Preliminary Observations of Synthesized WS_2 and Various Synthesis Techniques for Preparation of Nanomaterials

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1 Introduction

All the technological advancements of the future that seem impossible right now can indeed become a reality by the discoveries of today. These discoveries in the field of nanotechnology have a very promising future where the arrangement of atoms in the desired way can show some amazing results. There are a large number of pieces of evidence that show how the world's smallest materials are changing our lives including the nano-machines that defeat the cancer cells, tiny computer chips, a few inches long high definition cameras and others. Synthesis of these nanomaterials is in itself a huge topic of research where the change in a single parameter like temperature can also make a difference in the structure and morphology of the product [1]. There are various synthesis techniques with different working principles that give very different products at specific conditions [2]. The hunt for new tiny gadgets creates a need for new and better synthesis techniques to get products of high purity and controlled dimensions. Initially, it was believed that 2-D materials are not stable but after the successful synthesis of graphene as a 2-D material, the search for the other 2-D materials with enhanced properties like wider band-gap began. We got other potential materials in the form of Transition Metal Dichalcogenides (TMDs) with wonderful electronic and optical properties [3]. Amongst these, MoS_2 and WS_2 have attracted considerable attention because of the peculiar layered structure, an impressive rate of electron transfer and layer-dependent band-gap. Various applications of these materials include solid lubrication, optical devices, gas sensing, and others [4, 5]. The schematic structure of WS_2 is shown in Fig. 1.

1.1 Hydrothermal and Solvothermal Method

These are two promising inorganic synthesis methods that involve the synthesis via chemical reaction as shown in Fig. 2a. These are the green processes as the reaction takes place in a sealed reactor known as autoclave shown in Fig. 2b. The autoclave is generally made up of metal and is employed with Teflon or alloy lining to protect it from highly corrosive solvent. These processes offer numerous advantages over other techniques apart from being the green processes: (a) these are relatively low-cost processes,

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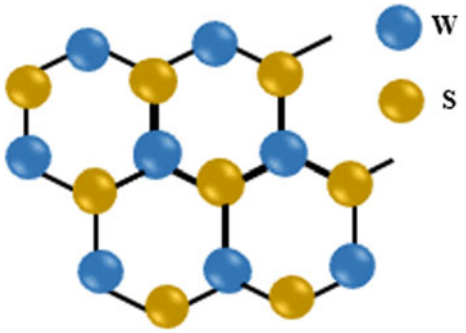

Fig. 1 The schematic layered structure of WS_2

(b) an environment-friendly process as it takes place inside a sealed reactor and (c) high purity products are formed [6]. In the hydrothermal method, the solvent used is water while the solvothermal process uses aqueous and non-aqueous organic solvents like ethylenediamine, ethanol, diethylenetriamine [7], polyethylene glycol [8], etc. Furthermore, the solvothermal process has some additional advantages over the hydrothermal process: (a) it requires relatively low temperature and pressure, (b) precursors which are sensitive to water can be used in this process and (c) the crystallinity of products formed is very well controlled in this process.

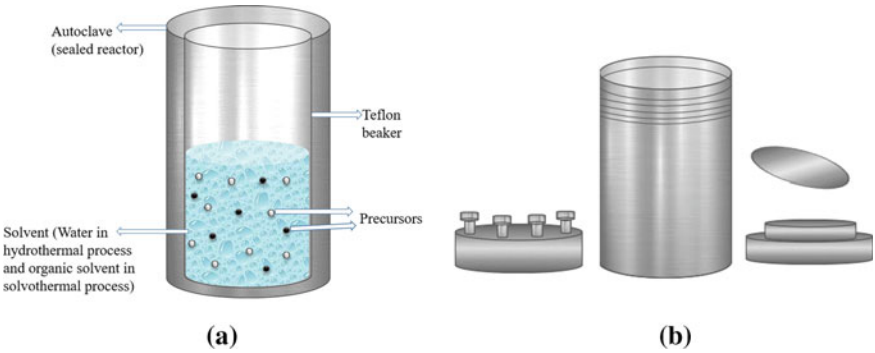

Fig. 2 **a** A diagrammatical representation of hydrothermal/solvothermal synthesis **b** A diagrammatical representation of an autoclave in nanomaterials research laboratory (NRL), DTU, India

