Phase dependent catalytic activity of nickel sulfide nanoparticle by hot injection method
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1. Introduction
Environmental friendly transitional metal chalcogenides received much attention in recent years due to the current requirement for energy applications [1]. The complexity in nickel sulfide phases (NiS (α-NiS and β-NiS), Ni₃S₂, NiS₂, Ni₃S₄, Ni₆S₉, and Ni₇S₈) make unique in its properties over other metal sulfides [2]. Nickel sulfides with different phases and morphologies were discussed by several research groups, but to date, the complexity still remains for the phase control and its corresponding morphological control for applications. We have investigated the synthesis of phase controlled nickel sulfide hierarchical structures by hydrothermal method [3]. However, phase and size control of the synthesized product is important in the case of catalytic reduction applications. In the present work, nickel sulfide nanoparticles were synthesized with the sizes of less than 20 nm were synthesized by single-step hot injection method. The role of oleylamine as a solvent and surfactant were investigated with respect to the nickel and sulfur source concentrations. For the first time, we have investigated the catalytic reduction reaction of 4-nitrophenol by fabricating low cost phase controlled nickel sulfide nanoparticles.

2. Experimental method
Nickel nitrate hexahydrate (Ni (NO₃)₂. 6H₂O) (1 mmol) was mixed with oleylamine (10 mL) in a 100 mL three-necked flask (A). The solution was heated at 100 °C for 1 h to remove moisture and O₂ in the oleylamine. Elemental sulfur (1 mmol) and oleylamine (10 mL) were placed in a separate 100 mL three-necked flask (B) and heated at 70 °C for 30 min to form a sulfur–amine mixture. The transparent yellow sulfur–oleyamine solution (B) was loaded into a glass syringe and injected into the nickel–oleyamine solution mixture (A). This mixture of the sources in a concentration ratio of 1:1 resulted in the NiS phase. The temperature was raised to 210 °C and the mixture was continually stirred for 1 h under a N₂ atmosphere to initiate the reaction. After cooling, the particles were collected by centrifugation, washed with ethanol, and dried under vacuum for 1 h. The particles were dispersed in an organic solvent and stored in a tightly closed container. Synthesized nickel sulfide materials were characterized by XRD, TEM, FTIR and XPS analysis. Aqueous solutions of 4-Nitrophenol and NaBH₄ in a concentration ratio of 1:10 were mixed with nickel sulfide nanoparticles (4.0 mg). The mixture was placed in a quartz cuvette and the reaction was monitored using UV-vis spectroscopy.

3. Results and discussion
Fig. 1 (a) shows the XRD pattern of NiS phase. The use of a 1:1 concentration ratio of nickel to sulfur in the presence of oleylamine resulted in formation of a nickel monosulfide phase. The TEM image of Fig. 1 (b) shows that the sizes of the spherical nanoparticles ranged from 8 to 10 nm. The HRTEM image shows that the distance between the atomic layers was 2.94 Å, which matches the d-spacing of the (100) plane of the NiS phase (Fig. 1 c). A single phase with good crystallinity was obtained in a single step at 210 °C. Oleylamine helped to make the particle size distribution uniform. The other nickel sulfide phases NiS₂, Ni₃S₄ and Ni₇S₈ were synthesized with their corresponding nickel to sulfur concentrations (1:2, 3:4 and 3:2). Synthesized materials were utilized for the catalytic reduction of 4-nitrophenol to 4-aminophenol as shown in Fig.1 (d). The best activity was observed for NiS phase over other phases (NiS, Ni₃S₄ and Ni₇S₈) with the reaction rate of 8.949 × 10⁻³ s⁻¹.

[Reference]