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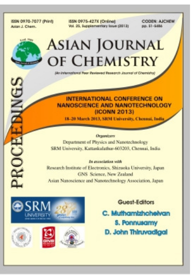

Wet Chemical Synthesis of Nickel Nanostructures Using Different Capping Agents†

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In this work, encapsulated nickel nanostructure were synthesized by wet chemical synthesis technique, using five different capping agents *viz.*, cetyltrimethyl ammonium bromide (CTAB), starch, poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) (PVP), zeolite. Experiments were performed by varying the type and the concentration of the capping agents and the changes in morphology and crystallinity of the nickel nanostructures were observed. Morphology and crystallinity of the nanostructures obtained in these experiments were analyzed using field emission scanning electron microscopy (FESEM) and X-ray difractometry (XRD). The results incurred from these experiments suggest that the morphology and the crystallinity of the nickel nanoparticles can be controlled by using appropriate capping agent of appropriate concentration.

Key Words: Nanostructures, Capping agent, Morphology, Crystallinity.

INTRODUCTION

Size controlled synthesis of metal nanoparticles can be achieved by various physical and chemical techniques like mechanical milling[1], solvothermal, hydrothermal synthesis[2-4], microemulsion[5-10], sonochemical[11,12] and capped precipitation from aqueous solutions[13-17]. However, synthesis of metal nanoparticles having definite morphology and crystallinity is always challenging. Hence, physical and chemical property of the metal nanoparticle depends on the morphology and crystallinity of it, in order to have a better control over these properties, researchers around the world are exploring novel synthesis technique and post synthesis processing techniques. Learning from the previous works reported on synthesis of nanoparticles using capping agent, by using cetyltrimethyl ammonium bromide (CTAB) as the capping agent the agglomeration of the synthesizing metal nanoparticle can be prevented and also structures like nanochains can be achieved[18,19], by using starch as the capping agent core/shell nanoparticles can be achieved[20]. By using poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG) as the capping agents core/shell structure/hybrid structure can be achieved[21]. Also, by using poly(vinyl pyrrolidone) as capping agent, agglomeration of catalyst material and its crystallization can be prevented during synthesis[22,23]. This work reports the effect of using five different capping agents *viz.*, cetyltrimethyl ammonium bromide, starch, poly(ethylene glycol), poly(vinyl pyrrolidone), zeolite, at different concentration, during the wet chemical synthesis of nickel nanostructure.

EXPERIMENTAL

Nickel chloride hexahydrate [$NiCl_2 \cdot 6H_2O$] analytical grade acquired from Loba Chemie. Acetone [CH_3COCH_3] analytical grade acquired from Rankem. Sodium borohydride, CTAB, starch and zeolite acquired from Sigma Aldrich, PEG, PVP acquired from Alfa Aesar.

Experimental procedure: Deionized water was used as solvent in all experiment. Solution A was made in 10 mL of deionized water by mixing 0.4 M nickel chloride and 'x' gram of capping agent (were x = 0.05, 0.1, 0.5, 1, 1.5, 2). Solution B was made in 10 mL of deionized water by mixing 0.8 M sodium borohydride. Solution B was titrated into solution A for 0.5 h. This procedure was performed with CTAB, starch, PEG, PVP, zeolite as the capping agents. The resultant solutions were always dark black precipitate. The obtained black precipitates were cleaned by centrifuging and dried at 200 ºC for 4 h. After drying, all samples turned to be black coloured powder.

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RESULTS AND DISCUSSION

Reaction mechanism for nickel formation:

$$NiCl_2 + 2NaBH_4 + \text{capping agent} \rightarrow (\text{encapsulated Ni}) + 2NaCl + H_2 + 2BH_3$$

The nickel chloride was reduced using sodium borohydride.

FESEM results: The FESEM results were obtained using FEI Company, Quanta FEG 200 FESEM.

Cetyltrimethyl ammonium bromide: The FESEM results of samples synthesized using 0.05 and 0.1 g CTAB yielded spherical nickel nanoparticles of *ca.* 35 nm diameter. The samples synthesized using 0.5, 1, 1.5 and 2 g of CTAB yielded fibrous nanostructures of *ca.* 35 nm wide and *ca.* 100 nm long. Although there were fibers, 1.5 and 2 g of CTAB yielded scale like structure without any definite shape or size (Fig. 1).