1.2 Sonochemical Method

This is a method which neither requires high temperature and pressure nor long reaction times. In this process, the precursors are mixed and put together in solution form and then the sonochemical treatment is given. It involves passing ultrasonic waves through the solution using an ultrasonicator as shown in Fig. 3. In this way, the hotspots are generated

which can achieve very high pressure and temperature. The hotspots are the places where the reaction takes place at sufficiently high temperature and pressure conditions and the products are formed [9]. It is a powerful tool for synthesis or modification of nanomaterials where even a little variation in the reaction conditions can lead us to the change in morphologies and compositions of the product formed.

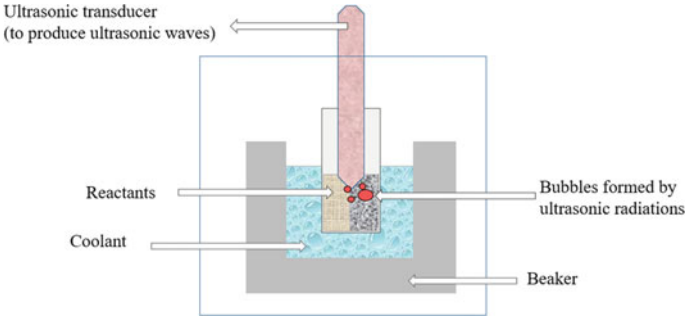

Fig. 3 A diagrammatical representation of the sonochemical method

1.3 Chemical Vapour Deposition (CVD)

It is a vacuum deposition method that involves a chemical reaction inside a vacuum chamber. It is used for the production of various materials like alloys, carbides, oxides, nanoparticles, etc. Layers of materials are deposited on a solid surface called substrate below atmospheric pressure, i.e. vacuum. There are many types of CVD's namely, Thermal CVD, Metal–Organic CVD (MOCVD), Plasma Enhanced CVD (PECVD),

Atomic Layer CVD (ALCVD), etc. [10, 11]. Amongst these CVD variants, Double Zone Thermal CVD and PECVD are present in our Lab at DTU whose diagrammatical images are as shown in Fig. 4a, b, respectively. The technical details and working of the above two instruments are reported in detail in our previous work, *'Double Zone Thermal CVD and Plasma Enhanced CVD Systems for Deposition of Films/Coatings with Eminent Conformal Coverage'*. This bottom-up approach involves the deposition of one or more stable solid films on a substrate at high temperatures by a suitable chemical reaction as shown in Fig. 5.

1.4 Sol–Gel Method

The Sol–Gel method or Chemical Solution Deposition Method is a low-temperature, nanomaterial synthesis process in which solid materials are produced from small molecules. It is a bottom-up approach for material synthesis whose working principle is shown in Fig. 6. The sol–gel method, as is evident from the name, involves two materials, i.e. 'sols' (solid particles suspended in liquid) and 'gels' (porous network of particles having liquid between the pores). First, sols are formed inside a liquid which are then connected after some process to form a network of gels. The liquid then gets

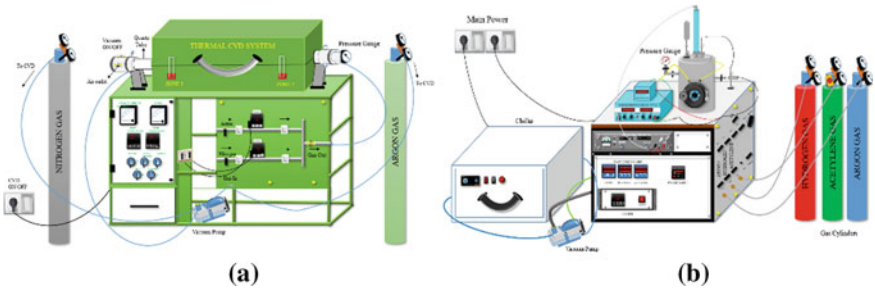

Fig. 4 **a** Labelled diagram of Double Zone Thermal CVD at NRL, DTU, Delhi, India. **b** Labelled diagram of PECVD in NRL, DTU, Delhi, India

evaporated and we are left with the powder or thin-film formation. This method requires less energy consumption leading to less pollution and is generally used to generate highly pure and well-contained ceramic materials [10, 12].

