

## **Synthesis of Fe-nano Particles Obtained by Borohydride Reduction with Solvent**

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**ABSTRACT:** In this study, we investigated the synthesis of nano-size iron particle using a borohydride reduction of ferric ion in the presence of solvent containing carbonyl groups. When we varied the contents of solvent, there is a corresponding variation of synthesis and iron form. Each sample of synthesized iron particles was characterized by transmission electron microscope (TEM) and powder X-ray diffractometer (XRD). The contents of zero-valent iron (ZVI) in the synthesized particles were measured to investigate the effect of solvent proportions in aqueous-organic solvent system reducing iron particles. As the solvent added, ZVI proportion in the synthesized particle was decreased forming well dispersed iron particle suspension. Their dispersity were also characterized by light scattering particle size analyzer, which led us to confirm the change of dispersing characteristics of wet synthesized iron particles in multi component system.

### **INTRODUCTION**

Iron nanoparticles have been synthesized to form magnetic recording media, ferrofluids, medical contrast agent, and environmental remediants (Li et al., 2006; Lu et al., 2007; Masciangioli and Zhang, 2003). In environmental field, iron has been widely used as reactive catalyst on account of its effectiveness, non-toxic, ubiquitous, and low price. Among the various synthetic methods, wet-chemical synthesis using borohydride has been the most common ways to synthesize nano-scale transitional metal. In recent, several results reported ferric salt reducing method using borohydride derivatives to get a simple and controllable fabrication of environmental nanoiron (Wang and Zhang, 1997). These nanostructures have become the focus of intensive research because nanostructures provide a better system to the mechanical properties on size reduction (Cain et al., 1996). However, synthesized nanomaterials faced great challenge for applications due to their strong tendency of agglomeration and consequently occurring consolidation (Bonini et al., 2007; Kantrell et al. 1997). In field application, Saleh et al. reported the problem of conventionally reduced nano-scale iron which occurs pore plugging (Saleh et al., 2007). Various efforts have been attributed to prepare a stable suspension of reactive nano-scale iron (Bonder et al., 2007; Cha et al., 2007). Although these dispersing methods using additives can partially reduce the aggregation and sedimentation of particles, method of preparing stabilized iron particle dispersion is still necessary. Because dispersing step and additives could occur deformation or wasteful reaction before the expected reaction. Furthermore, additives can make secondary pollution during the remediation.

The goal of this research would be to develop a process that would get the enhanced colloidal nanoiron for in situ remediation with water-solvent system.

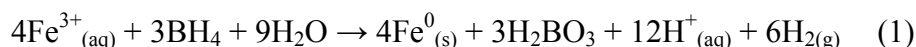
## MATERIALS AND METHODS

**Reagents.** The following chemicals were used without further purification: FeCl<sub>3</sub>•6H<sub>2</sub>O (extra pure, Kanto chemical, Japan), NaBH<sub>4</sub> (98%, Aldrich, USA), acetone (HPLC grade, J-T baker, USA).

All aqueous stock solutions were prepared using Ar purged DI water. In a typical process, 0.1M ferric solution (solution 1) and 0.15M borohydride was prepared. Excessive borohydride is typically deployed to perform the perfect synthesis reaction.

Solution 1 was aerated with Ar gas before the reaction. For modification, solvent should be added and mixed with solution during the bubbling of solution 1. To make enhanced dispersity and reduced particle size, additives would be aprotic, containing carbonyl group that would disturb the reduction reaction, and well mixed with water. In this paper, acetone was added to solution 1. After addition, under the Ar flow, borohydride solution was added at rates of smaller than 0.02 mL/s for the mild synthesis. During the addition, the solutions were mixed by mechanical stirrer and shaken by hand to reduce induced aggregation during the synthesis.

**Procedure.** Ferric ion is reduced by mixing sodium borohydride as the reductant, following the reaction (Glavee et al., 1995).



The black precipitates on the surface after (1) reaction, they were allowed to settle down. The separated black precipitates were washed with deionized water and acetone with triplicate. Finally precipitates were dried under Ar flow.

**Characterization.** The amount of zero-valent iron species in synthesized iron particle was measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES; IRIS-AP, Thermo Elemental). Excessive Fe ions were quantified by classical chemical titration method using o-Phenanthroline. The pH and reduction potential was measured using a pH-ORP meter (Orion, ROSS ultra combination electrode: 8102BNUWP).

