

Size-Controlled Synthesis of Chromium Nanospheres and Conversion into Multipods, Rods, Rectangular Blocks, Complex Structures and Superlattice Self-Assemblies

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Summary: In this paper we report for the first time, size-controlled synthesis of chromium nanospheres from common precursors and manipulated polyol method. These nanospheres have been further converted into multipods, nanorods, rectangular nanoblocks and micron size complex structures by simple and rapid microwave irradiations heat assisted methodology. Moreover, two dimensional (2D) superlattice self-assemblies containing monolayered mesoscopic particles have been fabricated using a solvent combination approach and the aluminum substrate without application of special polymer matrix.

Introduction

The great interest in nanoparticles and nanocrystalline films is due to their potential applications in nanoscience and nanotechnology [1-4]. One dimensional and advanced shape nanostructures (rods, wires, tubes, ribbons, plates, blocks, multipods etc) of metal, metal oxide and semi-conductors have recently attracted special attention because of their unique optical, magnetic, electrical, mechanical and chemical properties [5-10]. Such nanostructures play an important role as interconnections in "bottom-up" self-assembly approach toward further nanodevices and nanocircuits. Therefore, several methods have been applied for the synthesis of nanostructures with monodispersed sizes and well defined morphologies. Among these, the microwave irradiation (MWI) methodology offers great advantage as a simple and fast procedure [8]. However, most of the studies have been limited to the synthesis of metal oxides and semiconductors or those metal nanostructures which can be easily prepared at relatively low temperature [5-10]. Hence, the construction of close-packed two (2D) or three dimensional (3D) building blocks containing mesoscopic particles has been a vital topic of research for the fabrication of ultra-high density data storage media, catalysts, biosensors etc [11-14].

Chromium based compounds/chromium metal are the classic examples of primary catalysts [15-17] and itinerant magnetic materials [18-19]. Although, morphological controlled chromium

nanostructures are expected to exhibit more significant physical and chemical properties, there have been few reports limited to the synthesis of spherical nanostructures [20-22]. This is perhaps due to the difficulty of controlling shape under high temperature reaction conditions required for the reduction of Cr⁺³ precursors to Cr⁰ nanostructures. Therefore, to develop a versatile route towards the advanced metal nanostructures and their building blocks is of some urgency. Herein we report for the first time, size-controlled synthesis of chromium nanospheres and their conversion into multipods, rods, blocks and complex structures by modified polyol reduction and microwave irradiation (MWI) assisted procedure, respectively. We have also fabricated chromium superlattices containing monolayered mesoscopic particles via self-assembly.

Results and Discussion

The size of nanospheres has been controlled by changing the molar ratio of PVP (Polyvinyl pyrrolidone), reaction temperature and the solvent used. For example, at 6:1 ratio of PVP (5.4×10^{-2} M, monomeric unit) and chromium acetate precursor (8.8×10^{-3} , precious metal) was refluxed in diethylene glycol at 245 °C and 1.0-7.5 nm diameter spherical or little elongated nanostructures were formed (Fig. 1A). The increase either in growth temperature or the heating time increases the size of nanoparticles. For instance when temperature was raised to 285 °C using

