Fabrication of Organic/Inorganic Core/Shell Nanocomposites with Controlled Crystallite size

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Abstract

In the present work, different metal oxide and metal chalcogenide are used as the core materials with the controlled grain size which coated by the polymer. Metal nanoparticles used as various types of catalysts, adsorbents, and sensors. They have applications in optical, electronic and magnetic devices. Most of these applications vitally depend on the size of the nanoparticles. Therefore the synthesis of controlled crystallite size nanoparticles important for above mentioned applications. Here, lead sulfide (PbS), tin oxide (SnO_2), and Cadmium Sulfide (CdS) core materials coated by the polypyrrole (PPy). To form the core and the shell set the diameter fixed and measured theoretically. Weight is proportional to the product of volume and density. The theory behind this is to calculate the amount of precursor. The calculated amount is used to prepare the core as well as the shell which is formed by simple wet chemical method and addition polymerization. The XRD studies are used to determine the crystallite size of the core/shell nanocomposites. Thus the desired crystallite size is successfully obtained. Transmission Electron Microscope also confirms the formation of core/shell structure directly.

Keywords: Core, Shell, nanocomposites, polypyrrole, TEM

1. Introduction

In recent years, nanoparticles have been the center of attention of researchers in the field as the transition from micro particles to nanoparticles was seen to lead to immense changes in the physical and chemical properties of a material. Nanoparticles can be categorized based on single or multiple materials into simple and core/shell or composite nanoparticles. In general, simple nanoparticles are made from a single material; whereas, as the name implies, composite and core/shell particles are composed of two or more materials [1]. The core/shell type nanoparticles can be broadly defined as comprising a core (inner material) and a shell (outer layer material). These can consist of a wide range of different combinations in close interaction, including inorganic/inorganic, inorganic/organic,

organic/inorganic, and organic/organic materials [2]. The choices of shell material of the core/shell nanocomposites are generally strongly dependent on the end application and use [3, 4]. The core/shell nanocomposites and nanostructure may be with different sizes and different shapes of core and shell thickness with different surface morphology. It may be spherical, centric, eccentric, star-like, or tubular in shape. Depending on the size and shape, their properties tune from material to another. Individual core/shell nanocomposites have various applications. Whenever the surface of the nanoparticles is modified by functional groups or molecules or coated with a thin layer of other materials (with different constituents), they show enhanced properties compared to the uncoated particles [5,6].

These core/shell nanoparticles are produced by various synthesis approaches like hydrothermal synthesis, solvothermal synthesis, sol-gel method, emulsion polymerization, microemulsion polymerization, and so forth. On the basis of the core and shell of the materials, the synthesis techniques, their properties, and morphologies can be modified. The necessity and advantage to shift to core-shell nanoparticle can be summarized as follows; (i) the size of the nanoparticles and the shell material can be optimized such that the agglomeration of particles can be prevented. (ii) This structure enhances the thermal and chemical stability of the nanoparticle. (iii) Improves solubility, make them less cytotoxic. (iv) Allows conjugation of other molecule to these particles. (v) The shell can also prevent the oxidation of the core material [7].

Composite structures with these core/shell particles embedded in a matrix material are in use. Because the polymeric or inorganic layer would provide the hybrid structure with an additional property on top of the function/property of the core hence synergistically position [8]. Metal oxide, and metal chalcogenide materials have a wide variety of applications. Both metal oxide and metal chalcogenide materials can be semiconducting, which leads to applications in sensors, electronics, and solar cells [9].

In the case of organic materials polymers play a vital role because of the following advantages (i) They have light weight (ii) They are resistant to corrosion effects and are chemically inert (iii) Polymers have easy workability and toughness (iv) It absorb the mechanical shocks and show resistance to abrasion effects. Along with that polypyrrole is a conducting polymer and mechanical properties can be improved by adding polypyrrole with the core material [10]. So we choose polypyrrole as a shell. Various methods are used for the preparation of polymeric nanoparticles, namely, solvent evaporation, spontaneous emulsification, solvent diffusion, or polymerization. Several formulation and process parameters that affect size, release profile, and stability of the polymeric nanoparticles are solubility of drug, drug-to-polymer ratio, molecular weight, composition of the polymer, solvent, pH, homogenization speed, and mixing time [11].

To obtain the desired thickness of the core and the shell material the following hypothesis made. To shape the core and the shell fixed the diameter of the core has to be experimentally calculated and fixed already. So as to find the weight of the core, the following relations are used.

