An aqueous-phase synthetic route for ruthenium nanoparticles in cellulose nitrate fibres

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Abstract

Ruthenium nanoparticles were prepared in thin membranes made of cellulose nitrate fibres via a straightforward method of impregnation-reduction of metal ions at ambient conditions. TEM and HRTEM results showed that ruthenium nanoparticles were homogenously dispersed in the cellulose nitrate fibres. XPS studies confirmed the influences of the cellulose nitrate fibres functionality for the formation and stabilization of Ru nanoparticles.

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1. Introduction

Natural cellulose fibres have a porous structure; such morphological features may provide a unique reaction vessel for synthesizing nanoparticles [1]. Composites made of metal nanoparticles immobilized or synthesized *in situ* on supports, such as a polymers [2], oxide surfaces [3], proteins [4], microspheres [5], and carbon nanotubes [6], have recently attracted much interest because of their broad range of potential applications in optical, electrical, catalytic, magnetism, and sensing technologies [7]. Microfibres such as natural cellulose fibres [8], polyaniline fibres [9] and poly(4-vinylpyridine) fibres [10] have also been reported to be utilized as substrates for the adsorption of different metal ions and *in situ* formation of metal nanoparticles. Ruthenium has been known to exhibit a very unique and interesting activity as a catalyst, however, for most of the catalytic applications, it is necessary to prepare small ruthenium nanoparticles supported on a matrix and several strategies have been explored for this purpose [11].

Reduction of Ru salts either in water, using $NaBH_4$ [12], or in alcohols that act both as solvents and reducing agents [13], have been employed for synthesizing Ru nanoparticles. Reduction of $RuCl_3$ in 1,2-propanediol [14] and in a liquid polyol [15], have resulted in good methods for obtaining Ru nanoparticles too. Herein, we report an easy and "green" synthetic route to produce less than 10 nm Ru nanoparticles employing a facile immersion and reduction method and using porous cellulose nitrate fibres as nanoreactors.

2. Experimental

In a typical experiment, cellulose nitrate-fibre membranes (Millipore Co., 150 µm thick and 0.22 µm average diameter pores) were impregnated with ruthenium ions by immersing the membranes in aqueous $RuCl_3$ (0.1 mM) for 1 min, followed by rinsing with ethanol for ca. 30 s. Then, cellulose nitrate membranes were immersed in aqueous $NaBH_4$ (3 mM) for 30 min and subsequently rinsed with water for 1 min, to finally vacuum-dry them overnight at room temperature. SEM observations were performed on a Philips XL30 electron-scanning microscope. HRTEM images were carried out with a JEOL JEM-2010F instrument with a point resolution of 1.9 Å and

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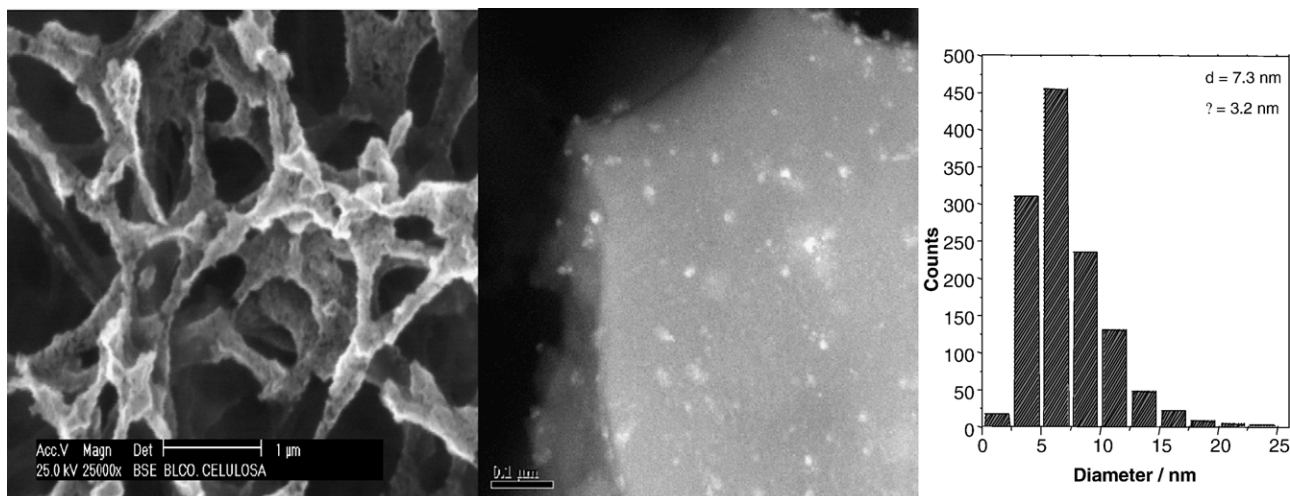*E-mail address:* vsm@uaemex.mx (V. Sánchez-Mendieta).