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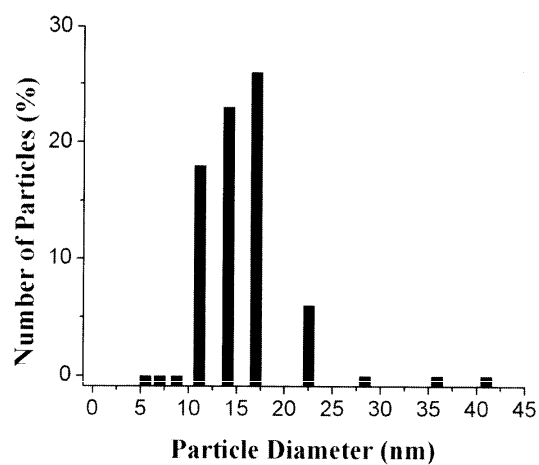
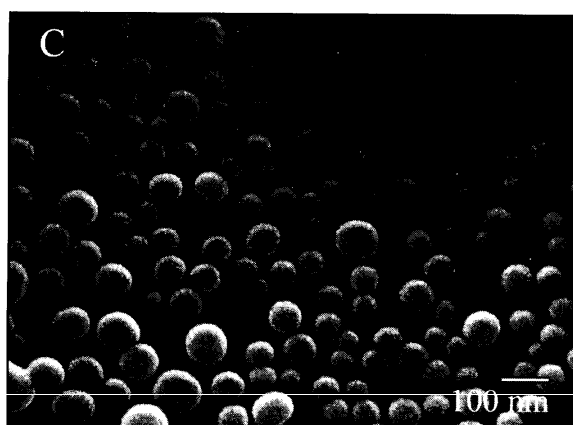
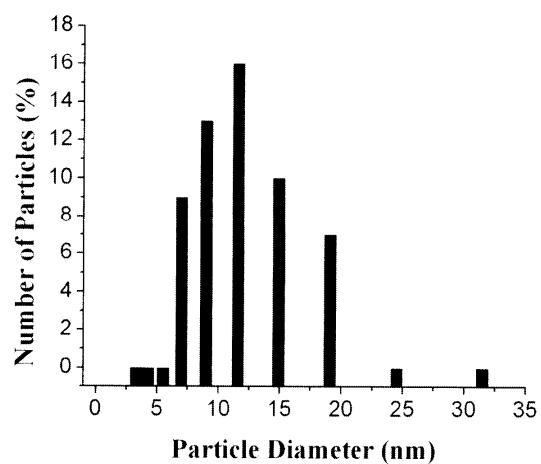
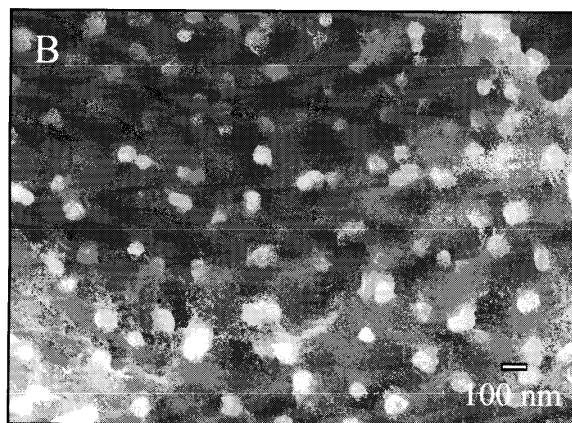
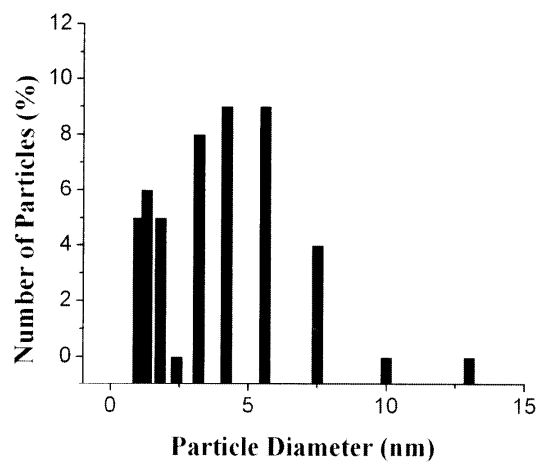
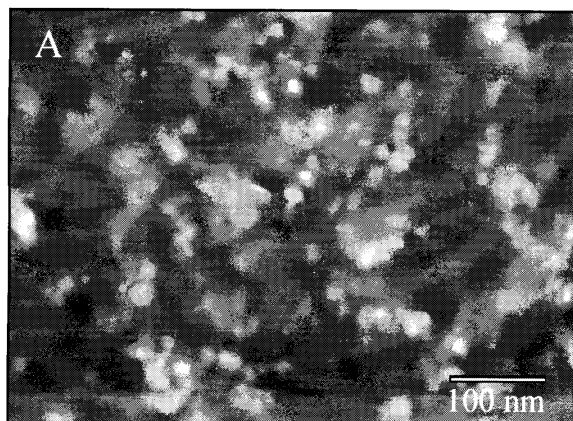


