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SONOCHEMISTRY

A Suitable Method for Synthesis of Nano-Structured Materials

Chemistry Research and Applications

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CHEMISTRY RESEARCH AND APPLICATIONS

SONOCHEMISTRY: A SUITABLE METHOD FOR SYNTHESIS OF NANO-STRUCTURED MATERIALS

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Nova Science Publishers, Inc.
New York

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA

Mousavi, M. F.
Sonochemistry : a suitable method for synthesis of nano-structured materials / M.F. Mousavi and S. Ghasemi.
p. cm.
Includes index.
ISBN 978-1-61761-310-4 (softcover)
1. Sonochemistry. 2. Nanostructured materials. I. Ghasemi, S. II. Title.

QD801.M68 2010
541'.3--dc22

2010048362

Published by Nova Science Publishers, Inc. † New York

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PREFACE

Recently, sonochemistry has been employed extensively in the synthesis of nano-structured materials. Rapid reaction rate, controllable reaction conditions, simplicity and safety of the technique as well as the uniform shape, narrow size distribution, and high purity of prepared nano-sized materials are some of the main advantage of sonochemistry. Sonochemistry uses the ultrasonic irradiation to induce the formation of particles with smaller size and high surface area [1].

Because of its importance, sonochemistry has experienced a large promotion in various fields concerned with production of new nano-structured materials and improvement of their properties during the recent years. However, it has encountered limitations in the case of production of some nano-materials with specific morphology, size and properties, but the growth of the number of researches and published articles in the field of sonochemistry during the recent years shows a large interest and attempt to apply sonochemistry in nanotechnology. The improvement of shape, size, purity and some other chemical and physical properties of such produced materials has been the scope of the researchers recently [2].

Sonochemistry uses the powerful ultrasound irradiation (20 kHz to 10 MHz) to induce chemical reaction of molecules. During the ultrasonic irradiation, the acoustic cavitations will occur which consist of the formation, growth and implosive collapse of bubbles in a liquid. The implosive collapse of the bubbles generates a localized hotspot or shock wave formation within the gas phase of the collapsing bubbles (The hot-spot theory) [3].

This chapter is planned to deal with the application of sonochemistry for the synthesis of various nano-structured materials such as metals, metal carbides, metal oxides, chalcogenides and nanocomposites with unique

properties. The effect of different ultrasonic parameters on the prepared structures including their size, morphology and properties are investigated. Also, some applications of prepared nano-materials are introduced, e.g. electrochemical energy storage, catalysis, biosensor and electrooxidation.

CONTENTS

Chapter 1

INTRODUCTION

When ultrasound radiations interact with molecules, chemical reactions can be initiated. Sonochemistry is an interesting research area deal with the processes occurs during the application of powerful ultrasound (20 KHz–10 MHz). Sonochemistry arises from acoustic cavitations. Bubbles undergo the formation, growth, and implosive collapse in a liquid under ultrasonic irradiation. Bubble growth occurs through the diffusion of solute vapor into the bubble. A bubble can be included evaporated water molecules and dissolved gas molecules. When the bubble size reaches to a radius down to several μm, the bubbles collapse provides extreme conditions of transient high temperature(as high as 5000K) and high pressure (up to ~1800 atm) within the collapsing bubbles, shock wave generation, and radical formation. The collapsing bubbles provide reaction sites,named hot spots.At this sites, sonolysis of water molecules to hydrogen radicals (H•) and hydroxyl radicals (OH•) is occurred which is responsible to sonochemical reaction. Also, organic molecules in solution can form organic radicals with a reducing ability. The size of a bubble depends on ultrasonic frequency and intensity. Bubbles collapse occurs in very short time (nanosecond) and cooling rate of 1011 K/s is obtained. The fast kinetics of such process can hinders the growth of nuclei produced during the collapse of bubbles. This may be the reason of formation of nanostructured materials.

Sonochemical synthesis of different types of nanostructured materials consisted of metals and their oxides, alloy, semiconductors, carbon carbonic and polymeric materials and their nanocomposite have received much attention in recent years.