Fig. 1. SEM image (left) of cellulose nitrate fibres and Ru nanoparticles TEM histogram and Z-contrast image (right) of nanoparticles lower than 20 nm and homogeneously distributed in the cellulose nitrate fibre.

equipped with high-angle annular dark-field or Z-contrast detector. XPS was performed using an UHV system of VG Microtech ESCA2000 Multilab, with an Al K_α X-ray source (1486.60 eV), and CLAM4 MCD analyser. The surface of the samples was etched for 10 s with 3 kV Ar$^+$ at 0.16 μA/mm^2. The XPS spectrum was obtained at 55° of the normal surface in the constant pass energy mode, $E_0 = 50$ eV and 20 eV for survey and high resolution narrow scan, respectively.

3. Results and discussion

Membranes used in this study are composed of cellulose nitrate fibres of approximately 200–300 nm in width, as obtained by SEM as shown in

Fig. 1. Surface of fibres is rough and has pores with diameters lower than 70 nm. These pores allow guest molecules and ions to penetrate into inner spaces, and provide the required chemical conditions to function as nanoreactors for the formation and stabilization of Ru nanoparticles. Ru nanoparticles generated in the cellulose nitrate fibres were obtained in different sizes, ranging from 3 to 20 nm, accordingly to TEM studies. A size distribution histogram for Ru nanoparticles was acquired by measuring 1253 particles. This histogram (Fig. 1) shows a unimodal particle size distribution of the synthesized Ru nanoparticles with average size of 7.3 nm and a standard deviation of 3.2 nm.

In Fig. 1, a Z-contrast image obtained in TEM is also shown. It reveals that Ru nanoparticles are homogeneously distributed throughout the fibres. HRTEM images in Fig. 2 show Ru semi-spherical shape nanoparticles with diameters between 2 and 3 nm. Several crystalline
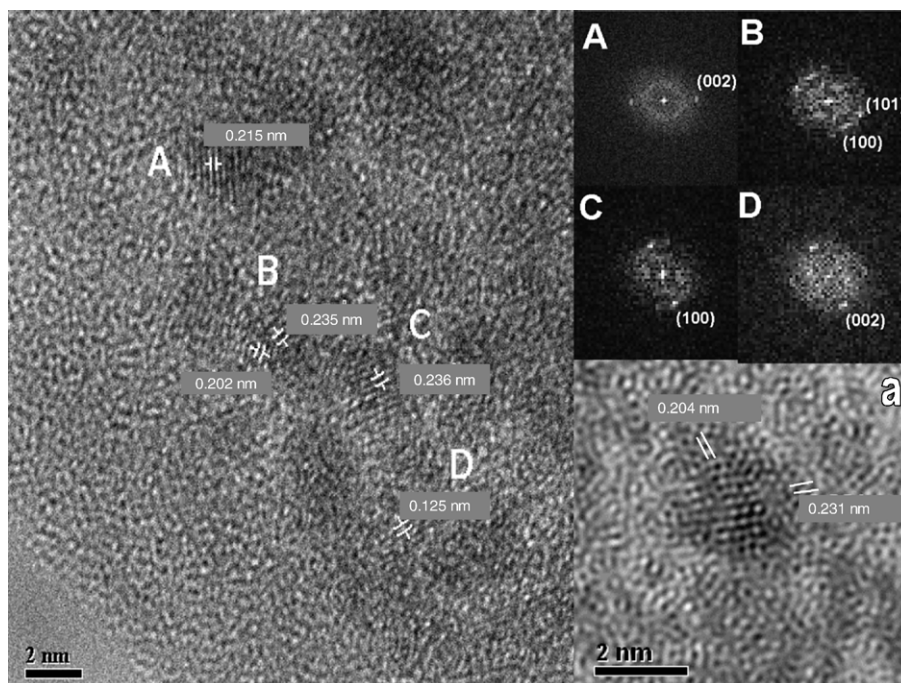