Weight of the core = $4/3 \times \pi \times r^3 \times$ density of the core material

Where, r is the radius of the core material. The following figure 1 represents the core and shell of various diameters. On fixing the shell diameter, the sum of the volume of the core and shell is calculated. After this the weight of the shell can be found out by the following relation.

Weight of the Shell= (Total volume of the core/shell – Volume of the core) x density of the shell

From this, the weight of the shell material can be calculated. To form a core/shell structure, during the polymerization the core materials have to be added. Thus the core material can be coated by the shell material. Using this hypothesis desired thickness can be obtained [12].

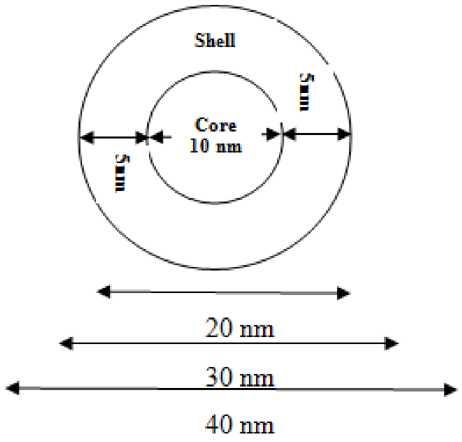

Fig: 1 Core /Shell nanostructure for different thickness

In this present work, inorganic organic hybrid core/shell nanocomposites are synthesized. The core materials are Lead sulfide (PbS), Tin oxide (SnO_2) and Cadmium Sulfide (CdS). The shell material is Polypyrrole (PPy).

2. Experimental

The following calculation shows the weight of the core and shell material. To start with the shell thickness is fixed as 12 nm. The crystallite size of PbS nanoparticles is 26 nm, which calculated from XRD and TEM studies.

Weight of the core (PbS) $= 4/3 \times \pi \times r^3 \times$ density of PbS

$= 4/3 \times \pi \times (26 \times 10^{-9}/2)^3 \times 7.60$

$= 69.9056 \times 10^{-24}$g

Weight of the shell (PPy) $= \{[4/3 \times \pi \times (50 \times 10^{-9}/2)^3 - 4/3 \times \pi \times (26 \times 10^{-9}/2)^3]\} \times 0.928$

$= 52.1708 \times 10^{-24}$g

In polymerization process the yield of the polypyrrole is 0.0926g. Hence the weight of the lead sulfide required to form PbS/PPy, core/shell structure having 26 nm core and 12 nm shell,

Weight of the core: Weight of the shell = Weight of the PbS: Yield of polypyrrole

$69.9056 \times 10^{-24} : 52.1708 \times 10^{-24}$ = Weight of the PbS: 0.0926

Weight of the PbS = 0.1241 g

Similarly, the weight of the SnO_2 (0.947 g) and CdS (0.1631 g) nanoparticles was calculated using the above hypothesis. In this synthesis, 0.03 M solution of pyrrole added to the 0.06 M solution of ammonium per sulfate and the reaction mixture was stirred continuously at the low temperature (5^oC - 10^oC). When the reaction mixture solution colour gets changed, the calculated amount of as prepared lead sulfide powder (0.1241 g) was added. The stirring process was carried out for 2 hours at a constant low temperature. The obtained composites were filtered and washed with water and then the composite dried at 60^oC. Similarly, the calculated amount of SnO_2 and CdS nanoparticles added to the above solution separately. Finally, the PbS/PPy, SnO_2/PPy and CdS/PPy core/shell nanocomposites were successfully synthesized.

3. Results and Discussion

3.1 X – Ray Diffraction Analysis

The XRD patterns of the samples PbS & PbS/PPy, SnO_2 & SnO_2/PPy and CdS & CdS/PPy nanoparticles are shown is fig 2. The X-ray diffraction pattern for PbS displays nine intense peaks in Fig. 2 (a). The values agree well with the standard value for PbS (JCPDS Card No.05-0592) [13]. The diffraction peaks observed at 2θ values of 26.69^o, 27.65, 29.66^o, 43.70^o and 44.55^o and the d spacing calculated indicates that the structure corresponds to the cubic rock salt structure of PbS. The broad peak with 2θ around 24^o is related to the diffraction of the polypyrrole indicates the presence of polypyrrole in this nanocomposite.