A number of factors can influence on cavitation efficiency and the properties of the products. The dissolved gas, ultrasonic power and frequency, temperature of the bulk solution, and type of solvent are all important factors that control the yield and properties of the synthesized materials.

In the field of sonochemistry, a number of book chapter and reviews have been published 4. Y. Mastai and A. Gedanken reviewed articles in the field of sonochemistry published before 2004 in a chapter of book entitled "Sonochemistry and Other Novel Methods Developed for the Synthesis of Nanoparticles" [2]. Also a review articles was published by Gedanken in 2004 entitled "Using sonochemistry for the fabrication of nanomaterials" focused on the typical shape of products obtained in sonochemistry [1]. Another review articles also published dealt with insertion of nanoparticles into mesoporous materials [5] and the sonochemical doping of various nanoparticles into ceramics and polymers [6].

In this chapter, we will present a literature survey on the various inorganic, organic/inorganic and inorganic/inorganic systems more recently have been synthesized by using ultrasonic method from January 2004 to January 2010s.

Chapter 2

SYNTHESIS OF NANOMETALS

Intensive works on metal nanostructures such as noble metals (Au, Pt, Pd) with various size and morphology have been achieved due to their potential applications in the fabrication of electronic, optical, optoelectronic, and magnetic devices. They can be obtained form sonication of solution containing related metal ion in the absence and presence of capping agents. With controlling size, shape, and crystallinity of nanometals, it can be possible to tune the intrinsic properties of a metal nanostructure.

2.1. GOLD

Gold and other noble metal nanoparticles have been extensively considered in recent years because of their potential applications in optics, electronics, and catalysis, etc. Okitsu et al reported the synthesis of Au nanoparticles and investigate the dependence of sonochemical reduction rate of Au(III) to Au nanoparticles in aqueous solutions containing 1-propanol as accelerator and their particle size to the ultrasound frequency so that the highest reduction rate was at 213 kHz in the range of 20 to 1062 kHz [7]. The average size of Au particles was 15.5 nm in 20 mM 1-propanol.

This group also synthesized Gold nanorods by using sonochemical reduction (frequency, 200 kHz; power, 200 W) of gold ions in aqueous solution (60 mL) containing of HAuCl4 and CTAB including 1.2 mL of AgNO3 (4.0 mM) and 240 μL of ascorbic acid (0.050 M) with pH 3.5 [8]. During the reaction, Au (III) is immediately reduced to Au (I) by reaction with the ascorbic acid. CTAB and AgNO3 act as effective capping agents for the

shape controlled growth of gold seeds. The solution was purged with argon for 15 min and then sonicated in a water bath (at 27 °C) by a water circulation system. In the presence of ultrasonic, the following reactions are proposed:

$$H_2O \xrightarrow{)))} H^{\bullet} + OH^{\bullet} \quad (1)$$

$$CTAB + OH^{\bullet}(H^{\bullet}) \rightarrow H_2O(H_2) + \text{reducing species} \quad (2)$$

$$CTAB + H_2O \rightarrow \text{pyrolysis radicals and unstable products} \quad (3)$$

$$Au^{+} + M \rightarrow Au^{0} + H^{+} + M' \quad (4)$$

$$nAu^{0} \rightarrow (Au^{0})_n \quad (5)$$

$$Au^{0} + (Au^{0})_n \rightarrow (Au^{0})_{n+1} \quad (6)$$

Where M corresponds to various reducing species, pyrolysis radicalsand unstable products. In reaction 3, pyrolysis radicals and unstable products are formed via pyrolysis of CTAB and water. The size of the sonochemically formed gold nanorods was less than 50 nm, and their average aspect ratio decreased with increasing pH of the solution.

At pH 7.7, irregular shaped gold nanoparticles were formed. At pH 9.8, most of the particles formed had a spherical shape with a smaller particle size than those formed in the lower pH solutions. Based on the obtained results, it was clear that the size and shape of the sonochemically formed gold nanoparticles are dramatically dependent on the pH value of the solution (Figure 1).

From the obtained results, it was demonstrated that longer gold nanorods would be obtained if the synthesis was performed in solution with acidic pH.

