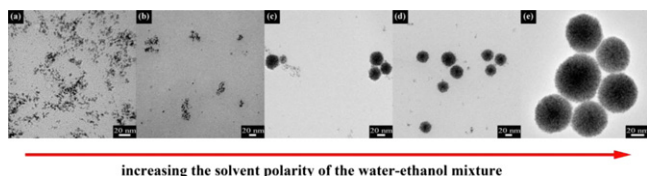


Effect of solvent polarity on the assembly behavior of PVP coated rhodium nanoparticles

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GRAPHICAL ABSTRACT



Highlights ► The solvent polarity effect on the assembly of Rh nanoparticles (RhNPs) was investigated. ► Discrete RhNPs and spherical aggregates were obtained in ethanol and water, respectively. ► RhNPs tended to form spherical assemblies with increasing solvent polarity. ► A particle generation step followed by an assembly step was observed in high-polar solvents. ► A mechanism was proposed to elucidate the assembly behavior of RhNPs.

ARTICLE INFO

Article history:

Received 13 June 2012

Received in revised form 1 October 2012

Accepted 16 October 2012

Available online 8 November 2012

Keywords:

Rhodium nanoparticle
Aggregation behavior
Self-assembly
Water–ethanol mixture
Solvent polarity

ABSTRACT

The rhodium nanoparticles (RhNPs) were prepared in aqueous, ethanol, and water–ethanol mixed solution using rhodium chloride, sodium borohydride and polyvinylpyrrolidone (PVP) as precursor, reducing agent and stabilizer, respectively. The effect of solvent polarity on the assembly behavior of PVP coated RhNPs was systematically investigated by varying the water-to-ethanol ratio in the solution. The main product changed from small separated RhNPs in ethanol to large spherical assemblies of RhNPs in water. The strong tendency for the RhNPs to form aggregates in high polarity solvent was clearly demonstrated by increasing the water-to-ethanol ratio in the reaction media. TEM characterization revealed a two-step formation process of the spherical RhNP assemblies in water: the initial rapid particle generation step followed by a slow particle aggregation step. A mechanism was proposed to elucidate the aggregation behavior of PVP coated RhNPs. The driving force for the aggregation of RhNPs is ascribed to the hydrophobic interaction of hydrocarbon chains of PVP, which can greatly reduce the surface energy of PVP coated RhNPs in high polarity solvents. This work shed light on how to control the formation of nanoparticle aggregates by modulating the polarity of solvent.

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1. Introduction

Shape and size controlled synthesis of noble metal nanoparticles has aroused great interests due to their unique optical and catalytic properties [1–3]. Different noble metal nanoparticles, such as Au, Pt, Pd, Ru and Ag, have been successfully prepared with controlled morphology and size in homogeneous solutions [4–8] or on solid substrates [9–13]. These nanoparticles demonstrated highly

size- and shape-dependent catalytic activities [5,9,14–17]. Organizing nanoparticles into two-dimensional assemblies [7,18–20] and three-dimensional complex structures [21,22] is very important for the applications of nanoparticles. Self assembly has been demonstrated to be an efficient approach for the spontaneous generation of ordered structures using nanoparticles as building blocks [23,24]. During self-assembly, the nanoparticles were organized through noncovalent interactions such as electrostatic attraction, hydrogen bonds, van der Waal's forces, and hydrophobic effects [25,26]. Nowadays, nanoparticle assemblies can be prepared by different strategies, and those integrating both synthesis and assembly into one single combined process are more promising

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