Fig. 1: SEM of chromium nanospheres synthesized by heating for 06 hrs at 245 °C (A); 285 °C (B); by heating for 12 hrs at 285 °C (C); Histograms showing particle size are shown on the right.

triethylene glycol solvent, 7.0-19.1 nm diameter spherical or little elongated particles were observed (Fig. 1B). While, the long time heating at same temperature converted the elongated particles to complete round shape, 11.1-22.5 nm spheres (Fig. 1C).

Since at low concentration of surfactant, the sufficient thermal energy either by applying high growth temperature or by heating for extended period of time, favors the more thermodynamically stable spheres through *intra-* or *inter-* particles ripping processes [10] which results in the increase in size. Alternatively, the concentration of PVP plays an important role in controlling the size of nanoparticles. Chromium nanospheres with gradual decrease in size could be obtained by gradually increasing the concentration ratio of PVP (see Table-1). In this case any surface adsorption is overwhelmed and the entire surface of the initially formed seed is covered with a thick coating of PVP.

Table-1: Size and corresponding reaction conditions for nanospheres.

Entry No.	PVP/M	Cr ³⁺ /M	Temp./°C	Time/hrs	Polyol	Range of Sizes
1	5.4x10 ⁻²	8.8x10 ⁻³	245	6	DEG	1.0–7.5 nm
2	5.4x10 ⁻²	8.8x10 ⁻³	285	6	TrEG	7.0–19.1 nm
3	5.4x10 ⁻²	8.8x10 ⁻³	285	12	TrEG	11.1–22.5 nm
4	6.9x10 ⁻²	8.8x10 ⁻³	285	6	TrEG	5.0–13.1 nm
5	8.7x10 ⁻²	8.8x10 ⁻³	285	6	TrEG	4.0–9.5 nm

The conversion of chromium acetate into chromium metal nanostructures was confirmed by FTIR spectroscopy. In the spectrum of chromium nanostructures, the IR vibrational bands due to Cr-O bond of chromium acetate that appeared in the 700-400 cm⁻¹ region were not observed (Fig. 2).

The conversion of chromium spheres into multipods, rods, blocks and complex structures was achieved by a modified microwave with heat assisted methodology reported earlier for the synthesis of 1D semiconductors [8]. In typical experiments, the nanospheres were employed a controlled rate of MWI and/or the heat energy to obtain different structures. For example, a high yield of multipods (~60-70 nm diameter and ~350-500 nm length, Fig. 3A) could be obtained at 15 s MWI followed by aging for 5hrs at 60 °C. Whereas, at 60 s MWI reaction time monorods (~90-130 nm diameter and ~450-800 nm length, Fig. 3B) were formed. Nanoblocks (~600 nm length, ~200 nm width and ~90 nm thickness, Fig. 3C) were

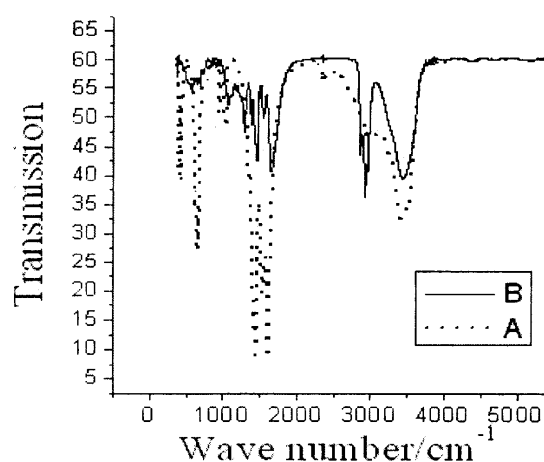


Fig. 2: IR Spectra, of Chromium acetate before reduction (A) and after reduction into Chromium nanostructures (B).

produced at 90 s MWI followed by heating for 5min at 80 °C. While, 120 s MWI resulted a highly complicated micron size structures (Fig. 3D).

