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Priority Communication

Synthesis of ruthenium particles by photoreduction in polymer solutions

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ABSTRACT

Colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected ruthenium (Ru) particles have been synthesized by the photoreduction of Ru(III) ionic solutions in the presence of photo-activator such as benzophenone and benzoin. The size and the structure of the synthesized particles have been extensively investigated by UV–vis, transmission electron micrograph (TEM) and extended X-ray absorption fine structure (EXAFS). Metallic Ru particles with an average diameter of 1.3 nm were successfully synthesized in the presence of benzophenone, although mixtures of partly oxidized Ru particles and metallic Ru particles were synthesized in the presence of benzoin. Photoreduction of Ru(III) ionic precursors to Ru atoms was promoted by ketyl radicals, which is more efficiently generated by the photoirradiation of benzophenone than by that of benzoin. The photoirradiation of benzophenone in the Ru(III) ionic solutions is an efficient and convenient method to produce metallic Ru particles in polymer solutions rather than the refluxing and the hydrothermal method of ionic solutions of Ru.

1. Introduction

Colloidal metal particles of the nanometer size have been of wide interest both academically and industrially, because of numerous applications such as electronics, optics, and catalysis [1]. Control of the size and shape of metal particles is significantly important in the practical synthesis of particles since the properties of particles strongly depend on their size and shape. The colloidal dispersions of Ru particles have been prepared by various methods, such as thermal reduction [2,3], reduction with microwave irradiation [4,5], $NaBH_4$ reduction [6], hydrogen reduction [7], and so on. Yan et al. [2] reported that polymer-stabilized Ru particles were prepared by the reduction of $RuCl_3$ at 160–285 °C and their average diameters were controlled in the range of 1.8–7.4 nm with relative standard deviations of less than 0.3 by changing the sort of polyols, the reduction temperature and the amount of protective polymer. Microwave synthesis [4] was also used to prepare polymer-stabilized Ru particles with an average diameter of 1.4 nm in ethylene glycol. Yang et al. [6] prepared alkylamine-stabilized Ru particles (average diameter of 3.5 nm) in toluene using $NaBH_4$ as the reducing agent.

A number of groups have been involved in synthesizing metal particles by using the photochemical reduction method [8,9]. Aqueous metal particles have been previously synthesized photochemically using ketyl radicals [10–13], as photo-activators such as benzoin [10], benzophenone [11] or acetophenone [12], in aqueous solution of polymers, dendrimers, and surfactant micelles. Scaiano et al. [14] have recently reported that silver nanoparticles are synthesized using ketyl radicals generated by the photoirradiation of benzophenone. They found that ketyl radicals, produced in the photoreduction of ketone analogues [15], are excellent reducing agents and efficiently convert Ag^+ to Ag^0 in surfactant micelles. We recently demonstrated that the photochemical reduction of platinum (Pt(IV)) and gold (Au(III)) under the existence of PVP in water and ethanol mixture could produce a colloidal dispersions of Pt and Au particles [16]. However, to the best of our knowledge, there are no reports in the literature on the preparation of the colloidal dispersions of noble metals such as Pd, Rh, Ru, etc., which are useful elements for the catalysis, in the presence of photo-activator by means of the photochemical reduction.

In this paper we present the preparation of metallic Ru particles by photochemical reduction method in the presence of photo-activator and compare the particle size and its structure with those of the particles prepared by the refluxing method [2,3,17] and the thermal reduction method [4,5,18]. Previously the structure of Ru particles produced by the reflux of Ru(III) solution of water and ethanol under normal pressure (0.1 MPa) at 100 °C as well as under high pressure (30 MPa) above 200 °C has been analyzed. According to this analysis, the particles produced at 100 °C were completely metallic and had an average particle diameter of 1.7 nm [17]. The particles produced above 200 °C were metallic and the average particle diameter was around 2.0 nm [18]. In the present study we have successfully synthesized metallic Ru particles using by the photochemical reduction with assistance of photo-activator and the photochemical reduction of Ru(III) ionic solution is found

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to be an efficient and convenient method to produce metallic Ru particles in polymer solutions.

2. Experimental

2.1. Materials

Ruthenium(III) chloride hydrate ($RuCl_3 \cdot nH_2O$, MW = 207.43), benzoin, benzophenone, ethanol (guaranteed reagent, 99.5%), and distilled water were purchased from Nacalai Tesque, and PVP (K-30) was purchased from Tokyo Kasei Kogyo Co., Ltd. The average molecular weight of PVP used here was 40000. Ruthenium powder and anhydrous ruthenium(IV) oxide were purchased from Aldrich and used as reference samples. All the chemicals were used without further purification.

2.2. Preparation and characterization of colloidal dispersions of Ru particles

Colloidal dispersions of Ru particles ([Ru] = 25 mM) were synthesized from a $RuCl_3 \cdot nH_2O$ mixture solution (1/1 v/v) of water and ethanol in the presence of PVP and photo-activator such as benzoin and benzophenone by irradiation with a 500 W super-high-pressure mercury lamp. The concentration of PVP in water/ethanol (1/1) solutions was at [PVP monomeric unit]/[Ru] = 40. Briefly, for the preparation of Ru colloidal particles, 10 mL of a 50 mM ethanol solution of $RuCl_3 \cdot nH_2O$ was added to 10 mL of a 2 M aqueous solution of PVP, and 52 mg of benzoin and 45 mg of benzophenone was added to the mixture solution with the simultaneous ultrasonication in the case of benzoin and benzophenone, respectively. N_2 gas was then bubbled into the solution in a Pyrex glass vessel, and vigorous stirring was carried out during 10–15 min to remove the dissolved O_2. Subsequently, the solution was poured into a quartz cell and photo-irradiated with continuous stirring. The reduced samples prepared with a designated reduction time of up to 9 h were measured by a UV–vis spectrophotometer.