Fig. 2. HRTEM image of less than 5 nm Ru nanoparticles and their corresponding Fast Fourier transforms (FFT) (left and top right images, respectively). HRTEM image of 2 nm Ru nanoparticles in [010] direction (a, bottom right image).
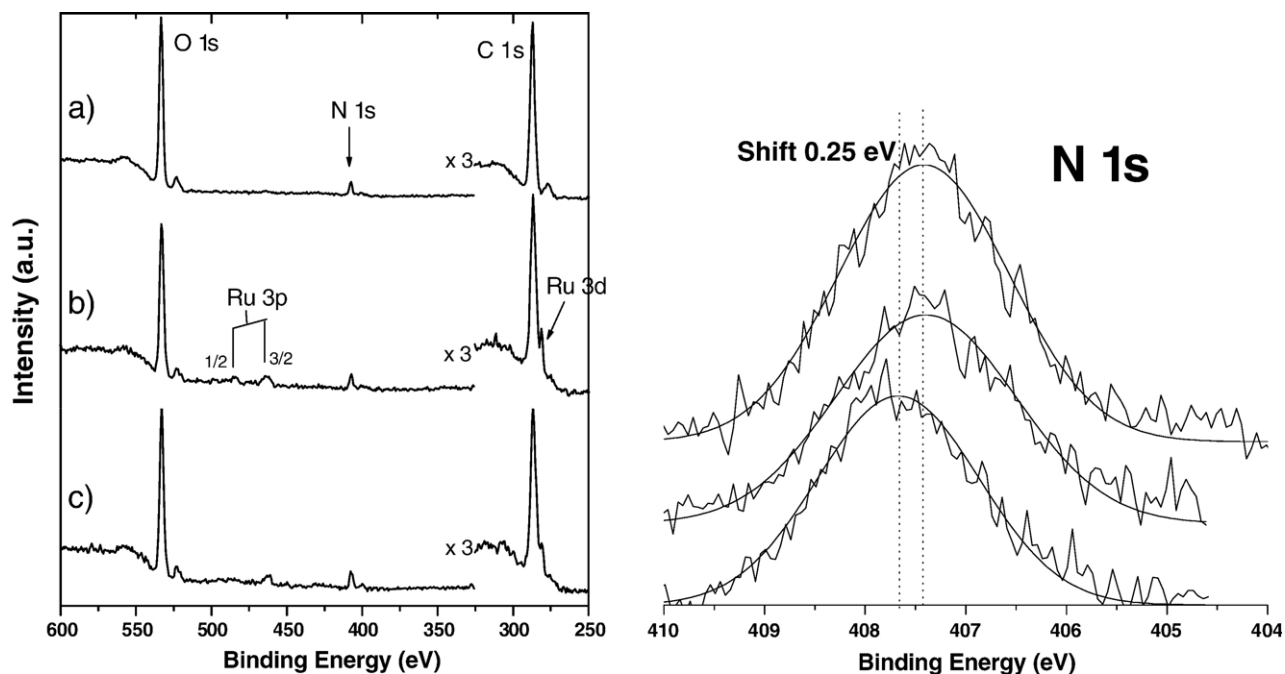