The formation of various shapes is likely the outcome of the interplay between the faceting tendency of the capping agent during the initial seed formation and then further growth along different crystallographic faces under the rate of supply of MWI and/or thermal energy. It is believed that, the PVP molecules bind more strongly to the (100) and (110) faces than to (001) [23] face of the initial seed. So that, the (001) direction of the seed appears to be more solvent accessible than those of others. Therefore, in ethanol, the 15 s MWI followed by equilibrium at low temperature aging, favored very smooth growth of the wurtzite arms in the (001) direction on (111) faces of the zinc blend core leading to the formation of multipods. The formation of tree growing like network seems to be governed by the multipods on basic skeleton (Fig. 3A) through van der Waals interactions. However, when the growth rate was increased by 60 s MWI, avoiding the equilibrium, the nonsynchronous growth of wurtzite arm from one of the (111) faces of the seed occurred resulting to the irregular monorods [24]. The extension in MWI time to 90 s followed by 5 min heating at 80 °C, activated the crystallographic faces according to their energy order leading to the formation of nanoblocks (Fig. 3C). While the further increase in MWI to 120 s resulted in extreme growth

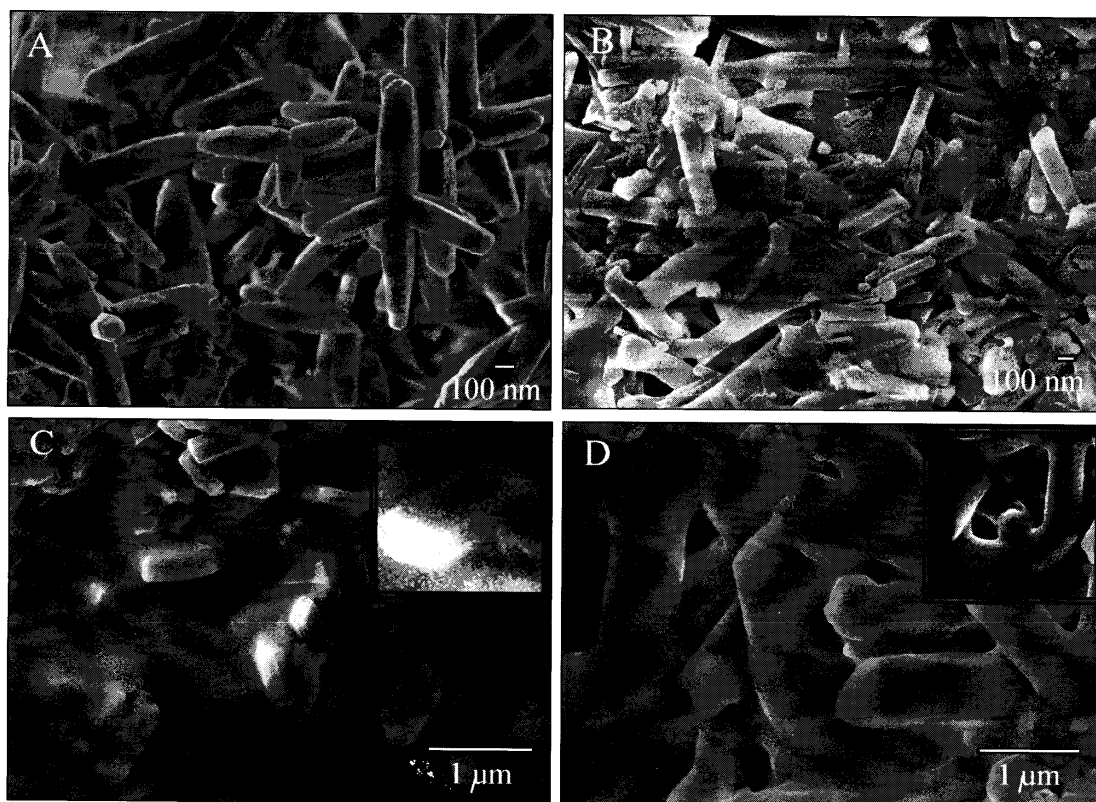


Fig. 3: SEM of chromium multipods prepared from spheres at 15 s. MWI followed by aging for 5 hrs at 60 °C (A); monorods at 60 s. MWI (B); blocks at 90 s. MWI followed by heating for 5min at 80 °C and inset enlarged single block (C) and complex micron size structures at 120 s MWI and inset enlarged single structure (D).

along all of the faces producing micron size complex structures (Fig. 3D).

