Large Scale Manufacturing of WS_2 Nanomaterials and Their Application in Polymer Nanocomposites

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

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Abstract

With size down to nanoscale, nanomaterials exhibit novel properties exceeding or differing significantly from their bulk counterparts. In particular, amongst a wide range of interesting new nanostructures, tungsten based nanomaterials have demonstrated super physical, chemical, electronical and mechanical properties in a diverse range of applications which has been comprehensively reviewed. However, challenges still remain high on the effective processes to scale up the manufacturing of such nanomaterials, with desired shape, size and quality. These tungsten based nanomaterials are thus become the research subject of this project, and the study on continuous manufacturing of specifically inorganic fullerene WS_2 (IF-WS_2) nanoparticles, and their potential exploration as fillers to polymer matrix to fabricate nanocomposites with improved mechanical properties are the main objectives of this research.

After a thorough assessment of the extremely promising potentials of tungsten based nanostructures, and review of the current bottleneck for large quantity production of IF-WS_2, a generic experimental methodology and techniques used for the investigations have been described in experimental methodology part. In the following chapters, this thesis demonstrates the following research works:

A novel rotary furnace for continuous scaling up manufacturing of IF-WS_2 nanoparticles has been designed, constructed, tested and refined in this work. The new furnace consists of several key components: a tube furnace, self-contained rotary system, dynamic seal system, modified new tube with baffle, and a continuous gas-blow feeding system. Test results show that the rotary reactor has improved the lab scale manufacturing of IF-WS_2 from sub-gram to several tens of grams per batch without agglomeration, which makes this technique a promising alternative for the replacement of the existing tall fluidised tower processing in industrial level production.

As an important precursor for IF-WS_2 nanomaterials production, the synthesis of WO_x nanoparticles by high temperature thermal decomposition of Ammonium Paratungstate (APT) has been investigated, and the parameters have been optimised (with Ar flow at 6 L/min at 1350°C) for achieving desired sizes. Further studies on the creation of uniform and ultra-thin WO_x nanowires were carried out using solvothermal technique. The

solvent concentrations, reaction time and solvent types have been systematically investigated, and the resulting WO_x nanowires from tungsten chloride precursor in mixed cyclohexanol and ethanol solvent exhibited a record high specific surface area of 275 m^2/g. This is fundamentally significant for their applications in sensor and electro-chromic devices.

Reverse patterned growth of WO_x nanorods was realised for the first time on an Au-coated W foil by a simple W-water vapour reaction. The resulting nanorods of different diameters, lengths and patterns have been created by tuning the growth parameters. Further nitriding under NH_3 atmosphere at elevated temperature, converted the WO_x nanorods, as a template, to WO_xN_y nanorods. The WO_xN_y nanorods have been found to inherit the patterns on the substrate and kept the size and shape of WO_x nanorods. An interesting morphology revolution for the conversion of WO_x to WO_xN_y nanorods was observed, and a mechanism has been proposed accordingly to account for the growth. This result represents a simple, innovative and efficient process for the reverse-patterned growth of new nanomaterials.

Further development of the rotary furnace has led to a unique new class of core-shell composite nanoparticles, carbon (C)-coated IF-WS_2 hollow nanoparticles, by continuous chemical vapour deposition (CVD) production. The composite nanoparticles exhibited a uniform and adjustable C coating, with little or no agglomeration. Importantly, the thermal stability of the core-shell C-coated IF-WS_2 against oxidation in air has been improved by about 70°C, compared to the pristine IF-WS_2. This new material could find applications where thermal stability is critical.

Exploration of 0-4 wt% IF-WS_2 as reinforcement in nylon 12 matrix nanocomposites has been carried out for the first time, using a combination of ultrasonic dispersion and magnetic stirring technique to achieve excellent IF-WS_2 dispersion in the matrix. Tensile and bending test results showed moderate improvements of 27% and 28% respectively, with a 2 wt% IF-WS_2 addition, but a staggering 185% and 148% improvement in toughness for the addition of 0.25 and 0.5 wt% IF-WS_2 samples, against pure nylon 12, suggesting that such composites are promising candidates for structural and ballistic fibre applications.

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