



# Size-dependent and intra-band photoluminescence of NiS<sub>2</sub> nano-alloys synthesized by microwave assisted hydrothermal technique

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## ABSTRACT

Synthesis of nickel disulfide (NiS<sub>2</sub>) nano-alloys capped and uncapped with hexadecylamine (HDA) was carried out. A cubic phase NiS<sub>2</sub> formation was confirmed by X-ray diffraction (XRD) analysis. An average crystallite size of 35 nm was obtained for the uncapped nanostructures and 9 nm was obtained for the capped nanostructures estimated using the Scherrer equation. Unexpected ultra-violet (UV) emission as well as near infrared (IR) emissions were attributed to intra-band energy state transitions that occur as a result of the porous structure of the material. Enhanced UV and near IR PL emissions due to the smaller crystallite size of the capped NiS<sub>2</sub> nanostructures was also observed. Band energy and local density of states calculation for NiS<sub>2</sub> were used to support the experimentally observed luminescence results. The luminescence features at wavelengths of 400 nm (3.10 eV), 428 nm (2.90 eV), 447 nm (2.77 eV) and 464 nm (2.67 eV) can be attributed to some of those electrons de-exciting from S (3p) levels down to the Ni (3d) (blue to UV emission) whereas those features at wavelengths of 710 nm (1.75 eV), 751 nm (1.65 eV), 754 nm (1.64 eV), [NiS<sub>2</sub>/HDA-capped NiS<sub>2</sub>] and 784 nm (1.58 eV) respectively seem to result from de-excitations between either Ni(3d) or S (3s, 3p) levels and Ni–S hybridization levels (red to near IR emission).

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## 1. Introduction

Transition metal chalcogenide nanomaterials e.g., CdS, ZnO, ZnS, SnO, SnS, CoS, CuS, CuS<sub>2</sub>, FeS<sub>2</sub>, CoS<sub>2</sub> and NiS<sub>2</sub> have received considerable attention over the years owing to the novel properties observed when compared to their bulk counterparts which results from a quantum confinement effect [1–6]. These material's properties such as opto-electronic, mechanical and chemical properties have aroused intensive investigations for new applications including use in catalysis and in optical and magnetic devices. The nickel disulfide (NiS<sub>2</sub>) alloy adopts a pyrite structure and it is known to be an antiferromagnetic insulator with a band gap of about 0.3 eV. Its narrow band gap has attracted attention for possible applications in the semiconductor industry especially in infrared emitters and detectors [7]. Methods that have been used to synthesize these types of materials include chemical vapor deposition, solid-state reactions and wet chemical thermal techniques [8–12]. The microwave assisted hydrothermal technique has become one of the methods for nanoscale synthesis [13]. This is because microwave addition to hydrothermal reactions provides quick, straightforward, and

inexpensive ways of attaining the desired products from a given chemical reaction. Also, the solvents used can be green; hazardous by-products are prevented. Information on the PL properties of NiS<sub>2</sub> is rare in literature and we have not yet come across a report that shows UV and near IR PL emissions due to NiS<sub>2</sub>. In this report we show the UV and near IR PL emissions of NiS<sub>2</sub> and enhanced PL emission of HDA-capped NiS<sub>2</sub> nanostructures.

## 2. Experimental

### 2.1. Reagents and sample preparation

All reagents used were purchased from the Sigma Aldrich chemical company and were used as received without any further purification. To synthesize NiS<sub>2</sub> nanostructures, 1.552 g Ni (CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O was added to an ethanol solution containing 0.400 g sulfur. The mixture was then transferred to a Multiwave 3000 microwave oven that was operated at 600 W for 30 min and fan cooled to room temperature for 20 min. The black precipitate formed was washed several times with ethanol and dried in an oven at 90 °C for 6 h. To optimize for NiS<sub>2</sub> formation, the reaction was repeated and the power used was changed to 700 W and 800 W. Further, the reaction was repeated in the presence of 5.00 g HDA in order to control the size of the nanostructures formed.