During self-assembly experiments, one drop (5 μ l) of concentrated suspension of chromium nanospheres (4.0-9.5 nm or 5.0-13.1 nm) dispersed in chloroform/ethanol (4:1) was placed on aluminum foil and allowed to evaporate in open air. SEM micrograph (Fig. 4A) showed superlattice poly-balls of diameter approximately 1400-2000 nm sizes. In some of the balls hollow cavity was observed (Fig. 4A).

The enlarged SEM image revealed that the concentration of particles inside the cavities is smaller than the concentration out side (Fig. 4B). The formation of cavities might be due to the hole opening by the volatile solvent in particle layer pushing them aside. When the half concentration of

same particles in same solvent was applied, the resulted superlattice poly-balls were four time smaller in size (~500 nm) and without cavities (Fig. 4C). The enlarged SEM image (Fig. 4D) of superlattice showed that the particles were in compact and mono-layered array. But in case of pure methanol or ethanol as a solvent, the particles were found either aggregated or randomly dispersed on the surface of the substrate. At this stage we can expect that the chloroform with ethanol in open atmospheres might induce dipolar interactions at the surface of the metal chromium nanostructures leading to the formation of well arranged superlattice self-assemblies. However several factors such as, particle-particle interactions, particle-substrate interactions, magnetic forces etc. have been reported to be a responsible for the different self-organizations [11-14]. Therefore a detailed study in future research will show more clearly the role of every component