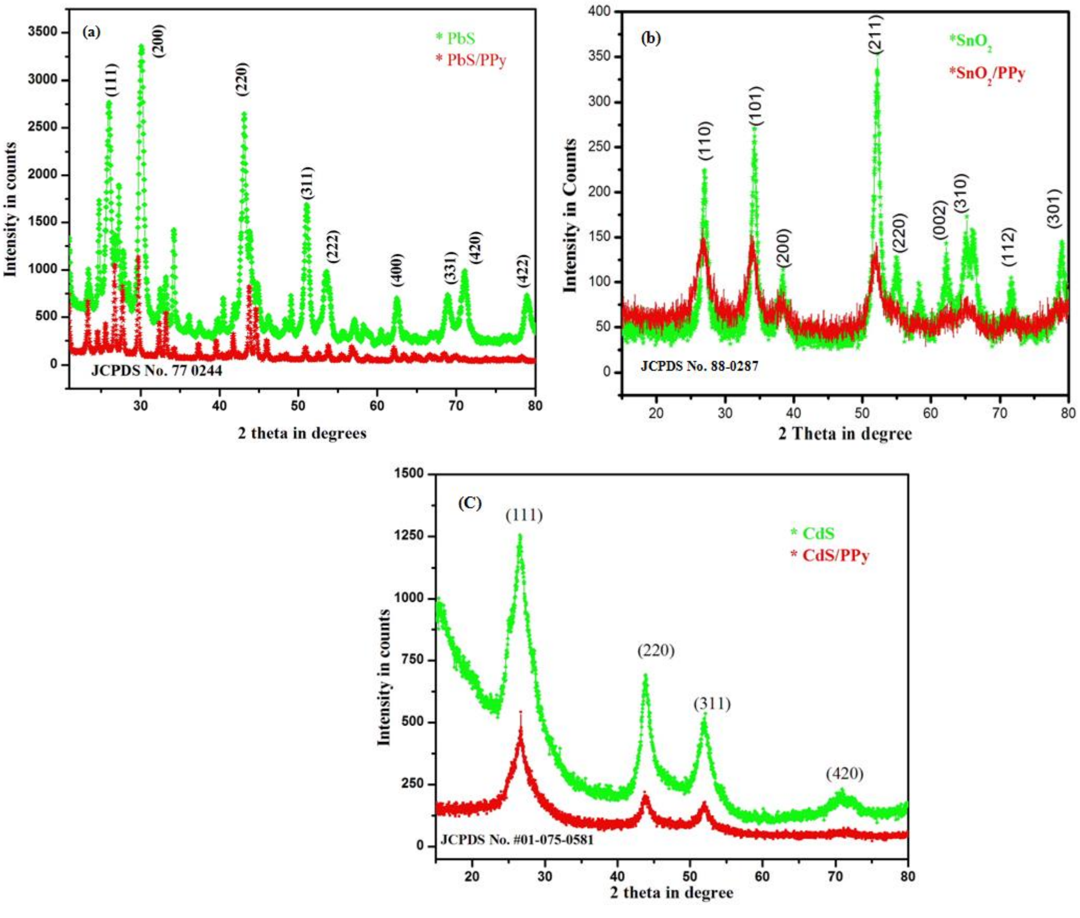

Fig: 2. XRD pattern of (a) PbS & PbS/PPy, (b) SnO_2 & SnO_2/PPy and (c) CdS & CdS/PPy

The X-ray diffraction pattern for SnO_2 displays more than seven intense peaks which is shown in Fig. 2(b). The XRD pattern matches well with the standard values for tin oxide (JCPDS Card No. 88-0287) [14]. The diffraction peaks observed at 2θ values of 26.6°, 33.8°, 51.9°, 54.7° and 64.7° can be associated with (110), (101), (200), (211) and (220) respectively. It shows tetragonal structure. SnO_2/PPy nanocomposite displays three intense peaks along with the lump around 24° which indicate the presence of polypyrrole.

The X-ray diffraction pattern for CdS displays four intense peaks which is shown in Fig. 2(c). The XRD pattern matches well with the standard values for cadmium sulfide (JCPDS Card No. 01-075-0581)[15]

The diffraction peaks observed at 2θ values of 26.55°, 43.7°, 52.1° and 70.87° can be associated with (111), (220), (311) and (420) respectively. It shows cubic structure. CdS/PPy nanocomposite displays the same peaks but decreased intensity along with the lump around 24° which indicate the presence of polypyrrole.[16]

From the XRD results, the average crystallite sizes were calculated using Scherrer formula. Calculated average sizes were tabulated in table.1. The above results confirm the formation of core/shell nanocomposites with desirable thickness.