### 2.2. Characterization

The phases of the as-synthesized materials were investigated using X-ray diffraction [Philips PW 1830 X-ray diffractometer with a Cu Kα (λ = 0.154 nm)]. Sample morphologies were studied using SEM (JOEL 2000) and high resolution transmission electron microscopy (HR-TEM Joel-Jem 2100). The PL spectra of the

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as-synthesized samples were recorded at room temperature from 310 nm to 800 nm using a Horiba Jobin Yvon HR320 Spectro-fulorometer by exciting the samples with the 300 nm line of a deuterium lamp. The emission was detected with a Jobin–Yvon MPT detector.

We carried out density functional theory simulations using the generalized gradient approximation (GGA) [14] for the exchange and correlation functional, as implemented in the CASTEP code [15]. The interaction between the ionic cores and the valence electrons is described using the ultrasoft pseudo potential of Vanderbilt [16]. The Brillouin zone is sampled using the scheme of Monkhorst and Pack [17]. This  $k$ -points sampling gives a good convergence to the total energy calculations. A kinetic energy cut-off of 300 eV was used for the plane wave expansion of the wavefunctions. The positions of all atoms in the  $\text{NiS}_2$  unit cell were relaxed using the conjugate gradient algorithm with a tolerance of  $2 \times 10^{-5}$  eV for maximal change in total energy. Calculations were considered converged when the residual forces were less than 0.05 eV/Å. The electronic states were occupied in accordance with the Fermi distribution function using a Fermi smearing parameter of  $k_B T = 0.20$  eV.

### 3. Results

#### 3.1. Phase analysis

In order to confirm the product phase synthesized, XRD analysis was carried out. Cubic phase  $\text{NiS}_2$  product was confirmed by XRD analysis which corresponds to the literature data ( $\text{NiS}_2$ : JCPDS Card number 11-0099) with the cell constant  $a = 5.68$  Å. It can be seen from Fig. 1 that the  $\text{NiS}_2$  formation was optimized at 800 W microwave power level. The increased microwave power level increases the rate at which the product is formed. The crystallite size for the sample synthesized at 800 W was estimated using the Scherrer equation given in Eq. (1).

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $D$  is the average dimension of the crystallites,  $K$  is a constant (usually applied as 0.9),  $\lambda$  (0.154 nm) is the wavelength of the  $\text{Cu K}\alpha_1$  X-ray,  $\beta$  is the full width at half maximum of the diffraction peak (inaccuracies associated with stress and instrumental broadening are expected), and  $\theta$  is the Bragg angle. The average crystallite size for  $\text{NiS}_2$  was estimated using the reflections shown in Table 1 and the average obtained was 35 nm. This suggests that the  $\text{NiS}_2$  materials prepared are in the nano-range.

The same phase was also obtained when HDA capping agent was added to the reaction. It can be observed from Fig. 2 that the

**Table 1**

Average crystallite size of the  $\text{NiS}_2$  nanostructures using the Scherrer equation.

| Peak    | D (Scherrer = $k\lambda/\beta \cos\theta$ ) (nm) |            |
|---------|--------------------------------------------------|------------|
|         | Uncapped                                         | HDA-capped |
| 111     | 43                                               | 14         |
| 200     | 41                                               | 9.5        |
| 210     | 32                                               | 9.5        |
| 211     | 27                                               | 3          |
| 220     | 31                                               | 7          |
| Average | 35 (+/–6)                                        | 9 (+/–4)   |

diffraction peak widths are broad, which is an indication of a small crystallite size. For the HDA-capped  $\text{NiS}_2$  the average crystallite size was estimated by the Scherrer equation to be 9 nm as shown in Table 1. This is a size control effect of the capping agent on the nanostructures.