X-ray powder diffraction patterns were obtained on a RIGAKU X-ray diffractometer with Cu K $\alpha$  radiation. The microstructures of synthesized particles were characterized using a Philips CM-200. An electrophoretical light scattering measurement (Photal, Otsuka Electronics) provided particle size distributions in the submicron range.

## RESULTS AND DISCUSSION

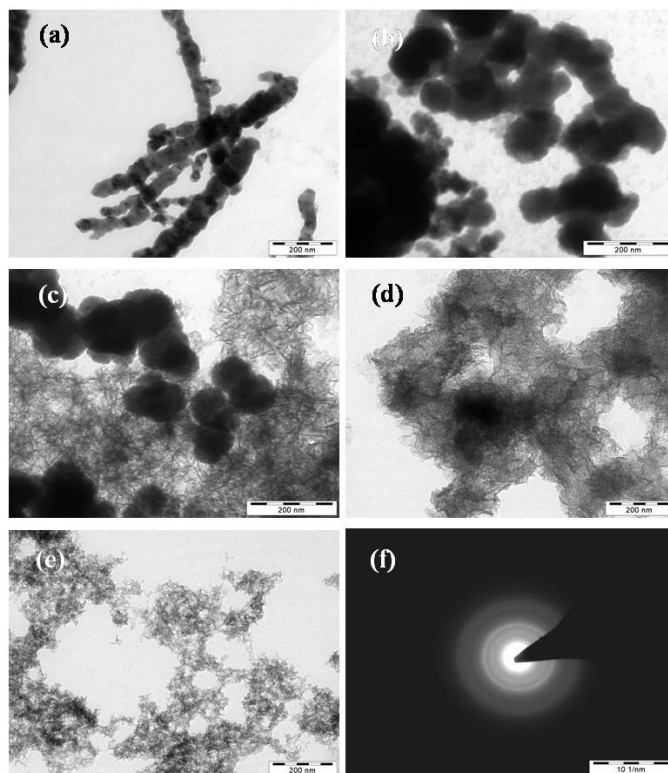
Reduction of iron ion with borohydride derivatives in solvent is a simple and mild reaction which can be done safely. Moreover, a key advantage of this reaction is that various iron sources can be used for the intended reaction. The different conditions for preparing the nanoiron particles with multi-component solvent system were listed in Table 1. Several parameters could significantly affect the formation of nanoiron. Arriagada and Osseo-Asare summarized five aspects to be taken into consideration for particle synthesis, which are phase behavior and solubilization, average concentration of the reacting species in the aqueous phase, intermolecular interactions, dynamic behavior of the multi-component system, and water to co-solvent ratio (Arriagada and Osseo-Asare; 1992).

**TABLE 1. Multi-component system of nano iron synthesis.**

Trial	Water (wt%)	Acetone (wt%)	$W^*$
1	100	0	0
2	75	25	2.22
3	50	50	1.35
4	25	75	0.22
5	0	100	

\*the molar ratio of water to solvent

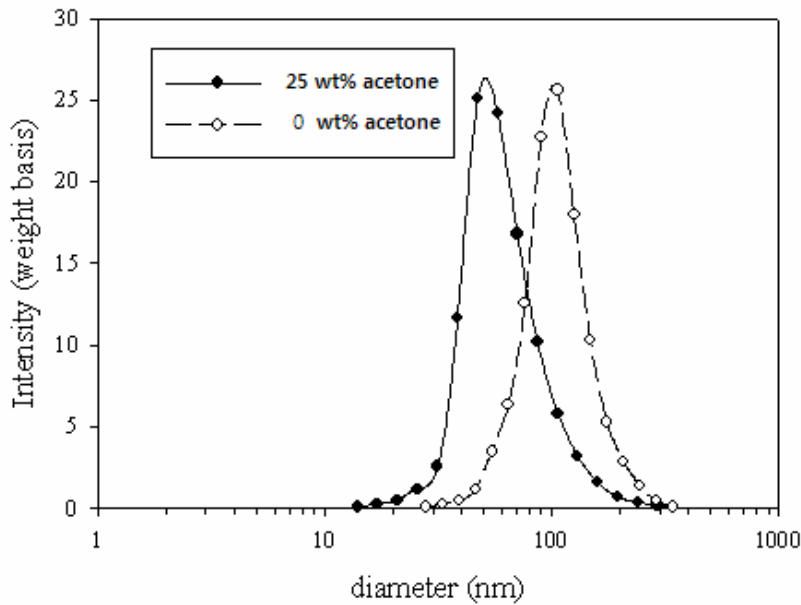
The water-solvent ratio is the most important parameter. Without the acetone addition, no other iron form occurred except zero-valent iron based on the titration result. When the acetone amount was dramatically increased, iron particles lost their magnetism and turned into a green pudding-like gel. The iron particles did not show any zero-valent iron on the titration result. This indicated that the addition of acetone occurred insufficient reduction of ferric ion which could help improve dispersal of iron particles and modify the characteristics of as-synthesized nanoiron particles. When the amount of acetone was over 75 wt% of solvent system, the suspended green gel was obtained without black precipitation.