Li et al. reported the synthesis of single-crystal Au nanoprisms with triangular or hexagonal shape, 30-40 nm planar dimensions, and 6-10 nm thickness from solution of HAuCl4 and PVP in ethylene glycol solution [9]. Ethylene glycol, the surfactant poly(vinylpyrrolidone), and ultrasonic irradiation play important roles in the formation of Au nanoprisms.

Single-crystalline gold nanobelts have been prepared sonochemically from aqueous solution of HAuCl4 in the presence of α-D-glucose, a biological directing agent, under ambient conditions (Figure 2).

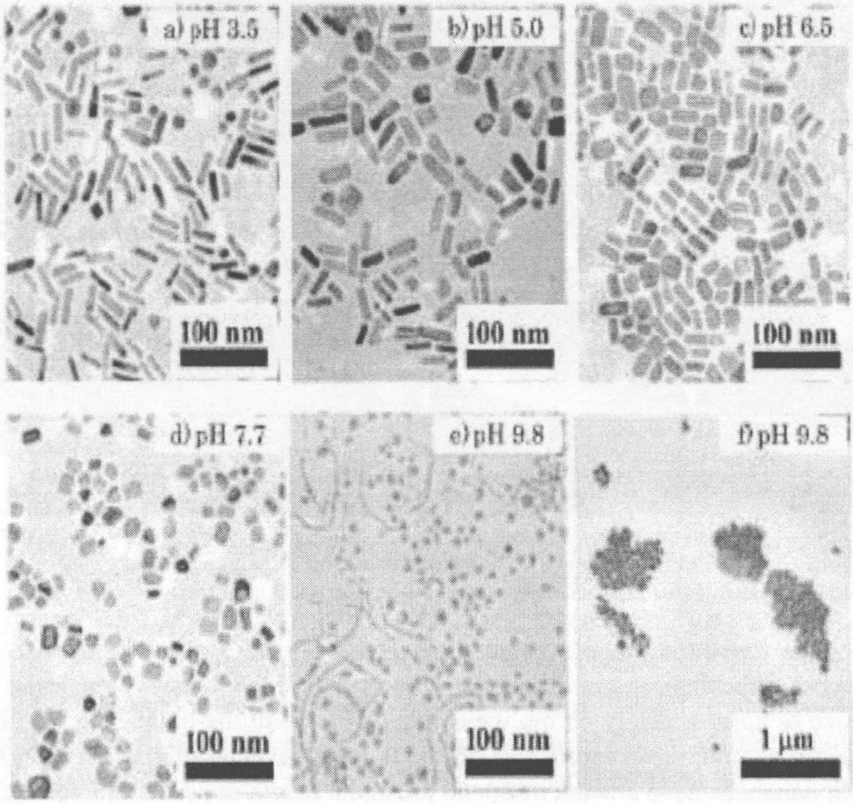

Figure 1. TEM images of gold nanorods and nanoparticles formed in different pH solutions of (a) pH 3.5, (b) pH 5.0, (c) pH 6.5, (d) pH 7.7, and (e) pH 9.8 after 180 min irradiation under argon. (f) TEM image of gold nanoparticles formed in pH 9.8 without ultrasonic irradiation.

