Instantaneous Synthesis of Stable Zerovalent Metal Nanoparticles under Standard Reaction Conditions†

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In this report is discussed a novel, easy, and general synthesis method to prepare zerovalent iron (ZVI) and copper (ZV Cu) nanoparticles (NPs), from colloid dispersions in an environmental friendly organic solvent, ethylene glycol (EG). Conventional metallic salts are used as nanoparticle precursors; sodium borohydride ($NaBH_4$) is the reducing agent, and triethylamine (TEA) is used as the nanoparticle stabilizer. The chemical changes take place instantaneously under normal reaction conditions. Small iron (α-Fe^0 phase) and copper (*fcc* phase) NPs with average diameters of 10.2 ± 3.3 and 9.5 ± 2.5 nm, respectively, were obtained. In both cases, the experimental evidence reveals the absence of any metal oxide shell coating the particle surfaces, and their powders remain stable, under aerobic conditions at least for 3 weeks. ZVI NPs were characterized by X-RD, Mössbauer, and Raman spectroscopies and by EELS coupled to HR-TEM. Otherwise, copper NPs were characterized by X-RD, Z-contrast, and HR-TEM. This synthesis pathway is particularly suitable for large-scale and high-quality zerovalent metallic nanoparticle (ZV M NP) production due to its simple process and low cost.

Introduction

Nanoparticle applications are closely related with their *sui generis* properties, due to their high surface/volume ratios which are determined by their shape, size, and size distribution.[1] In comparison with the macro and polycrystalline materials, physical and chemical nanoparticle properties drastically change due to quantum confinement effects.[2]

Most applications of ZV M nanoparticles are based on their large surface area and metallic high reactivity, the latter being a function of the zerovalent metallic element content. It is generally assumed that ZVI and ZV Cu NPs have core−shell morphology, with an iron or copper core and iron oxide/hydroxide or copper oxide shells. In particular, zerovalent iron nanoparticles have many attractive applications[3] mainly in optics,[4] magnetism,[5] electrical,[6] electrocatalysis,[7] and environmental remediation.[8] Moreover, copper nanoparticles (Cu NPs) have been used in optical,[9] magnetic,[10] and sensor devices,[11] in catalysis[12] and environmental remediation,[13] as well as in antifungal and bacteriostatic agents.[14] These applications depend on the novel properties that are acquired when the particle size is of the nanoscale dimensions.

ZVI NPs have been prepared by different procedures such as microemulsion,[7a] sonochemical,[15] chemical vapor condensation,[5c,16] reverse micelles,[5d] thermal decomposition,[17] and chemical reduction.[5e,7b,18]

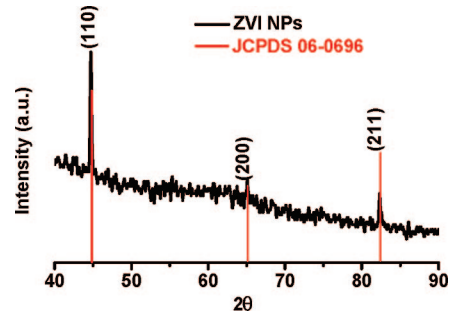

Figure 1. X-ray diffraction pattern of ZVI nanocrystallites, obtained from $FeBr_2$ (1×10^{-2} M), $NaBH_4$ (1×10^{-1} M), and TEA (1×10^{-1} M), in EG, after 15 days of storage.

In order to compare the synthesis pathway of ZVI NPs discussed in this paper with the information already reported in the literature, we have identified six general zerovalent iron nanoparticle preparation methodologies. Table 1 summarizes some of the main attributes of these reported preparation procedures. It is worth stating that in this table only some representative references where zerovalent iron nanoclusters with average sizes under 15 nm have been obtained are included.

On the other hand, to obtain ZV CuNPs, gas phase,[19] sonochemical and thermal reduction,[20] reverse micelle,[21] electroreduction,[22] microwave assisted reduction,[23] irradiation,[24] lithography,[25] metallic vapor synthesis,[26] frame spray,[27] and chemical reduction[12h,i,28] methods have been used.

A similar comparison related with the published ZV Cu nanocluster preparation procedures is shown in Table 2. In this case, we have selected some references where zerovalent copper nanoparticles have been synthesized, with average sizes under 300 nm.

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