Table: 1 Crystallite Size by Scherrer formula

Material	**Expected Crystallite Size in nm**	**Obtained Crystallite Size in nm**
PbS/PPy	**50**	**55**
SnO_2/PPy	**30**	**29**
CdS/PPy	**15**	**19**

3.2 TEM Analysis

TEM images were obtained using a TALOS F200S G2 Transmission Electron Microscope. The TEM image of PbS/PPy, SnO_2/PPy and CdS/PPy nanocomposites is shown in fig. 3 (a), (b) & (c), reveal that the obtained nanoparticles have core/shell structure. It has been found that PbS/PPy, SnO_2/PPy and CdS/PPy nanocomposites are almost spherical in shape with an average size of 50 nm, 29 nm and 17 nm respectively. The particle size distribution histogram, which is shown in fig.4 (a), (b) and (c), gives the corresponding particle size of the PbS/PPy, SnO_2/PPy and CdS/PPy nanocomposites which are harmonized with data obtained from XRD studies using Scherrer formula. By comparison between TEM images, it can result that the facile synthesis method had a considerable influence on the size of the nanoparticles and played the main role in the control size process. Obtained particle sizes are tabulated in table 2.

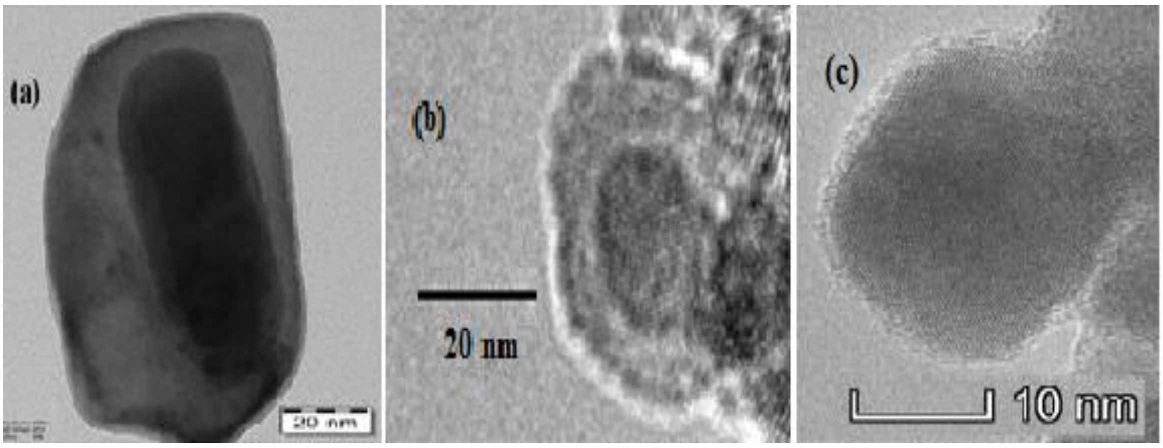

Fig. 3: TEM images of (a) PbS/PPy, (b) SnO_2/PPy and (c) CdS/PPy

Table: 2 Particle Size from histogram

Material	Obtained Particle Size in nm
PbS/PPy	**49.9**
SnO_2/PPy	**28.5**
CdS/PPy	**16.6**