Fig. 3. XPS survey scans of cellulose nitrate fibres membrane before (a) and after (b and c) formation of Ru nanoparticles (left figure). N 1s XPS spectra of cellulose nitrate fibres membrane before (bottom) and after (top and medium) formation of Ru nanoparticles (right figure).
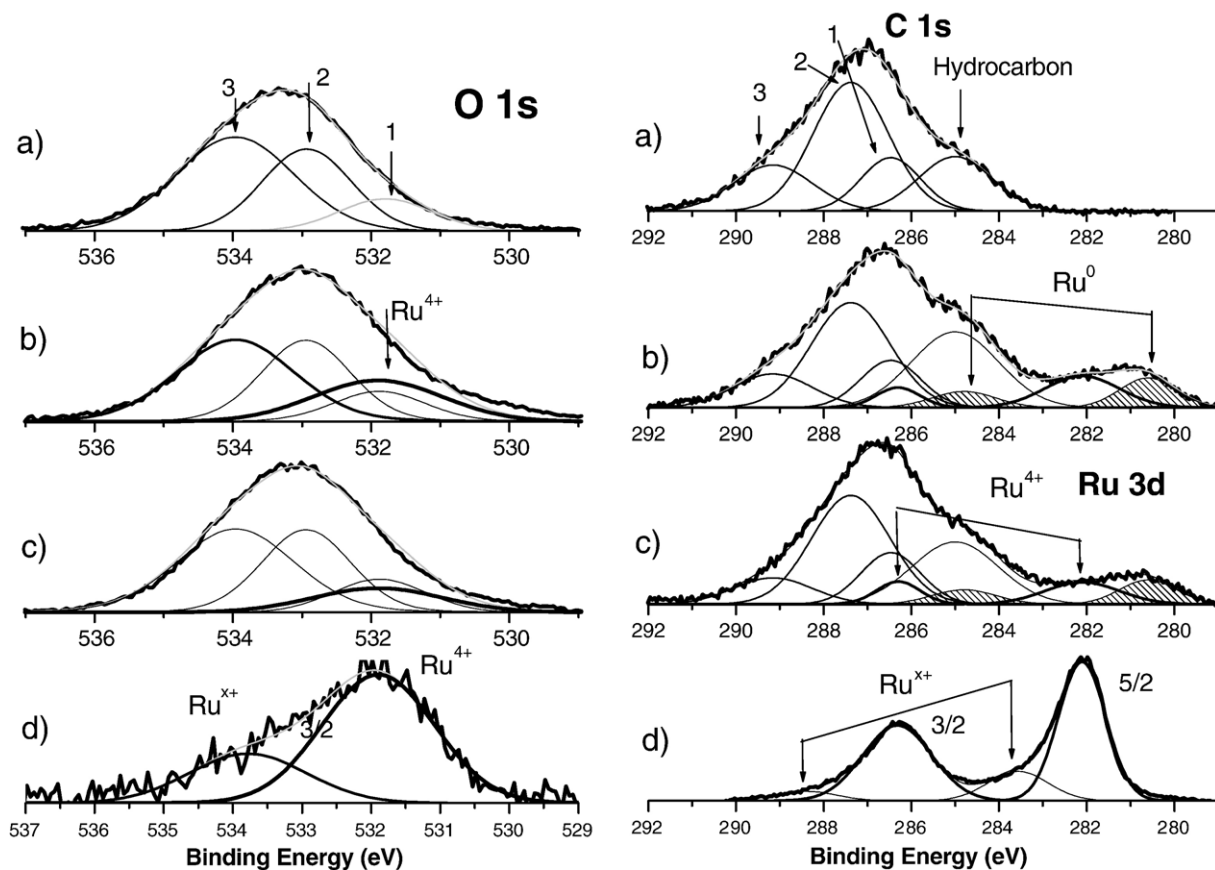