1.5 Chemical Exfoliation Method

It is a top-down nanomaterials synthesis process where the reduction of interlayer forces takes place followed by the formation of intercalated compounds and then exfoliation occurs by rapid heating and sonication. This synthesis mechanism (as shown in Fig. 7) is mainly done for graphene as the process produces a large amount of graphene at low temperatures [13]. Exfoliation is a phase transition, which takes place when there is a layer to solvent molecule charge transfer and a minimum mixing enthalpy at well-defined elevated temperatures.

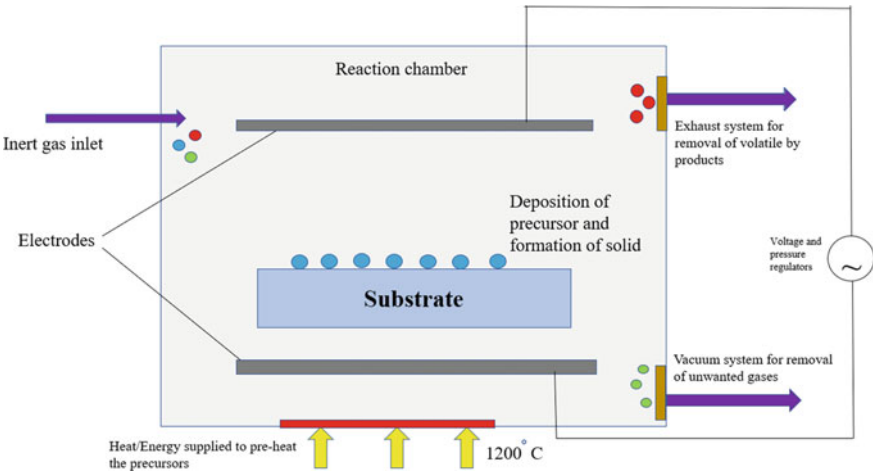

Fig. 5 A diagrammatic representation of the working principle of the CVD process

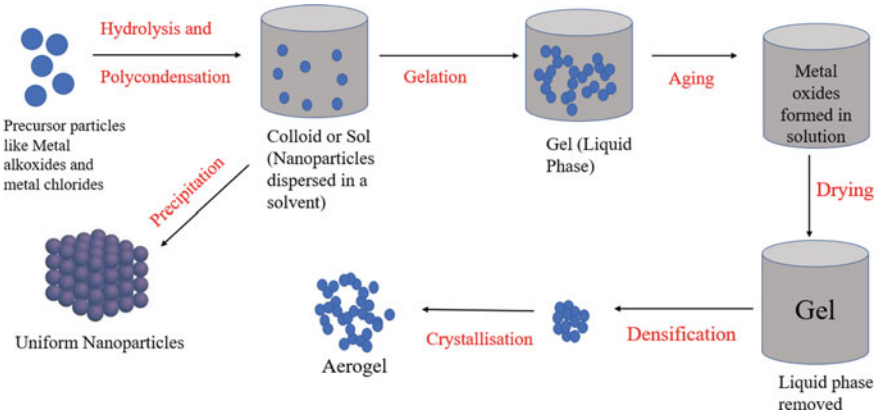

Fig. 6 A diagrammatical representation of the working principle of the Sol–Gel process

2 Experimental

2.1 Chemicals and Materials

Tungsten Hexa-chloride (WCl_6) and Thioacetamide or TAA (C_2H_5NS) were purchased from Sigma Aldrich. Acetone was purchased from Rankem. Ethanol was purchased from Merck. We have used Milli-Q water, (18.2 MΩ cm) as the solvent during our synthesis. All the chemicals used here had an analytical grading and were taken without any further purifications being done.