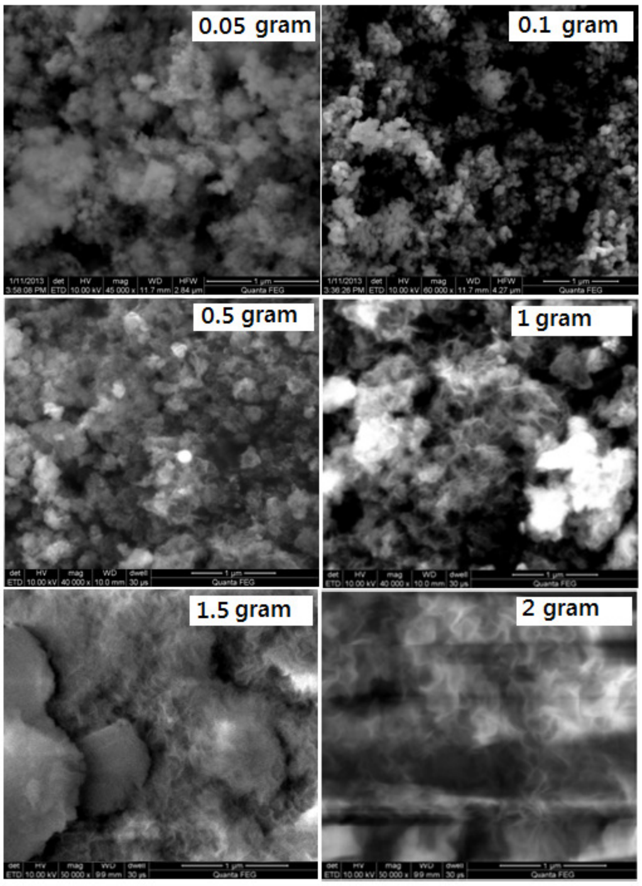

Fig. 1. FESEM images of CTAB encapsulated nickel nanoparticles

Starch: The FESEM result of the sample synthesis using 0.05-1 g of starch yielded to spherical nanostructures of *ca.* 20-100 nm. It is observed that the size of the nanostructures increased in proportion with the concentration of starch. The samples synthesized using 1.5 and 2 g starch yielded to unsymmetrical morphology with scale like structure (Fig. 2).

Poly ethylene glycol: The FESEM result of the sample synthesis using 0.05 - 1 g of PEG yielded to fine spherical nanostructures of *ca.* 20-40 nm. It is observed that the size of the nanostructures increased in proportion with the concentration of PEG. The samples synthesized using 1.5 and 2 g of PEG yielded to unsymmetrical morphology with scale like structure (Fig. 3).

