



High yield production of photoluminescent tungsten disulphide nanoparticles

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ABSTRACT

Single and few layered tungsten disulphide (WS₂) nanoparticles were prepared using a surfactant assisted ultrasonication exfoliation technique with concentrations of up to 0.4 mg/mL. The lateral dimension of the particles was in the range of 100–250 nm. The exfoliated WS₂ was stabilised against re-aggregation through adsorption of a tri-block non-ionic polymeric surfactant (PEO–PPO–PEO). These nanoparticles were characterised by absorption, Raman and photoluminescence spectroscopy (PL). Broadening of the E_{2g} peak in the Raman spectrum was observed due to phonon confinement within a single layer of WS₂. The exfoliated particles have significantly different properties than the bulk WS₂ material, in particular, the emergence of strong photoluminescence at 1.97 eV in energy coincidental with the excitonic peak in the UV–Vis spectrum. The emergent PL emission suggests that the monolayer WS₂ is a direct gap material analogous to other dichalcogenides such as MoS₂.

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1. Introduction

Atomically thin materials have received great attention, the most commonly cited example being graphene [1–3]. Other van der Waals bonded solids though, such as the dichalcogenides, also have interesting optical and electronic properties particularly in the limit of 2D [4]. Chiefly among these, the transition metal dichalcogenide semiconductors molybdenite (MoS₂) and tungstenite (WS₂) have attracted interest for potential use in advanced applications such as photovoltaics and photocatalysis due to tunable band gaps depending on size. There is a strong push from the renewable energy interests to create materials with appropriate valence and conduction bands which allow the splitting of water to form hydrogen and oxygen through the utilisation of the maximum amount of incident solar radiation. Typically, TiO₂ has been used in such applications however the large band gap of 3.2 eV means less than 5% of the incident solar photons can be absorbed.

Both MoS₂ and WS₂ in the bulk form are indirect band gap semi-conducting materials with band gaps of 1.22 eV and 1.20 eV respectively. The magnitude of this gap is insufficient for many photocatalytic applications, specifically the photoelectrochemical splitting of water [5,6]. Thermodynamically, the minimum energy required is 1.23 eV but practical considerations means a band gap greater than 1.4 eV is needed. Furthermore, the positioning of the valence and conduction bands is such that the generation of hydroxyl radicals is also not possible reducing the potential for these materials to be used in many photocatalytic applications. Hence,

much effort has been taken in tuning the band gap properties of the dichalcogenides to more suitable values through quantum confinement effects [7]. 3D confinement has led to increased band gaps of up to 2.5 eV for crystallite sizes of 4–5 nm for MoS₂. Precipitation inside micelles has typically been used in order to produce these nanoparticles [8–10] and analogous WS₂ particles [11]. Recent studies have shown that confinement effects are also demonstrated by the 2D analogues of MoS₂ with emerging photoluminescence suggesting a transition to a direct band gap material [12–14]. Thus, it is timely that the methods used for generating large scale quantities of graphene be adapted for producing single and few layered materials of the transition metal dichalcogenides.

Many methods have been described for the production of 2D materials such as graphene [15]. Whilst large area graphene was first produced using exfoliation with adhesive tape [1,16,17], subsequent methods such as intercalation, reduction of graphene oxide [18], solvothermal techniques [19] and sonication in appropriate solvent systems [20–28] have all led to increased quantities of material. Aqueous solution processing has many advantages, particularly in terms of cost and the environment. One of the more promising techniques is the use of ultrasonic exfoliation of graphene and related materials in the presence of aqueous surfactant solutions [21,23,29]. The surfactant is necessary to promote exfoliation for two reasons. The first, it reduces the surface tension of the aqueous phase to a magnitude of the order of the cohesive energy required to separate the solid sheets. Secondly, it adsorbs onto the surface of the exfoliated particles creating an extra repulsive term that inhibits re-aggregation of the produced particles [30,31]. This surfactant assisted ultrasonication technique was recently adapted from the graphene system to other van der Waals bonded solids [32], including the semi-conducting dichalcogenides MoS₂ and

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WS₂. In this paper, a method for the high yield production of photoluminescent WS₂ nanoparticles under aqueous conditions is described. Surfactant is added continuously throughout the sonication thereby giving rise to a much greater concentration of exfoliated WS₂ particles. These particles have been characterised in terms of their size and their opto-electronic properties, with interesting photoluminescence observed.

2. Experimental section

2.1. Materials

Powdered Tungsten(IV) Sulphide with a bulk particle size of 2 μm was purchased from Sigma–Aldrich Australia and used as received. A tri-block co-polymeric surfactant, Pluronic F108 (BASF, Ludwigshafen) with a molecular weight of 14.6 kDa was used to stabilise the exfoliated particles as well as control the liquid–vapour interfacial tension. Milli-Q water was used in the preparation of all suspensions.