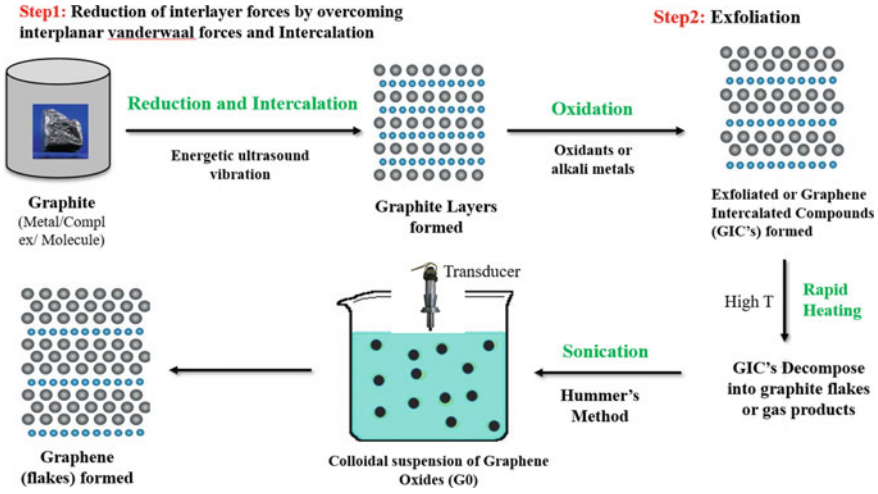

Fig. 7 A diagrammatical representation of the working principle of the chemical exfoliation method

2.2 WS_2 Nanostructure Synthesis

WS_2 nanostructures were synthesized via the hydrothermal method and their phase was checked using XRD characterization. Figure 8 gives an outline of the hydrothermal process used for WS_2 nanomaterial synthesis in NRL lab, DTU, Delhi, India.

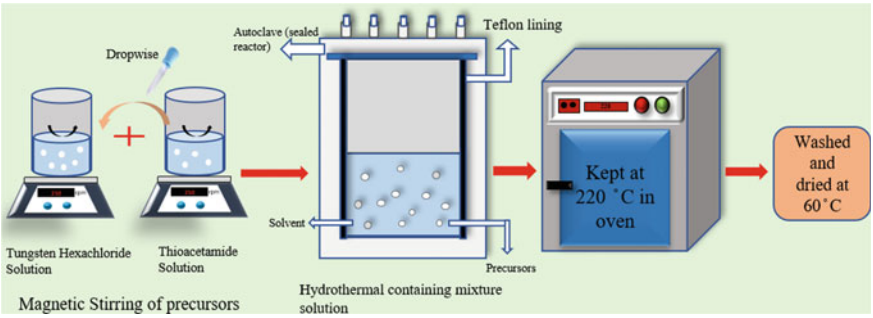

Fig. 8 A diagrammatical representation of the general hydrothermal process used for sample preparation in NRL, DTU, Delhi, India

We first weighed the salts/precursors, i.e. Tungsten Hexa-chloride and TAA, and added them to two different beakers containing water as solvent. Beakers were then kept for magnetic stirring at room temperature (27–30 °C) with varied revolutions per second for 1 h for mixing of salts in water. Two different approaches were followed for the synthesis of WS_2 nanostructures. In one approach of synthesis, the TAA solution was added dropwise into WCl_6 solution after one hour while in the other approach, the WCl_6 solution was added into TAA solution. After this, the mixed solutions were kept for stirring for 1 h. The pH of the solutions was regulated and optimized to the values ranging from 6 to 8 which was initially 2 by adding liquor ammonia drop by drop. The solution mixtures were then transferred to Teflon lined autoclaves of different capacities and kept in the oven for 20–24 h at 220 °C. Then centrifugation and washing of samples was done using De-ionized water (DI) and ethanol, 3 times with each. Drying of samples was done at 60 °C in an oven for 24 h. Then the samples were sent for XRD analysis. We tried 5 reaction attempts to synthesize the materials at varied conditions. In the following Table 1, we have summarised all 5 reaction attempts and their physical optimization conditions.

After 24 h, samples were cooled down to room temperature. Then the samples were collected via centrifugation at 7,000 rpm for 7 min after washing with DI water and ethanol before drying at 60 °C for 24 h. We then collected the formed samples in Eppendorfs after crushing and named them ‘S4’and ‘S5’, respectively.