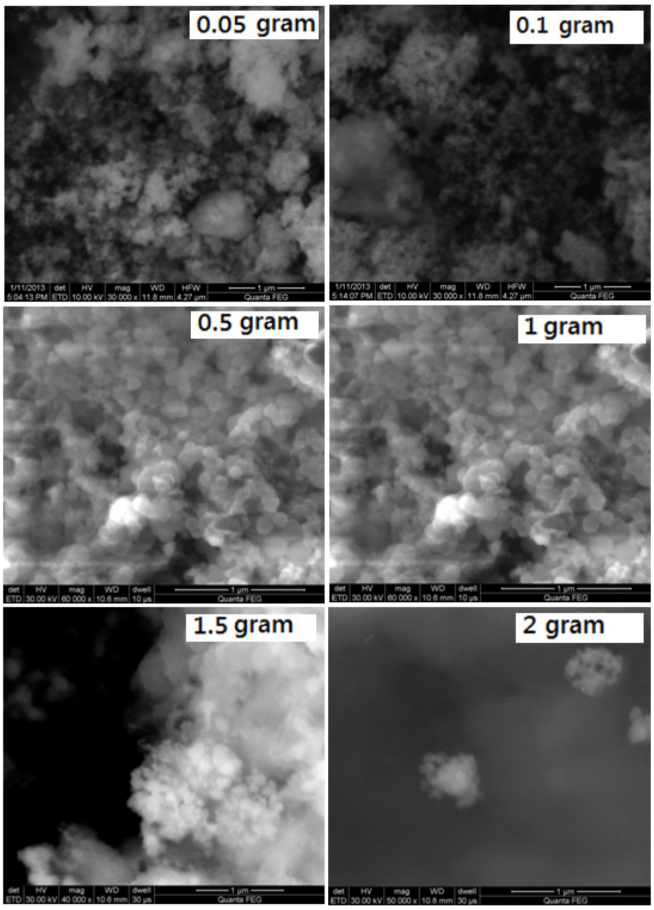

Fig. 2. FESEM images of STARCH encapsulated nickel nanoparticles

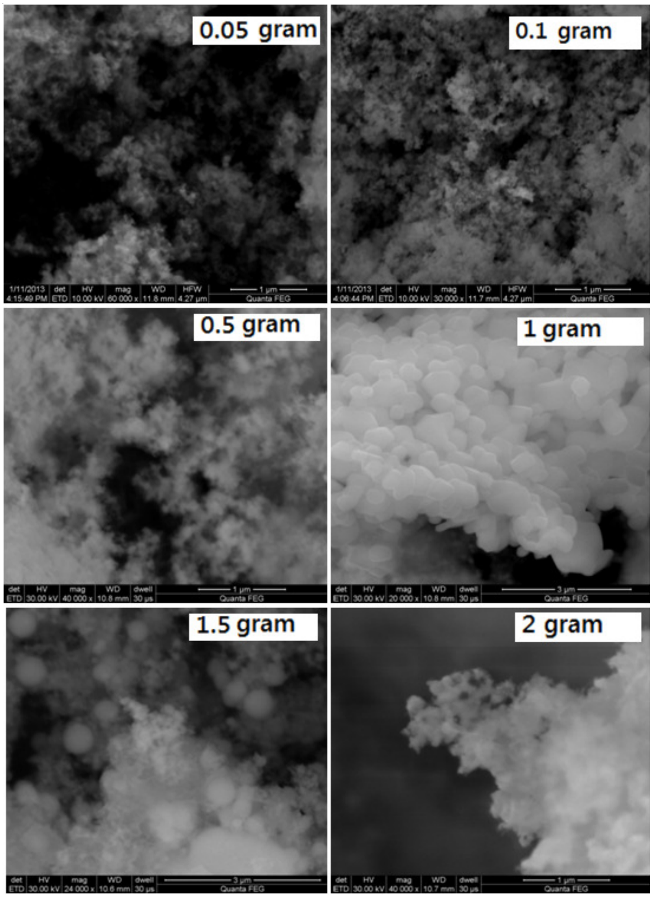

Fig. 3. FESEM images of PEG encapsulated nickel nanoparticles

Poly vinyl pyrolidone: The FESEM result of the sample synthesis using 0.05 and 0.1 g of PVP yielded to spherical nanostructures of *ca.* 20-30 nm. The samples synthesized using 0.5-2 g yielded to the formation of spherical nanoparticles *ca.* 50-100 nm with the mild existence of fibrous nanostructures. It is also observed that the average size of the nanostructures increased in proportion with the concentration of PVP (Fig. 4).