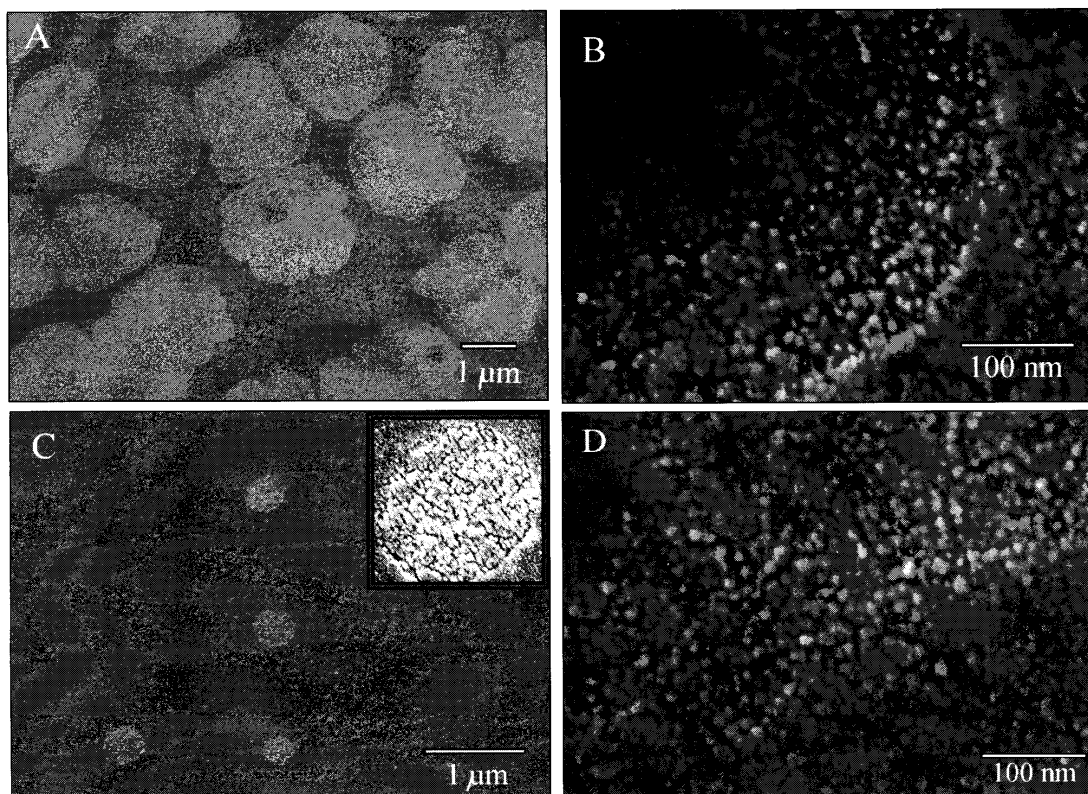


Fig. 4: SEM of superlattice poly-ball self-assemblies of spheres suspended in chloroform: ethanol (4:1) (A); magnified portion of cavity (B); superlattice poly-ball assemblies from dilute solution and inset enlarged single ball without cavity (C); and compact mono-layered array in superlattice (D).

involved in the formation of superlattices at aluminum substrate.

Experimental

In a typical synthesis, a desired amount of PVP was dissolved in 250 ml flask containing 60 ml of DEG (diethylene glycol) or TrEG (triethylene glycol) under constant stirring at 50 °C. Chromium acetate powder (8.8×10^{-3} M) was added with continuous shaking. The resulted suspension was heated at 120 °C for 20 min with constant magnetic stirring to dissolve solid chromium precursor as well as to remove any trace of water. The resulted homogeneous solution was cooled at room temperature. Then nitrogen gas was passed from solution for 10 min to replace air from the reaction flask. The resulted mixture was refluxed under vigorous stirring at required temperature. After 6 or 12 hrs a transparent dark brown homogeneous

colloidal solution of Cr^0 nanoparticles was obtained without any precipitate. Generally, as prepared polyol dispersions of Cr^0 structures were precipitated using anhydrous acetone. The precipitates were centrifuged for 20 min at 7000 rpm speed, washed with acetone and re-dispersed in methanol. The precipitation and washing processes were repeated many times to remove non-reacted materials and polyol. After washing the resulted solid was re-dispersed in methanol (60 ml) and stored for characterization. After washing, the solid nanospheres (Table-1, entry 1) were re-dispersed in 100 ml ethanol and then equally transferred into four conical flasks labeled as sample 1-4. Each sample was placed in a conventional microwave oven with power set to 50% of 1000W and operated for required time to prepare different advanced shape nanostructures.

For self-assemblies studies, 5 ml or 2.5 ml suspension of nanospheres (Table-1, entry 4 or 5)

was precipitated and centrifuged for 10 min at 6000 rpm speed. The resulted solid residue was washed and re-dispersed in 4:1 ml ratio of chloroform and ethanol, respectively. 5 μ l of this suspension was placed on aluminum foil and allowed to dry in open atmosphere.

FE-SEM images were obtained by Field Emission Scanning Electron Microscope (JSM-6700F, JEOL, JAPAN). After removing the surfactant and polyol, the nanoparticles were re-dispersed in suitable volume of appropriate solvent. 5 μ l of this solution was dropcast on the surface of aluminum foil and allowed to dry in open atmosphere. FT-IR spectra were recorded on Perkin Elmer Infrared Spectrometer using KBr disc at wavenumbers of 400-6000 cm^{-1} . Particle size was measured by Particle Analyzer (Brookhaven Instrument Corp.) using 90 Plus Particle Sizing Software Ver. 3.48. and further confirmed by FE-SEM.

Conclusions

We demonstrated the successful synthesis of size-controlled chromium nanospheres and their conversion into multipods, rods, blocks and micron size complex structures using common precursors and rapid MWI with heat assisted strategy.

We expect this procedure will provide an alternative route to advanced shape nanostructures that are difficult to achieve by conventional methods at high temperature.

We have also fabricated for the first time superlattice mono-layered arrays of mesoscopic particles via solvent combination approach at the surface of very cheap substrate without applying the special polymer matrix.

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