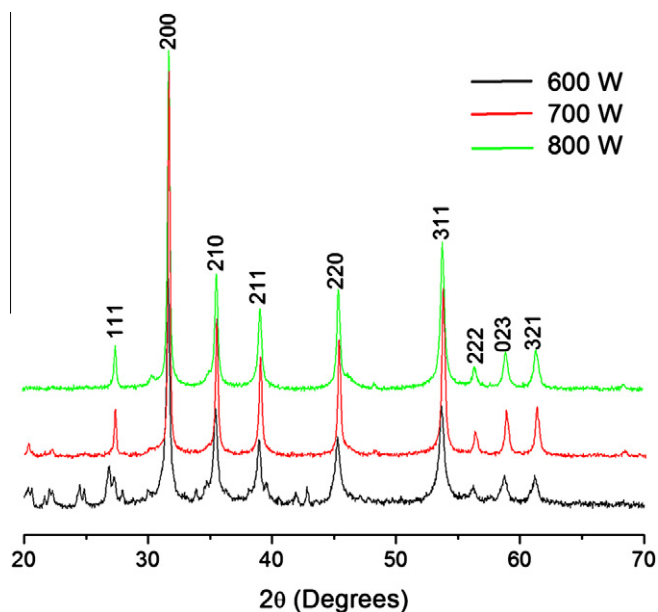
#### 3.2. Microscopy analysis

Evenly distributed hierarchal microparticles with rough surfaces were observed in the SEM images for all the samples synthesized at different microwave power levels without HDA addition. The images are shown in Fig. 3. The average particle size distribution was measured from the SEM images using the imageJ programme. It can be seen from the size distribution that the average size increases from about 300 nm to 500 nm with increased power level which is due to the increased microwave heating rate as the power is increased. From the rough surfaces it can be seen that these hierarchal microparticles are a result of small particles that assemble to form big agglomerates.

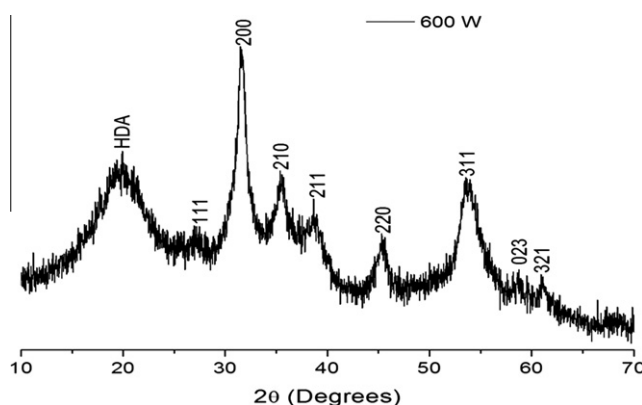
When HDA was added to the reaction to act as a capping agent, the size of the  $\text{NiS}_2$  structures was reduced to a nanometer scale as shown in Fig. 4(a) and (b). It was not possible to see the crystallites by SEM due to their small size. However, it can be seen in Fig. 4(a) that the sample looks like flakes which is a result of the presence of the HDA capping agent. HR-TEM analysis shown in Fig. 4(b) reveals that the  $\text{NiS}_2$  particles formed were spherical with an average crystallite size of about 3 nm. The small particle size is a result of the added HDA capping agent which prevented large particle growth as well as particle agglomeration.