The UV–vis absorption spectra of the colloidal dispersions of Ru particles were measured by a Hitachi U-3010 spectrophotometer to pursue the reduction of Ru(III) ions in the PVP solutions. To adjust the concentration of metal for the UV absorption measurements, 0.2 mL of the obtained samples were diluted in 3 mL of the 1:1 mixture solution of water and ethanol.

TEM of the colloidal dispersions were obtained using a JEM-2000FX instrument operated at 200 kV as the acceleration voltage. The high-resolution carbon-supported copper mesh was used to support the samples of colloidal dispersions. The diameter of each particle was determined from enlarged photographs. The histogram of the particle size distribution and the average diameter were obtained by measuring about 200 particles in arbitrarily chosen areas in the enlarged photograph.

2.3. EXAFS measurements and data analysis

EXAFS measurements at the Ru K-edge for the colloidal dispersions of Ru particles ([Ru] = 25 mM) were performed at room temperature in a transmission mode at Photon Factory, High Energy Accelerator Research Organization in Japan (KEK, PF-AR), using the BL-NW10A station [19]. The details of the EXAFS measurement are described elsewhere [17,18]. Briefly, for the EXAFS measurements, the sample solutions ([Ru] = 25 mM) were prepared from $RuCl_3 \cdot nH_2O$ and mixture solution (1/1 v/v) of water and ethanol with PVP by the same procedure mentioned above. The ionic solutions were poured into quartz cells (optical path length 50 mm) sealed with polyimide film (KAPTON-200H, 50 μm of thickness), and the irradiation of the 500 W super-high-pressure mercury lamp was started after N_2 bubbling. The solutions were continuously stirred and photoirradiated during a designated reduction time. The EXAFS spectra were collected after the designated reduction time. EXAFS spectra were analyzed by REX2000 vers. 2.0.7 program (supplied by Rigaku Co.) [20]. EXAFS analysis was performed as described in detail elsewhere [21]. The spectra were extracted using a cubic spline method and normalized to the edge height. The k^3-weighted EXAFS function was Fourier transformed into r space, and the Fourier transformation range was 30–160 nm^{-1}. The inverse Fourier transformed into k space was then performed. The Fourier filtered EXAFS functions were fitted with empirically-derived phase shift and amplitude functions obtained from the reference samples (Ru–Ru contribution from Ru powder, Ru–Cl contribution from $RuCl_3 \cdot nH_2O$ ethanol solution, and Ru–O contribution from RuO_2 powder). According to the previous reports, the coordination number and bond length of the first peak of Ru–O are 6 and 0.197 nm, respectively [22]. The coordination number and bond length of $RuCl_3$ (powder) are 6 and 0.237 nm [22], and those of $RuCl_3$ (in ethylene glycol solution) are 6 and 0.232 nm [23], respectively.

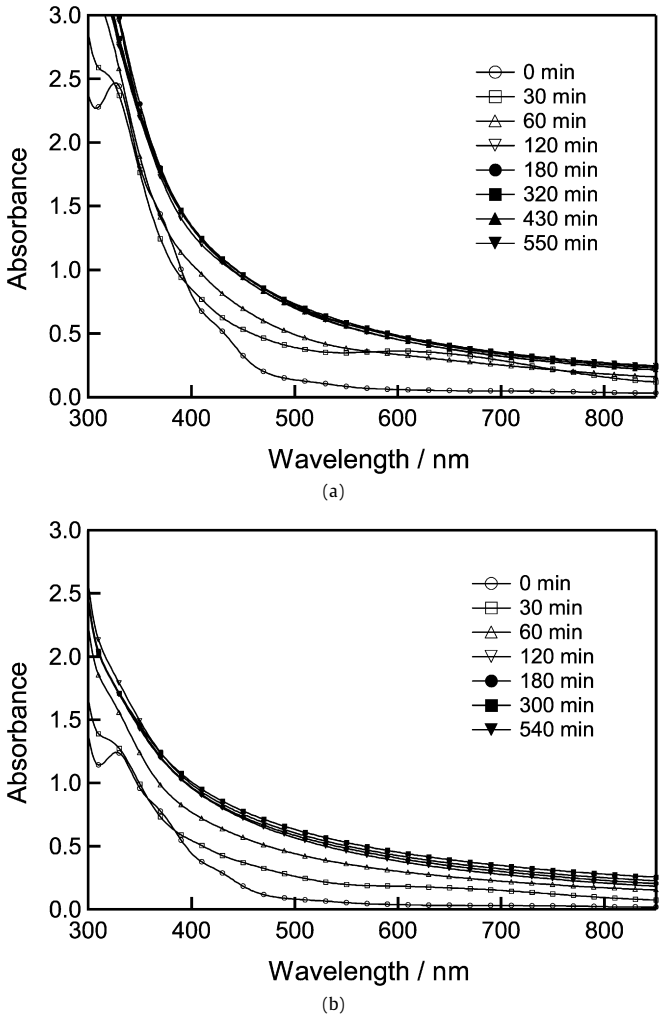

Fig. 1. UV–vis absorption spectra of the colloidal dispersions of Ru particles produced from PVP aqueous ethanol solutions by the photoreduction method in the presence of (a) benzoin and (b) benzophenone as a photo-activator. The time evolution was examined during the photoreduction up to 9 h.

3. Results and discussion

UV–vis measurements confirmed the photochemical reduction of Ru(III) ionic solutions by UV irradiation. Figs. 1a and 1b show