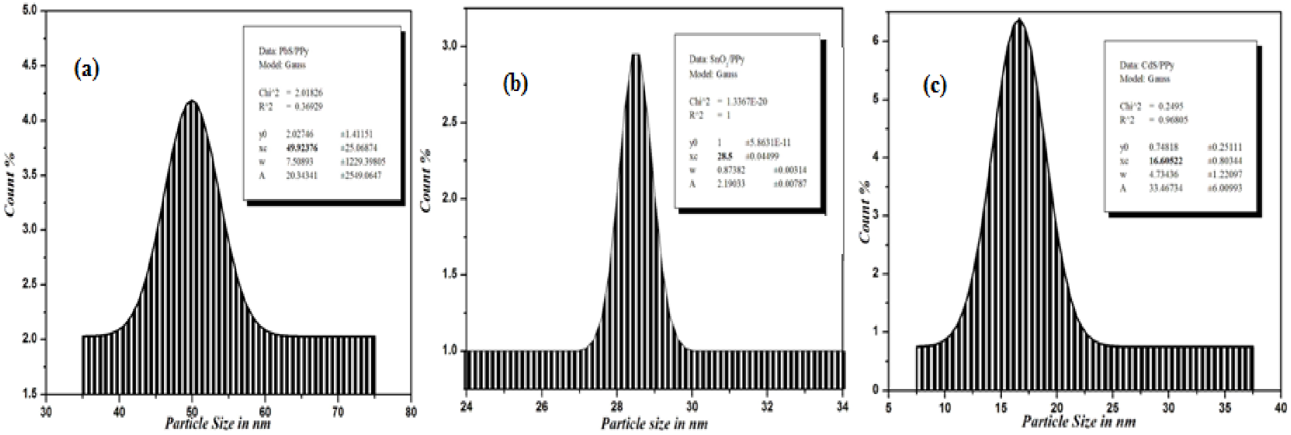

Fig. 4: Particle size distribution histogram (a) PbS/PPy, (b) SnO_2/PPy and (c) CdS/PPy

3.3 SAED Analysis

Selected Area Electron Diffraction pattern of PbS/PPy, SnO_2/PPy and CdS/PPy nanocomposites is shown in fig. 4 (a), (b) & (c). For this, a drop of the diluted prepared products is taken on the carbon coated copper grid and after evaporation has taken place, the corresponding SAED patterns of the PbS/PPy, SnO_2/PPy and CdS/PPy nanocomposites have been observed. These rings are in agreement with the peaks in the XRD spectra.[17, 18, 19] The images confirm the poly and nanocrystalline nature of the samples due to the spot and ring patterns. The concentric rings with spots in the SAED pattern clearly indicate the polycrystalline nature and good crystallinity of the prepared nanocomposites. .

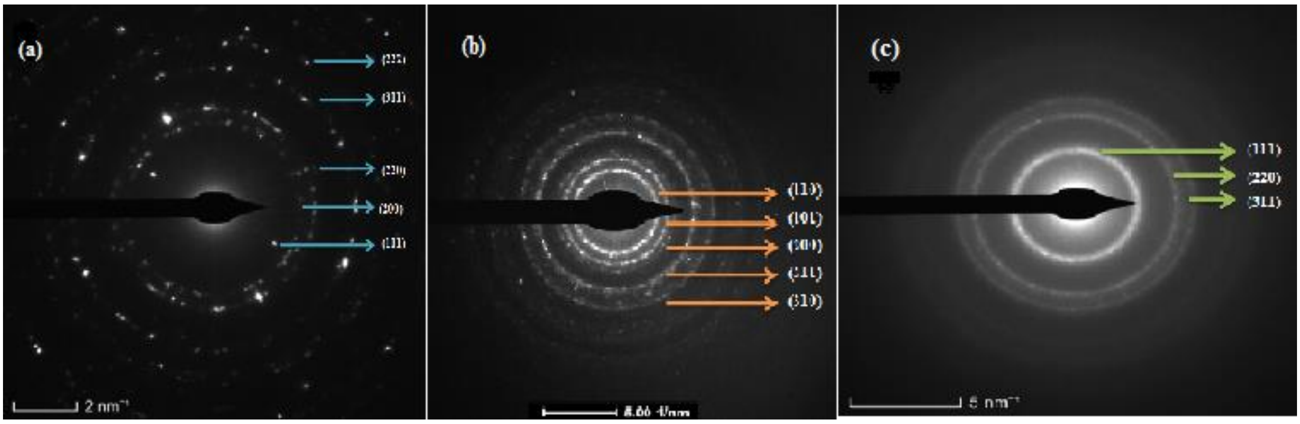

Fig. 5: SAED pattern of (a) PbS/PPy, (b) SnO_2/PPy and (c) CdS/PPy

Conclusion:

This hypothetical study seeks to emphasize how the core/shell nanocomposites are synthesized with desirable crystallite size. Using this method, we could fix the diameter of the core/shell nanocomposites. The above study reveals that the obtained crystallite size of core/shell nanoparticles having ± 5 nm with the expected crystallite size of the materials. The future is concerned, along with the development of new core/shell materials, insight into new mechanisms will be needed in order to facilitate the synthesis process. This is in turn should lead to new application areas, are expected to be fast-tracked from laboratory to scientific trials. The importance of process scalability from laboratory to a commercial scale should not be underestimated. Finally, with such advances in the experimental work, it is also expected that more theoretical studies will lead to a better understanding and facilitate experimental trials.

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