**FIGURE 1. TEM image of nanoscale iron particles as synthesized with (a) 0 wt%, (b) 25 wt%, (c) 50 wt%, (d) 75 wt%, (e) 100 wt% acetone in co-solvent system during the synthesis. (f) shows an electron diffraction pattern for the sample in (e) 100 wt%.**

Figure 1 shows the TEM images of nanoscale iron particles, with 0, 25, 50, 75 and 100 wt% of acetone addition during the synthesis, stabilized in alcohol media. In this media, the particles are well dispersed but in water media they are somewhat more aggregated observed by naked eyes. As shown in (f), no crystal structure observed at 100 wt% of acetone addition. This resolved TEM image confirmed forming of the gel-like iron precursor by adding of acetone in ferric solution.

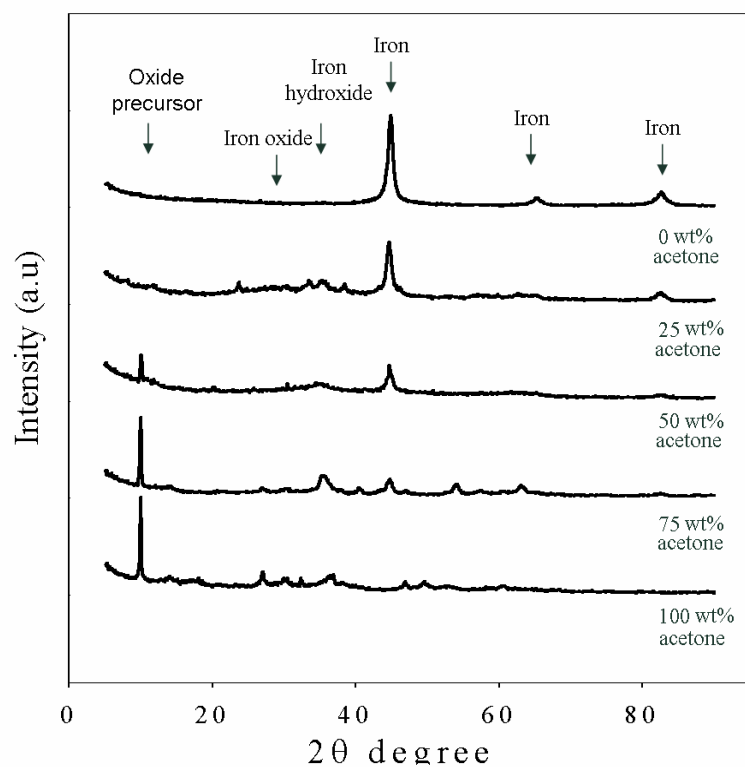
The prepared particles are largely spherical. A representative single particle size is around 60-80 nm. A few particles had size less than 50 nm or larger than 80 nm, whereas most (~90%) particles were in the range. TEM images also show that some particles formed chain-like aggregates. Granulometric particle size distribution results (Figure 2) confirmed the size of synthesized iron particles of 0 and 25wt% of acetone addition, which agree with TEM calculation.



**FIGURE 2. Weight-based particle size distribution determined by light-scattering measurement.**

Figure 3 shows the XRD patterns of the iron particles prepared using the 0, 25, 50, 75 and 100 wt% of acetone addition. The  $2\theta$  values of the peaks are compared with the standard data for iron oxide and hydroxide such as magnetite, lepidocrocite, and  $\alpha$ -Fe. The data cannot be assigned into one oxide because peaks are very weak and close to each other. Remarkable change was observed at  $10^\circ$  and  $44.2^\circ$ . Apparent peak at the  $2\theta$  of  $44.9^\circ$  indicate the presence of  $\alpha$ -Fe. Other apparent peaks show the presence of oxidized iron and iron precursor.