3 Results and Discussions

In the first three attempts, no sample was obtained at the bottom of the Teflon as shown in Fig. 9a but in the 4th attempt, as shown in Fig. 9b and 5th attempt, as shown in

Table 1 Reaction attempts summary for WS_2 synthesis

Sample	Precursor name	Amount (g)	DI water (mL)	Stirring conditions	pH
S1 (TAA into WCl_6)	WCl_6	0.522	30	stirred at 250 rpm, 30 °C	Initial: 2 Final: 6
	TAA	0.6	30	stirred until fully dissolved	
	TAA was added into WCl_6 and the mixture was stirred at 350 rpm at 30 °C				
	Solution mixture kept at 220 °C for 24 h in a 100 mL Teflon-lined autoclave				
S2 (WCl_6 into TAA)	WCl_6	0.522	18	stirred at 350 rpm, 27 °C	Initial: 2 Final: 8
	TAA	1.000	17	stirred at 250 rpm, 27 °C	
	WCl_6 was added into TAA and the mixture was stirred at 350 rpm at 27 °C				
	Solution mixture kept at 220 °C for 24 h in a 50 mL Teflon-lined autoclave				
S3 (TAA into WCl_6	WCl_6	1.044	18	stirred at 400 rpm, 27 °C	Initial: 2 Final: 8
	TAA	2.000	17	stirred at 250 rpm, 27 °C	
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27 °C				
	Solution mixture kept at 220 °C for 24 h in a 50 mL Teflon-lined autoclave				
S4 (TAA into WCl_6)	WCl_6	0.632	18	stirred at 400 rpm, 27 °C	Initial: 2 Final: 6
	TAA	1.211	17	stirred at 250 rpm, 27 °C	
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27 °C				
	Solution mixture kept at 220 °C for 20 h in a 50 mL Teflon-lined autoclave				
S5 (TAA into WCl_6)	WCl_6	1.566	17	stirred at 280 rpm, 27 °C	Initial: 2 Final: 6
	TAA	3.000	18	stirred at 400 rpm, 27 °C	
	TAA was added into WCl_6 and the mixture was stirred at 400 rpm at 27 °C				
	Solution mixture kept at 220 °C for 20 h in a 50 mL Teflon-lined autoclave				

Fig. 9c, an impressive amount of greyish coloured samples were formed. The suspected reason for failures is the manual or incomplete stirring of precursors due to unoptimized conditions. Here, we have included the XRD results of our 4th and 5th reaction attempts of the synthesis of WS_2 nanomaterial. The phases of the resultant nanomaterials obtained in the last 2 reactions are checked for the confirmation of WS_2 phase as can be interpreted from the preliminary XRD results.

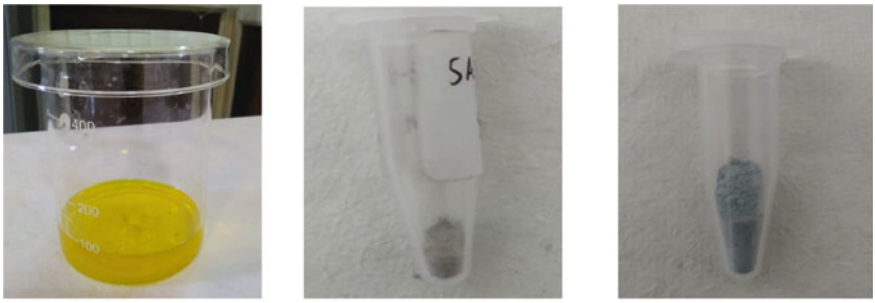

Fig. 9 **a** No sample obtained in first three attempts **b** sample formed in the fourth attempt **c** sample formed in the fifth attempt

3.1 Characterization

XRD patterns were recorded using Bruker 8-D Advance System using CuK{alpha) $\lambda =$ 1.54 Angstrom at 40 kV voltage and 20 mA current with a scan rate of 1 °per minute to study the phase of the as-prepared samples. In our results, we present the diffraction patterns as recorded within the 2θ scanning range of -5 to 90 degrees.

