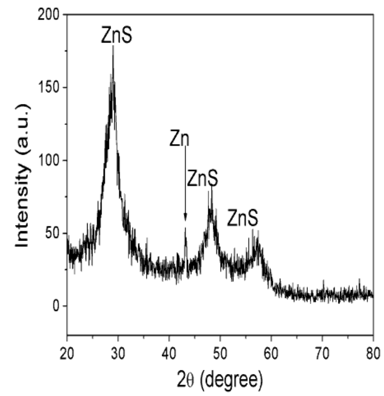


**Figure 1.** XRD patterns of the ZnS nanoparticles prepared by sonoelectrodeposition.

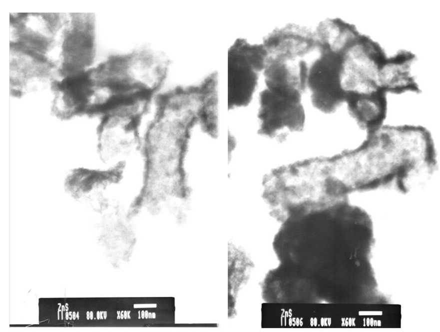

**Figure 2.** TEM micrographs of the ZnS materials prepared by sonoelectrodeposition.

## 4. OTHER PHYSICAL ASSISTANCES

Laser is a potential power source to promote chemical reactions. Using laser as a physical factor is very simple because laser sources are available in many laboratories. Experimental setup was simple [23]: a silver plate (99,9 %) was placed in a glass curvet filed with 10 ml aqueous solution of Trisodium citrate dihydrat. A second harmonic (532 nm) of the Quanta Ray Pro 230 Nd: YAG laser in Q-switch mode was focused on the silver plate by a lens with a 150 mm focal length. The laser was set to give the pulse duration of 8 ns, the repetition rate of 10 Hz and the pulse energy of 80 mJ. TEM images revealed the presence of silver nanoparticles with diameter of 4 – 12 nm.

Reaction under autogenic pressure at elevated temperature (RAPET) is another simple, efficient, and economical method. The reaction was occurred in a stainless steel Swagelok part heated to 750 C for 5 h. Using this technique, we have prepared high surface silicon (200 $m^2$/g) with unique properties [24].

## 5. CONCLUSSIONS

Chemical reactions with the help of physical factors can produce many types of nanoparticles with very interesting properties. These methods are simple and inexpensive which can scale-up for using in practice.

# CÁC HẠT NANO CHẾ TẠO BẰNG PHƯƠNG PHÁP HOÁ HỌC VỚI SỰ HỖ TRỢ CỦA CÁC TÁC ĐỘNG VẬT LÝ

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***TÓM TẮT:*** *Các phản ứng hóa học với sự tác động vật lý như sóng viba, sóng siêu âm, laser, nhiệt độ và áp suất cao đã được sử dụng để chế tạo silic có diện tích bề mặt lớn, các hạt ô xít sắt (tinh thể hoặc vô định hình), bạc, vàng, Fe-Pt, Co-Pt. Sóng viba thúc đẩy phản ứng thông qua quá trình gia nhiệt dung dịch nhanh và đồng nhất; sóng siêu âm phát ra từ còi siêu âm sẽ tạo ra sự tăng và giảm nhiệt vô cùng nhanh chóng nếu phát ở công suất cao và có vai trò như sóng cơ học nếu phát ra ở công suất thấp; laser có thể tạo ra hạt nano từ miếng kim loại; nhiệt độ và áp suất cao tạo môi trường đặc biệt để các phản ứng hóa học xảy ra. Các phương pháp chế tạo ở đây đều đơn giản, rẻ tiền nhưng vẫn tạo ra được các vật liệu nano với các tính chất thú vị.*

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