From the combined results of XRD and titration, the synthesized iron nanoparticles contain  $\alpha$ -Fe in the case of 0, 25, 50 wt% of acetone added system, while the nanoparticles derived from over 75 wt% of acetone contain oxidized Fe. The form of hydroxylation and oxidation on the particle surface may be occurred in aqueous solution during the synthesis.



**FIGURE 3. XRD patterns of synthesized iron particles. The solvent used in each case contained the amount of acetone indicated with the remained water.**

## CONCLUSION

From the experiments in synthesis of the nanoiron with acetone by borohydride, the following conclusions can be drawn:

- Stable and enhanced suspension (dispersion) of iron nanoparticles was achieved using a multi component system of ferric ion, water and acetone. The addition of acetone retarded borohydride's reduction potential, consequently form more oxidized phase iron.
- The solvent modified synthesis reduced iron particle size to well-dispersed nano-scale particles.
- A colloidal suspension of nanoscale iron particles which have an average size 60 to 80nm was easily synthesized through a one-pot reaction.

## ACKNOWLEDGMENTS

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## REFERENCES

- Arriagada, F.J, K. Osseo-Asare. 1992. Phase and dispersion stability effects in the synthesis of silica nanoparticles in a non-ionic reverse microemulsion. *Colloids and surfaces*. 69: 105-115
- Bonder M.J., Z.Y., K.L. Kiick, V. Papaefthymiou, and G.C. Hadjipanayis. 2007. Controlling synthesis of Fe nanoparticles with polyethylene glycol. *Journal of magnetism and magnetic materials*. 311: 658-664.
- Bonini, M., E. Fratini, and P. Baglioni. 2007. SAXS study of chain-like structures formed by magnetic nanoparticles. *Materials Science and Engineering C*. 27: 1377-1381.
- Cha, H.G., Y.H. Kim, C.W. Kim, and Y.S. Kang. 2007. Preparation of aqueous dispersion of colloidal  $\alpha$ -Fe nanoparticle by phase transfer. *Sensor and Actuator B: Chemical*. 126: 221-225.
- Cain Jason L., H. S. R., J.A. Nikles, and D.E. Nikles. 1996. Preparation of  $\alpha$ -Fe particles by reduction of ferrous ion in lecithin/cyclohexane/water association colloids. *Journal of magnetism and magnetic materials*. 155: 67-69.
- Cantrell, K.J., D.I. Kaplan, and T.J. Gilmore. 1997. Injection of colloidal Fe<sub>0</sub> particles in sand with shear-thinning fluids. *Journal of Environmental Engineering*. 123: 786-791.
- Glavee, G. N., K.J. Klabunde, C.M. Sorensen, and G.C. Hadjipanayis. 1995. Chemistry of Borohydride Reduction of Iron(II) and Iron(III) Ions in Aqueous and Nonaqueous Media. Formation of Nanoscale Fe, FeB, and Fe<sub>2</sub>B Powders. *Inorganic Chemistry*. 34: 28-35.
- Li, X.Q., D.W. Elliott, and W.X. Zhang. 2006. Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Review of Solid State Material Science*. 31: 111-122.
- Lu, L., Z. Ai, J. Li, Z. Zheng, Q. Li, and L. Zhang. 2007. Synthesis and characterization of Fe-Fe<sub>2</sub>O<sub>3</sub> core-shell nanowires and nanonecklaces. *Crystal Growth and Design*. 7: 459-464.
- Masciangioli, T., and W.X. Zhang. 2003. Environmental technologies at the nanoscale. *Environmental Science and Technology*. 37: 102A-108A.
- Saleh, N., K. Sirk, Y. Liu, T. Phenrat, B. Dufour, K. Matyjaszewski, R.D. Tilton, and G.V. Lowry. 2007. Surface modifications enhance nanoiron transport and NAPL targeting in saturated porous media. *Environmental Engineering Science*. 24: 45-57.
- Wang, C. B., and W.X. Zhang. 1997. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental Science and Technology*. 31: 2154-2156.