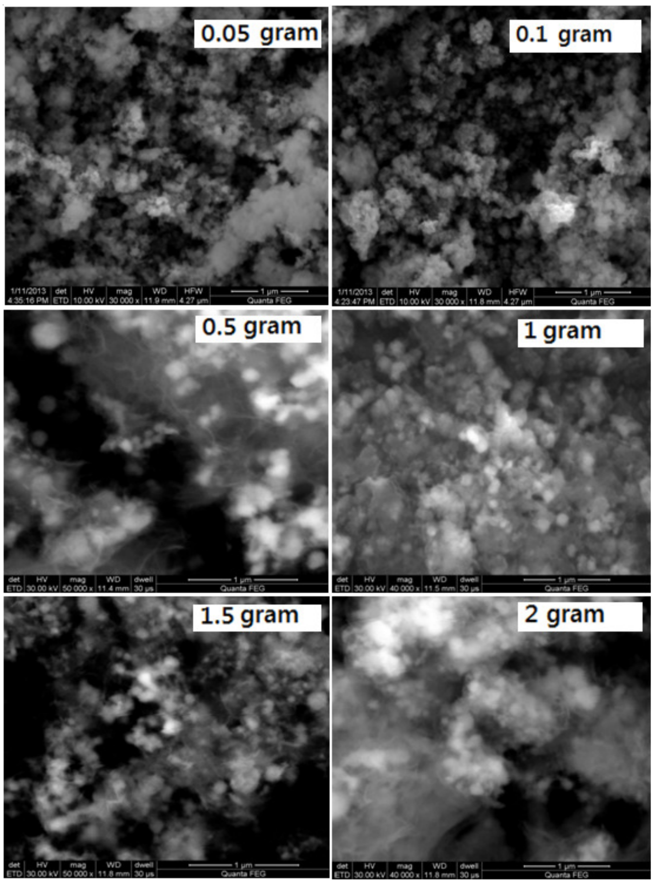

Fig. 4. FESEM images of PVP encapsulated nickel nanoparticles

Zeolite: The FESEM result of the sample synthesis using 0.05 and 0.1 g of zeolite yielded to spherical nanostructures of *ca.* 20-30 nm. The samples synthesized using 0.5 g yielded to the formation of spherical nanoparticles of 50-100 nm with rare fibrous structure. The samples synthesized using 1-2 g of zeolite yielded to scale like structure formation, with few spherical nanostructures over them. It is also observed that the size of the nanostructures increased in proportion with the concentration of zeolite (Fig. 5).

X-ray diffraction results: The X-ray diffraction patterns were obtained using PAN analytical XRD [X'pert] Pro, CuK$_\alpha$ radiation, with a graphite monochromator, at 45 KV tension, 40 mA current with a 0.04° step rate with 2θ ranging from 20°-90°.

The obtained X- ray diffraction data of the samples synthesized showed that the sample synthesized using CTAB as the capping agent were crystalline nickel (Cubic) [JCPDS# 70-0989] at low CTAB concentration and the peak intensity reduces as the concentration of CTAB increases. The rest of the sample obtained using PEG, PVP, zeolite and starch as capping agents completely led to amorphous nickel. The results obtained from the experiments done using zeolite as the capping agent have a peak at 2 theta 23.984°, which could correspond to (622) plane of Zeolite [JCPDS# 43-0142] (Fig. 6).

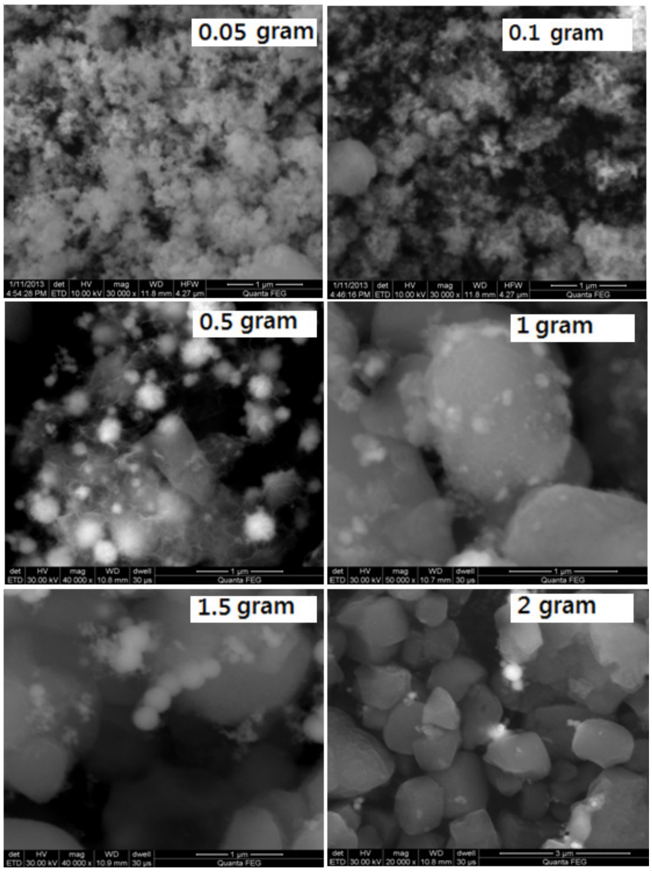

Fig. 5. FESEM images of zeolite encapsulated nickel nanoparticles

Conclusion

The results from these experiments showed that there is an effect of capping agents and its concentration on the morphology and crystallinity of nickel structures. In general, the particulate size is directly proportional to the concentration of the capping agent used in the reaction. It has to be noted that among all the capping agents used in this work, only CTAB yielded crystalline nickel nanostructures.