#### 3.3. Photoluminescence

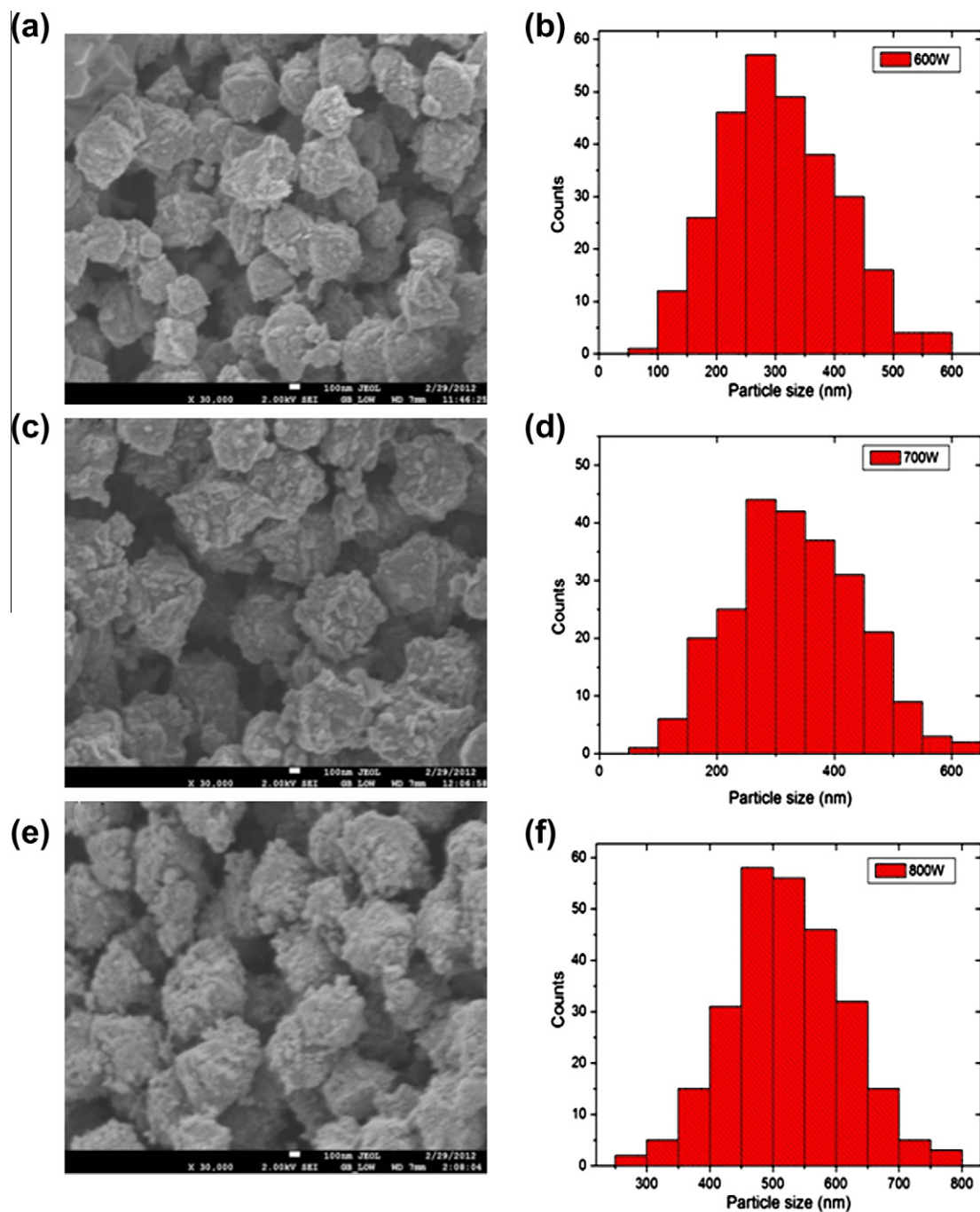
Fig. 5 shows room temperature PL spectra of the  $\text{NiS}_2$  hierarchical structures and HDA-capped  $\text{NiS}_2$  nanocrystals excited at



**Fig. 1.** XRD spectra of cubic  $\text{NiS}_2$  microstructures synthesized at various microwave power levels.



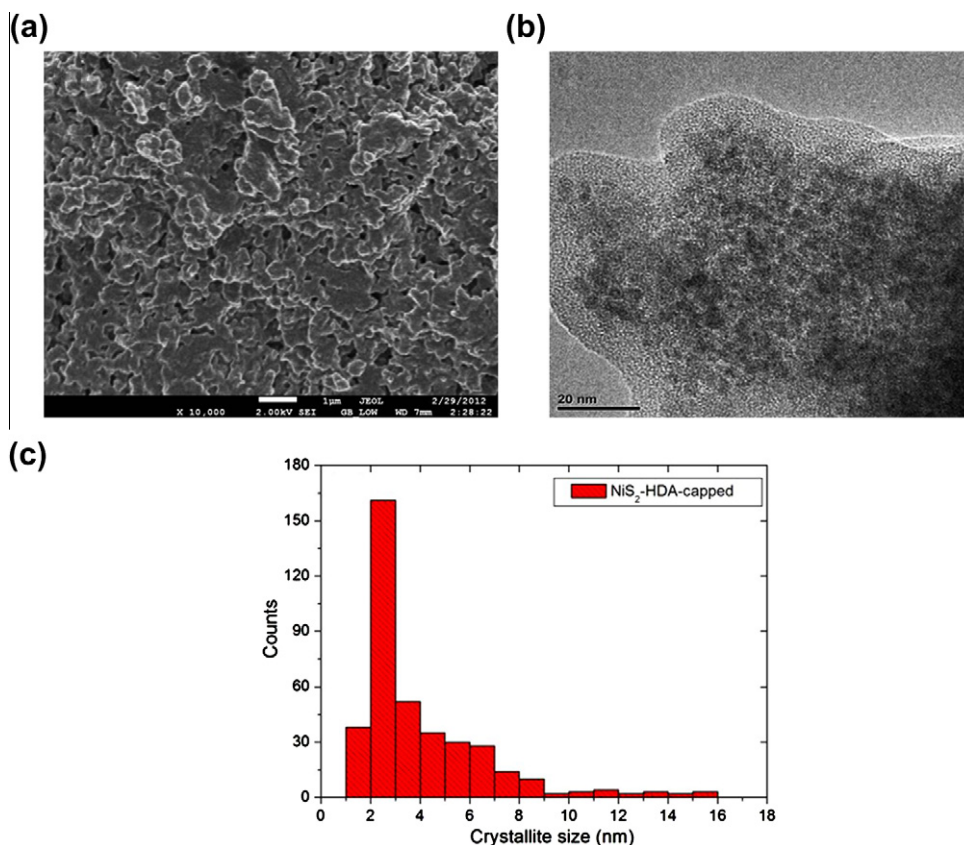
**Fig. 2.** XRD profile for the  $\text{NiS}_2$  material synthesized in the presence of 5 g HDA which acts as a capping agent.