2.2. Methods

2.2.1. Production of aqueous suspensions of WS₂ particles

WS₂ nanoparticle suspensions were prepared using the surfactant assisted ultrasonic exfoliation technique as previously described [21,23,27,29,31–34]. A 2% w/w suspension of bulk WS₂ was added to Milli-Q water. Under continuous sonication at 60 W using a “Cell Disruptor” Model W-220F (Heat Systems–Ultrasonics Inc) sonicator, non-ionic surfactant was added from a highly concentrated solution to maintain the concentration of surfactant in water at approximately 0.1% w/w. The exfoliation procedure results in a vast increase in solid–liquid surface area which leads to rapid depletion of the surfactant through adsorption to the particles surface. Thus, continuously adding surfactant during sonication leads to a significantly greater yield of nanoparticulate WS₂ [29]. This concentration of surfactant is suitable for maintaining the optimum surface tension as described previously at ~40–42 mJ/m² [32].

The resultant exfoliated suspension was then dialysed in Milli-Q water for 48 h to remove any non-adsorbed surfactant from the solution. The suspension was then typically centrifuged at 1500 rpm for 5 min to sediment further any large (non-exfoliated) particles. The supernatant was collected and was found to be stable for up to 3 months. Some sedimentation was observed due to the relatively high density of WS₂ (7.5 g/mL) but the particles could be readily re-dispersed through simple agitation. The particles were subsequently characterised in terms of size, charge and spectroscopic properties as described below. The yield of single and few layer WS₂ nanoparticles produced using this method was determined gravimetrically to be as high as 0.4 mg/mL depending on the rate of centrifugation. Furthermore, density measurements of the suspensions were also performed to confirm the concentration of WS₂ particles. The thickness of the WS₂ particles was typically characterised based upon the photoluminescence measurements. That is, the proportion of particles which demonstrated strong luminescence at 1.97 eV, with at least 100 particles measured.

2.2.2. Transmission Electron Microscopy (TEM) imaging

The dried suspension of WS₂ particles was imaged using TEM to confirm that single and few layered material was prepared as well as to determine the lateral sizes of the particles. A Hitachi H7100FA transmission electron microscope with an accelerating voltage of 125 kV was used. Furthermore, electron diffraction patterns of the particles were measured.

2.2.3. UV–Vis spectrophotometry

UV–Vis spectra of the diluted WS₂ suspensions were measured using a Shimadzu UV-3101PC spectrophotometer with matched quartz cuvettes over the wavelength range of 250–800 nm.

2.2.4. Raman spectroscopy and photoluminescence spectra

The synthesised WS₂ particles were characterised using Raman spectroscopy with a Horiba Jobin Yvon T64000 Raman system. Laser excitation at 532 nm was used. Typically, WS₂ particles were deposited onto an oxidised silicon wafer. The photoluminescence spectrum of the particles was also measured using the laser excitation at 532 nm.

2.2.5. Zeta potential measurements

The zeta potential of the WS₂ particles was determined using a Malvern Zetasizer Nano. The measurements were performed on the suspension in Milli-Q water (pH 6.5) after extensive dialysis to remove any unbound non-ionic surfactant.

3. Results and discussion

The surfactant assisted sonication method was used to exfoliate single and few layer WS₂ from the bulk particles in the presence of the non-ionic tri-block surfactant. This technique involves a relatively high powered sonicator probe however little oxidation was observed as determined through the measurement of the nanoparticle zeta potential. Typically, the ζ potential of the WS₂ at pH 6.5 was less than –5 mV. This particle charge is significantly lower than the graphene analogues however the dangling edges of the WS₂ are stabilised by sulphur atoms [35] leading to reduced overall charge in comparison to the graphene which is predominately stabilised through oxygen containing moieties. This overall surface charge is typically too low to stabilise the particles in suspension. However, the non-ionic surfactant adsorbs to the surface allowing stability of the WS₂ for in excess of 3 months. Fig. 1 shows an image of the nanoparticulate WS₂ suspension, which has a slight green/brown¹ colour.

The UV–Vis spectrum of a 100× diluted suspension of WS₂ nanoparticles was measured in the range of 250–800 nm. As can be seen in Fig. 1, the particles absorb strongly in the UV region and furthermore, a peak is observed at 627 nm (1.97 eV), commonly assigned as the “A exciton” and related to the direct excitonic transition at the *K* point of the Brillouin zone [13]. This peak at 627 nm is also present in the bulk material which demonstrates that there is no a significant shift in the spectrum as may be expected from simple two dimensional confinement. Wilcoxon et al. have demonstrated that changes in the adsorption edge only occur for confinement in three dimensions [8]. Furthermore, the spectrum shows strong absorption at wavelengths below 627 nm, particularly in the UV region in agreement with previous spectrophotometric studies [7]. Confinement in 3D leads to a shift in the absorption edge and decreases in the position of the exciton. It is clear however that although the size of the WS₂ particles are confined in terms of thickness, the relatively large lateral dimensions leads to maintenance of the position of the excitonic peak at 627 nm. Previous studies suggest that there is only a very small shift (~0.15 eV) due to confinement in 2D [8]. The peak associated with the indirect B excitonic transition is not as prominent as for the isomorphous MoS₂ analogues in either the bulk or exfoliated samples shown in Fig. 1. The difference in energies of the A and B excitons peaks upon exfoliation is not expected to change significantly under these 2D confinement conditions unlike in 3D con-

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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