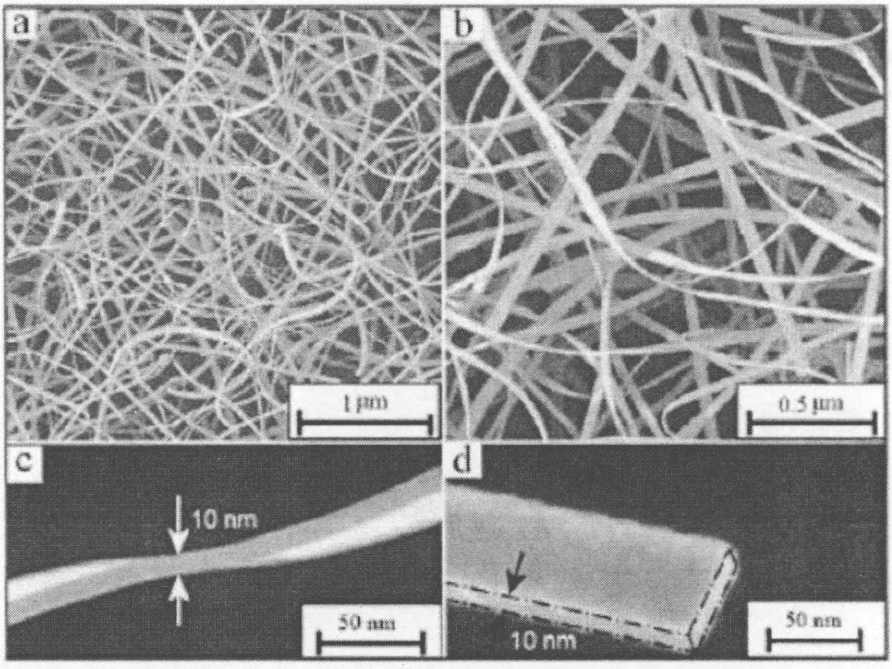

Figure 2. a,b) SEM images and c,d) high-magnification SEM images ofas-synthesized gold nanobelts; [$HAuCl_4$]=50 $mgmL^{-1}$, [α-D-glucose]= 0.2 m, ultrasound time=1 h.

The formation of gold nanobelts depends on the concentration of α-D-glucose. When its concentration was as low as 0.05 M, only gold particles with a size of approximately 40 nm were obtained [10]. In the dilute solution, the glucose can not provide effective coverage or passivation of gold facets. The gold nanobelts have a width of 30–50 nm and a length of several micrometers withhighly flexibility. Nanobelts have thickness of approximately 10 nm. Authors also showed that only spherical particles with a diameter of approximately 30 nm were obtained in the presence of β-cyclodextrin. It was mentioned that ultrasound irradiation can enhance the entanglement and rearrangement of the α-D-glucose molecules on gold crystals.

Park et al. showed the effects of concentration of stabilizer (sodium dodecylsulfate: SDS) and ultrasonic irradiation power on the formation of gold nanoparticles (Au-NPs) [11]. The multiple shapes and size distribution of Au-NPs are observed by different ratio of Au (III) ion/SDS and ultrasonic irradiation power.

A sonochemical method in preparation of gold nanoparticles capped by thiol-functionalized ionic liquid (TFIL) in the presence of hydrogen peroxide

as a reducing agent reported by Jin et al. [12]. It was demonstrated that the molar ratio of gold atom in chloroauric acid to thiol group in TFIL (Au/S) has great effects on the particles size and distribution of gold nanoparticles. Small gold nanoparticles size of 2.7±0.3 nm can be synthesized when ultrasound irradiation applied to a solution with the molar ratio of Au/S = 1:2 for 12 h.

2.2. PALLADIUM

Nemamcha et al reported the sonochemical synthesis of stable palladium nanoparticles by ultrasonic irradiation of palladium (II) nitrate solution in ethylene glycol and in the presence of poly(vinylpyrrolidone) (PVP) for 180 min [13].During theultrasonic irradiation of the palladium (II) nitrate mixture, the color of the solutions turned from the initial pale yellow to a dark brown. The following mechanism was proposed:

$$H_2O \xrightarrow{))))} OH^{\bullet} + H^{\bullet} \quad (7)$$

$$HOCH_2CH_2OH + OH^{\bullet}(OH^{\bullet}) \rightarrow HOCH_2C^{\bullet}HOH + H_2O(H_2) \quad (8)$$

$$nPd(II) + 2nHOCH_2C^{\bullet}HOH \rightarrow nPd(0) + 2nHOCH_2CHO + nH^{+} \quad (9)$$

The coordination of the PVP carbonyl group to the palladium atoms causes to the stabilization of the Pd nanoparticles in ethylene glycol. It has been shown by TEM that the increase of the Pd (II)/PVP molar ratio from 0.13 ×10-3 to 0.53 ×10-3 decreases the number of palladium nanoparticles with a slight increase in particle size. For the highest Pd (II)/PVP value, 0.53 × 10-3, the reduction reaction leads to the unexpected smallest aggregated nanoparticles.