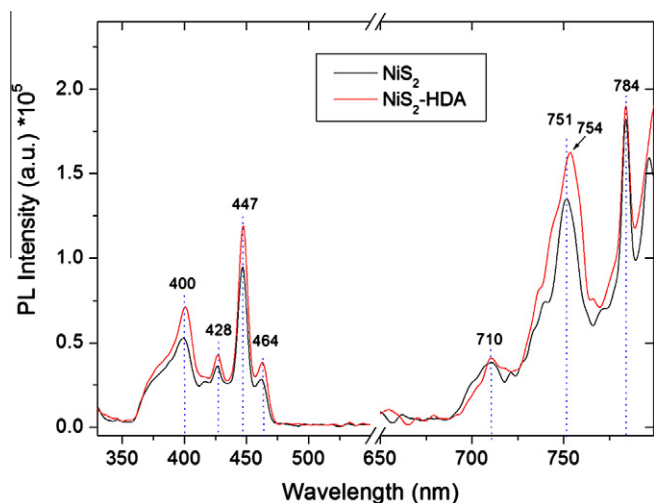
**Fig. 3.** SEM images of the samples synthesized at 600 W (a), 700 W (c), 800 W (e), and their corresponding particle size distribution in (b), (d) and (f) respectively.

300 nm. A UV broad emission peak which is comprised of four peaks located at about 400 nm (3.10 eV), 428 nm (2.90 eV), 447 nm (2.77 eV) and 464 nm (2.67 eV) was observed. The presence of more than one peak may be due to the presence of structural defects within the samples. A second and much more intense PL emission peak was observed in the near IR region. Three peaks were evident with emission maxima located at 710 nm (1.75 eV), 751 nm (1.65 eV), 754 nm (1.64 eV), [NiS<sub>2</sub>/HDA-capped NiS<sub>2</sub>] and 784 nm (1.58 eV). Both the UV and the near IR emissions observed in our study appear at a much higher energy when compared to the reported band gap of NiS<sub>2</sub> which is within the range 0.3–0.8 eV. The observed emissions can therefore be attributed to intra-band transitions that take place on the NiS<sub>2</sub> band structure

during excitation. The multi peaks could also be due to excess S induced energy state transitions. This observation has not been reported for NiS<sub>2</sub> structures before. Wang et al. reported PL results of NiS<sub>2</sub> microspheres of 5 micro-meters constructed of cuboids with 500 nm mean side length. Their fluorescence spectrum was recorded from 270 to 500 nm using an excitation wavelength of 277 nm [18]. Their spectrum (provided in the Supplementary material) did not show any fluorescence in this recorded region. So if we assume that bulk NiS<sub>2</sub> does not show fluorescence, we can then attribute the observed emissions to a nanosize effect. Further, most materials that are closely related to NiS<sub>2</sub> like FeS<sub>2</sub>, CoS<sub>2</sub> and CuS<sub>2</sub> do not show this behavior. However, the UV emission band with quadruple fine structure was reported by Denzler



**Fig. 4.** SEM (a) and HR-TEM (b) images of NiS<sub>2</sub> nanostructures synthesized at 600 W in the presence of 5 g HDA capping agent. The crystallite size distribution measured from the HR-TEM images is shown in (c).