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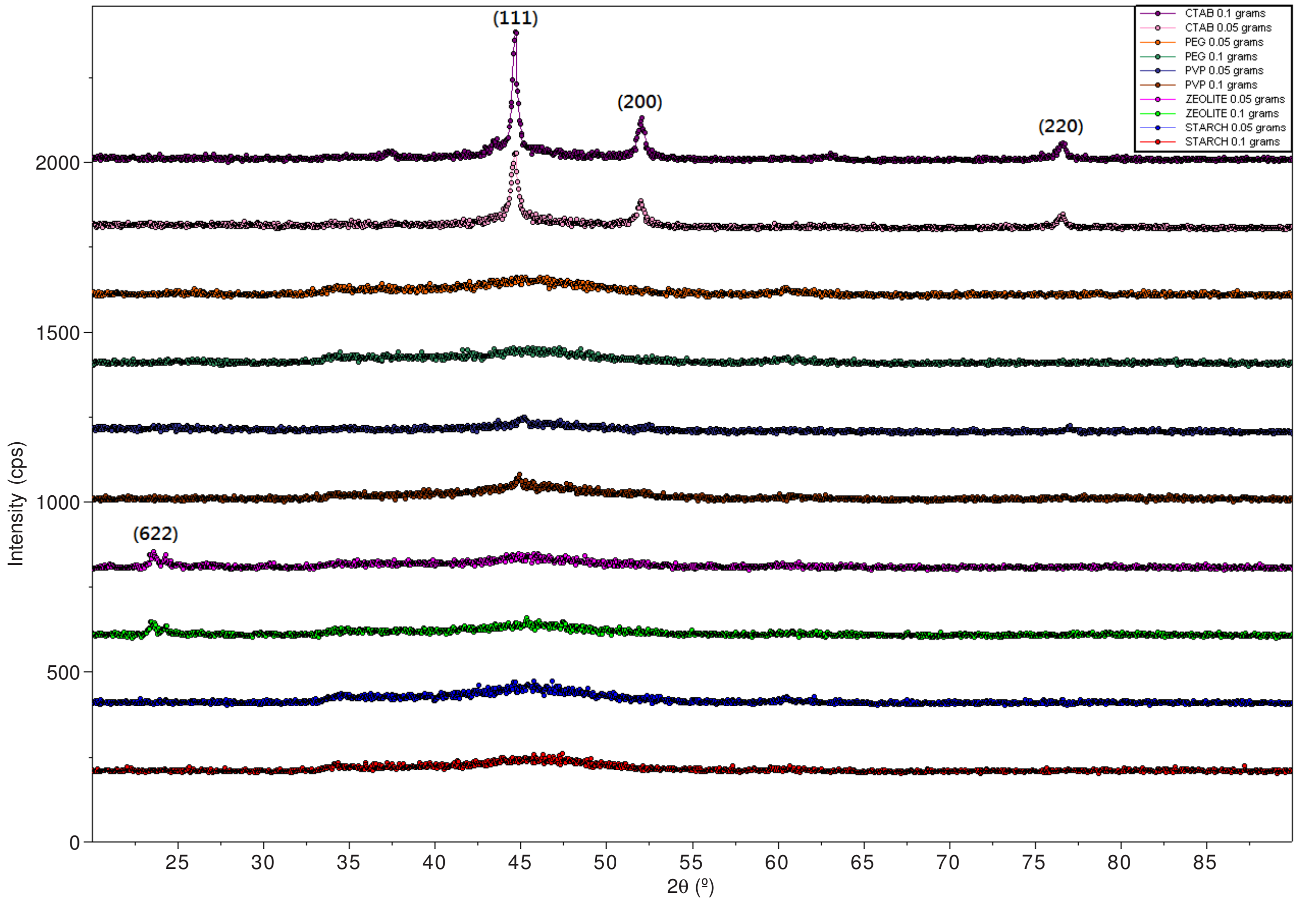

Fig. 6. Consolidate XRD data of samples obtained using low concentration (0.1 and 0.05 g) of different capping agents

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