2. 3. TELLURIUM

Crystalline tellurium nanorods and nanorod branched structures are successfully prepared at room temperature via an ultrasonic-induced process in alkaline aqueous solution containing tellurium nitrate, D-glucose and polyethylene glycol (PEG-400,CP)for 2 h treatment in an ultrasonic bath [14]. A yellow sol was produced and was kept in darkness for 24 h to allow the

growth of Te nanocrystals. The as-obtained nanorods are single crystalline with [0 0 1] growth orientation, and have 30–60 nm in diameter with 200–300 nm in length. Some branched architectures, consisting of several nanorods, are also found in the products. The formation of the branched structures is suggested to be the result of multi-nuclei growth in monomer colloid.

2.4. TIN

Metallic tin nanorods were synthesized by a sonochemical method employing the polyol process [15]. In the reaction a solution of SnCl2 in ethylene glycol was exposed to high-intense ultrasound irradiation. The crystallized metallic tin nanorods have diameters of 50–100 nm and lengths of up to 3 μm were synthesized. In the absence of the high-intensity ultrasonic irradiation, no reduction of tin ions occurs even at temperatures as high as 500 °C in a closed cell.

2.5. RUTHENIUM

Ruthenium nanoparticles have been prepared by sonochemical reduction of a ruthenium chloride solution in 0.1 M perchloric acid containing propanol and SDS foralmost 13 h [16]. The effects of differentultrasound frequencies in the range 20–1056 kHz were investigated. The Ru particles have diameters between 10 and 20 nm. The rate of Ru (III) reduction by the sonochemical method is very slow. The sonochemical reduction rate has been found to influence by ultrasound frequency. An optimum reduction rate was determined in the frequency range 213–355 kHz.

2.6. GERMANIUM

Wu et al. reported a method based on ultrasonic solution reduction of GeCl4 by metal hydride (LiAlH4 and NaBH4) or alkaline($N_2H_4 \cdot H_2O$) in tetrahydrofuran (THF) and in ambient condition [17]. The germanium nanocrystals have narrow size distribution with average grain sizes ranging from 3 to 10 nm. Octanol was used as capping agent. To prevent the formation

of GeO2 formed in the presence of water, the anhydrous salt is added to form a transparent ionic solution in THF.

2.7. SELENIUM

Single crystalline trigonal selenium (t-Se) nanotubes with diameters of less than 200 nm and nanowires with diameters of 20-50 nm have been synthesized by the reduction of H2SeO3 in different solvents with a sonochemical method [18]. The morphology of the products depends on the reaction conditions including ultrasonic parameters (e.g., frequency, power, and time), aging time, and solvent. Hydrazine hydrate was dissolved in ethylene glycol, water, etc. to form solutions. The solution was added dropwise to the corresponding selenious acid solution. At the same time, ultrasound was preceded to the solution, and the ultrasonic time is 30-60 min. Selenium nanotube and nanowire formation involved several stage:

$$H_2SeO_3 + N_2H_4 \xrightarrow{)))} Spherical(\alpha - Se) \xrightarrow{)))} Spherical-like(t - Se) \xrightarrow{)))} Nanowires(t - Se) \quad (10)$$

2.8. SILVER

Dendritic silver nanostructures were formed by means of ultrasonic irradiation[19] of an aqueous solution of silver nitrate with isopropanol as reducing agent and PEG400 as disperser for 2 h.

The side branches of the dendritic silver are constructed of well crystallized small nanorods (Figure 3). The selected area electron diffraction (SAED) image of dendritic silver nanostructures has single crystal nature with cubic phase and the side branch direction assembles along <011> direction.

The irradiation time, the concentration of Ag+ and the molar ratio of PEG to AgNO3 are parameters can influence the morphology of silver nanostructured. The low molar ratio of PEG400 to AgNO3 (1:4 ~ 1:1) result in the formation of silver dendritic nanostructures but the molar ratio of 10:1 will cause to formation of silver nanoparticles (in the range of 40–100 nm) instead of dendritic nanostructures. Only silver spheroidal nanoparticles were obtained at the beginning of the reaction but silver dendrites were observed with 1 h