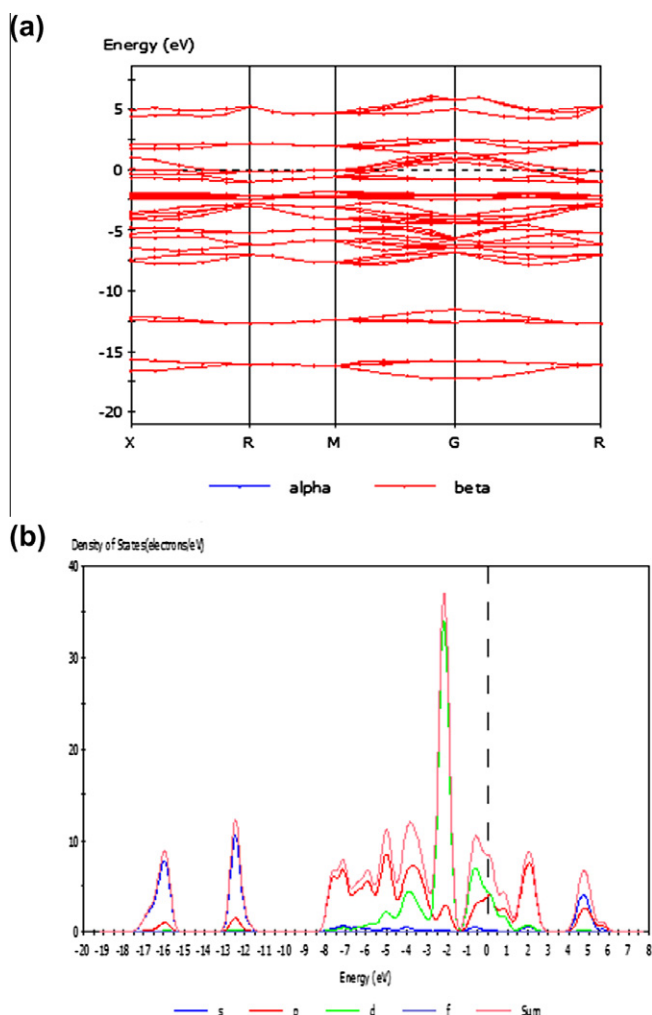
**Fig. 5.** Photoluminescence spectra of the as-synthesized hierarchical and the HDA-capped NiS<sub>2</sub> nanostructures excited at  $\lambda = 300$  nm.

et al. for colloidal ZnS nanocrystals. Their UV peaks appeared at 416, 424, 430, and 438 nm. They attributed the peaks to transitions that involve vacancy states and interstitial states for Zn and S atoms [19]. Further, they observed low intensity peaks in the IR region which they attributed to transitions between distinct localized states in the gap due to impurities and imperfections [19]. The intense emission peaks they observed in the UV region could also be supported by the wide band gap of ZnS, which is 3.7 eV.

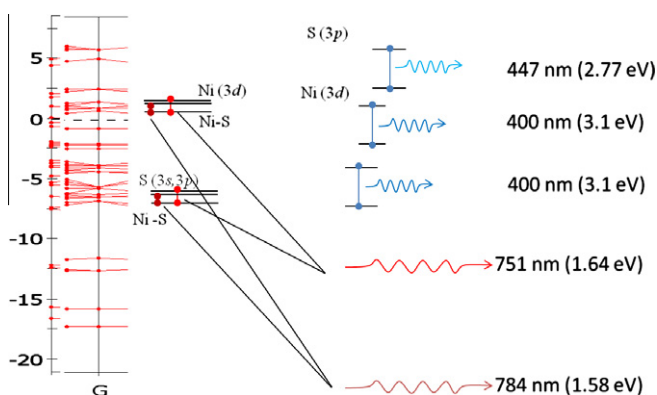
Intense emission peaks in the IR region in our case are due to the narrow band gap of our material. It can be observed for both emissions that the small size HDA-capped NiS<sub>2</sub> nanocrystals show enhanced emission when compared to the uncapped NiS<sub>2</sub> structures. This is due to the smaller size of the capped nanocrystals and is in good agreement with what has been reported for other nanomaterials in the literature [20]. The small shift of the HDA-capped nanoparticles could be attributed to an increased level of defects due to the smaller size of the NiS<sub>2</sub> particles.