3.1.1 XRD

XRD results of the prepared WS_2 sample numbers 4 (S4) and 5 (S5) are as shown in Fig. 10a, b. The crystal structure of these samples was interpreted using XRD spectra. In the XRD results of sample 4, diffraction peaks are obtained at 2θ angles of 15.05 °, 28.87 °, 32.12 °, 37.36 °, 46.20 °, 50.80 °and 71.26 ° whereas, for sample 5, the diffraction peaks are more prominent and are obtained at 2θ angles of 8.81 °, 13.80 °, 15.29 °, 29.00 °, 29.63 °, 30.63 °, 31.12 °, 37.23 °, 53.43 ° and 64.89 °. The diffraction peaks corresponding to these samples were plotted and labelled and using OriginPro-2021 software.

4 Conclusions

There are many physical and chemical synthesis techniques for the preparation of nanoparticles namely hydrothermal, solvothermal, sonochemical, CVD, sol–gel and chemical exfoliation techniques. Some are top-down approaches while others are

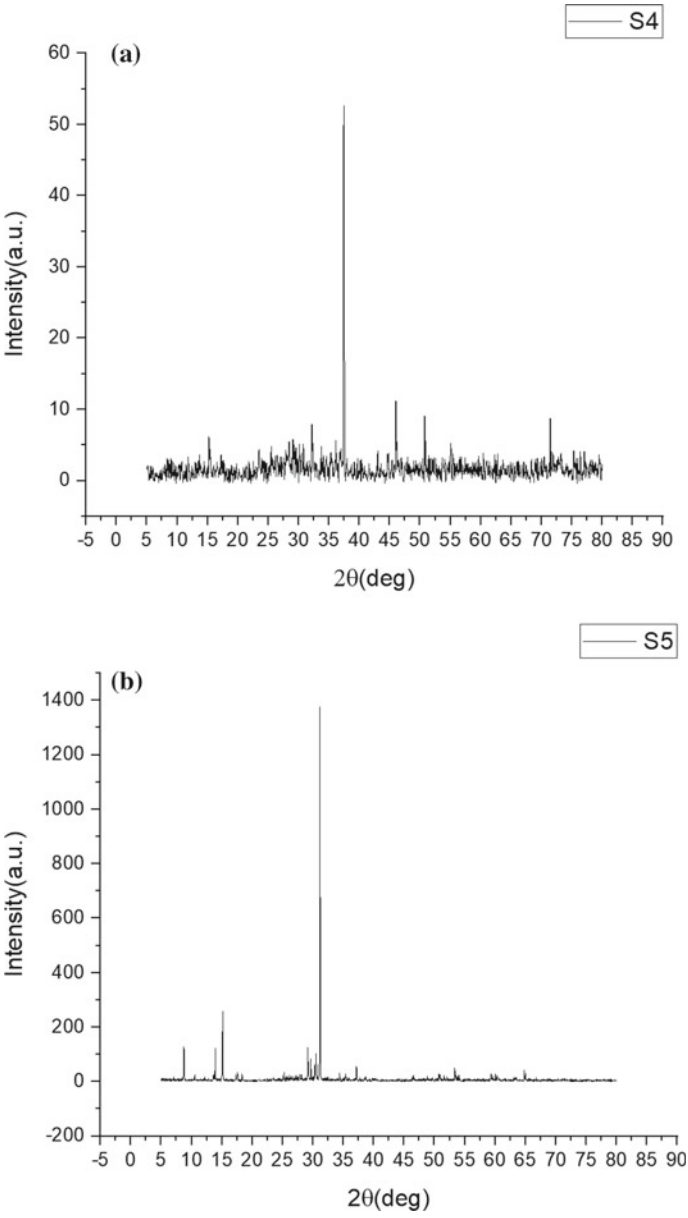

Fig. 10 XRD of **a** sample 4 (S4), **b** sample 4 (S5)

bottom-up approaches. Both types of techniques have their advantages and disadvantages offering a variety of options to the users. Different types of nanomaterials like metal oxides, TMDs, etc. can be prepared by these approaches. Here, various attempts of preparation of WS_2 via facile hydrothermal method are reported with XRD results. In some of the materials, no sample was formed while in some other attempts greyish coloured powder was obtained after centrifugation and washing. This material can be used for a variety of applications in which solid lubrication is a famous one. The adhesion between sulphur layers is relatively weak which results in the sliding of layers over each other.

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