The band energy structure and the local density of states (LDOS) calculated for NiS<sub>2</sub> are shown in Fig. 6(a) and (b). The LDOS spectra shows that the electrons near Fermi level energies ( $E_F$ ) are mostly from the Ni 3d and S 3p energy bands. It can also be seen that most electrons active at the lower bands are from 3p and 3s orbitals which are likely to belong to S atoms. This observation is in agreement with what has been reported in literature, where NiS<sub>2</sub> band opening was attributed to Ni eg-orbital splitting via LDA calculations combined with dynamic mean field theory (DMFT) [21]. Kunes et al. did similar calculations accompanied by experimental X-ray photoemission spectroscopy measurements [22]. Their NiS<sub>2</sub> spectral density also shows S-p density dominating far from the  $E_F$  which suggests dominant S contribution at these energies. This suggests that intra-band transition in the NiS<sub>2</sub> structure is likely due to the presence of S atoms.

In as far as the photoluminescence features appearing at various wavelengths, we consider the gamma,  $\Gamma$ , line of symmetry in the calculated band structure. Here we only truncate the bands around the gamma point  $\Gamma$  in the Brillouin zone of the NiS<sub>2</sub> system in Fig. 7. The gamma point (where  $\pi a/\lambda = 0$ ) being the centre of the Brillouin zone is appropriate when the photon wavelength,  $\lambda$ , of



**Fig. 6.** (a) The band energy structure of NiS<sub>2</sub> and (b) the electron states of Ni (3d), Ni-S hybridisation and S (3s and 3p) partial density of states.



**Fig. 7.** Band structure around the gamma point G of the Brillouin zone of the NiS<sub>2</sub> system. Both the 751 nm and 784 nm feature in the PL spectra are identified on this energy diagram as de-excitations either from Ni (3d) or S (3s, 3p) to Ni-S hybridization energy states whereas the luminescence features from 400–464 nm are attributed to S (3p) to Ni (3d) electron relaxations.

excitation (in this case 325 nm) is much longer than the lattice parameter of the NiS<sub>2</sub> system ( $a \sim 0.568$  nm).

We have carefully identified the energy differences in the band structure as truncated in Fig. 7 to the emission energies in the PL

spectra in Fig. 5. The luminescence features at wavelengths of 400 nm (3.10 eV), 428 nm (2.90 eV), 447 nm (2.77 eV) and 464 nm (2.67 eV) can be attributed to some of those electrons de-exciting from S (3p) levels down to the Ni (3d) (blue to UV emission) whereas those features at wavelengths of 710 nm (1.75 eV), 751 nm (1.65 eV), 754 nm (1.64 eV), [NiS<sub>2</sub>/HDA-capped NiS<sub>2</sub>] and 784 nm (1.58 eV) respectively seem to result from de-excitations between either Ni (3d) or S (3s, 3p) levels and Ni-S hybridization levels (red to near IR emission).

No band-to-band transitions are observed in the experimental PL which suggests that Ni (3d) electrons, being close to the Fermi level, do not participate in the visible, near IR and UV emissions. They may rather be emitting far into the infra-red region which was beyond the detection limits of our PL instrument.

#### 4. Conclusions

In conclusion, NiS<sub>2</sub> nanostructures have been synthesized through the microwave irradiated thermal technique by heating a mixture of nickel acetate and sulfur in methanol solution. Varying the microwave power level yielded different sized particles with bigger agglomerates of about 500 nm average particle size. XRD analysis showed that the crystallite size of the synthesized material was in the nano-range suggesting that the huge agglomerated particles observed during SEM analysis for the samples synthesized without HDA addition were self assembled smaller particles. Addition of HDA as a capping agent yielded a NiS<sub>2</sub> with smaller particle sizes of about 9 nm. The smaller size effect due to HDA addition was seen in the PL emission properties of the samples. HDA-capped NiS<sub>2</sub> nanostructures showed enhanced PL emission when compared to the uncapped and bigger size NiS<sub>2</sub>. The emissions in both samples were attributed to intra-band transitions mostly due to the sulfur content in the samples according to the calculated band energy structure and partial density of states.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jallcom.2012.10.102>.

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