Fig. 4. O 1s XPS spectra of the cellulose nitrate fibres before (a and c) and after formation of Ru nanoparticles (b and d). C 1s, Ru 3d XPS spectra of the cellulose nitrate fibres before (a) and after (b, c, d) formation of Ru nanoparticles.

planes are distinguishable and the interplanar distances were measured, as pointed out in Fig. 2. The interplanar distances shown in the micrograph were measured from the Fast Fourier Transform (FFT) of these nanoparticules (Fig. 2, top right image), where the corresponding crystalline planes are specified. The interplanar distances measured: 0.202 nm, 0.215 nm and 0.235 nm, correspond to planes: (101), (002) and (100) of metallic Ru (hcp) phase, respectively [14]. Coalescence between particles was not observed. A typical HRTEM image of a 2 nm Ru nanoparticle is also shown in Fig. 2a. The particle is oriented in [010] direction with interplanar distance $d1 = 0.204$ nm, $d2 = 0.231$ nm.

Ru nanoparticles/cellulose nitrate fibres composite, RuO_2 and cellulose nitrate (before formation of Ru nanoparticles) were analyzed as references by XPS. Chemical composition of the Ru nanoparticles/cellulose nitrate fibres composite resulted as follows: C 48.56, O 44.69, N 6.40, and Ru 0.34 at.%. Figs. 3 and 4 show the XPS spectra obtained after Ar^+ etching for 10 s. The C 1 s (binding energy, BE $= 285.00$ eV) was used as reference for binding energy calibration in all samples spectra. Fig. 3 exhibits XPS survey spectra of cellulose fibres without any treatment (spectrum a) and cellulose fibres containing Ru nanoparticles (spectra b and c). Fig. 4 show deconvoluted XPS spectra of C 1s, Ru 3d and O 1s, respectively. For cellulose nitrate, core level C 1s peaks 1, 2 and 3 are centred at 286.47, 287.38 and 289.16 eV, respectively. Ru nanoparticles (Ru^0) peaks correspond to core level Ru $3d_{5/2}$ 280.6 eV and Ru $3d_{3/2}$ 284.80 eV.

Ruthenium oxide peaks were obtained as follows: Ru^{4+}, Ru $3d_{5/2}$ 282.10 eV and Ru $3d_{3/2}$ 286.30 eV. RuO_2 is presumably formed by the superficial oxidation of Ru during handling of samples for characterization [15]. Moreover, in the reference material, RuO_x or RuO_2, there are additional peaks in Ru $3d_{5/2}$ at 283.56 eV and Ru $3d_{3/2}$ at 288.39 eV (Fig. 4, d), which can confirm that oxidation of Ru nanoparticles is only superficial. It is worthwhile to mention that the overlapping of the aliphatic C 1s and the Ru $3d_{3/2}$ peaks near 285 eV, brings difficulties to analyse this energy range accurately [15]. In Fig. 4, there are three peaks for O 1s in cellulose nitrate, before formation of Ru nanoparticles (spectra a and c), corresponding to 531.79, 532.93 and 533.97 eV, which is in concordance to oxygen chemical states reported in this polymer [1]. For RuO_2 the O 1s peaks are centred at 531.9 eV and RuO_x at 533.78 eV (Fig. 4, d). After Ru nanoparticles were formed in cellulose nitrate fibres, no appreciable changes were observed for the O 1s peaks in cellulose. The N 1s XPS spectra, conversely, before and after formation of Ru nanoparticles show peaks at 407.67 and 407.42 eV, respectively (Fig. 3, right). This small shift (0.25 eV) in binding energy could be attributed to the participation of the nitrogen atoms of cellulose nitrate in the stabilization of Ru nanocrystallites. Similar chemical shifts to the lower BE side in N 1s XPS spectra have been observed for the interaction of PVP with Pt nanoparticles [16]. Hence, porous cellulose nitrate fibres, where the oxygen atoms belonging to the ether and hydroxyl moieties and the nitrogen and oxygen in the nitrate groups, not only interrelate with the metal ions through ion-dipole bonds but once the reduction reaction occurs, they also stabilize the Ru nanoparticles throughout the interactions between the most superficial metal orbitals and the electron-donor atoms of the cellulose nitrate template.

4. Conclusion

We have demonstrated that using an aqueous, room temperature, ion impregnation–reduction synthetic route; formation of Ru nanoparticles can be carried out in cellulose nitrate fibres thin membranes. TEM, HRTEM and XPS studies confirmed the presence of Ru nanoparticles in the fibres, which have an average size of 7.3 nm and standard deviation of 3.2 nm.

References

[1] J. He, T. Kunitake, A. Nakao, Chem. Mater. 15 (2003) 4401.
[2] P.C. Morais, R.B. Acevedo, D. Rabelo, E.C.D. Lima, Chem. Mater. 15 (2003) 2485.
[3] J. He, I. Ichinose, T. Kunitake, A. Nakao, Y. Shirashi, N. Toshima, J. Am. Chem. Soc. 125 (2003) 11034.
[4] M. Okuda, Y. Kobayashi, K. Susuki, K. Sonoda, T. Kondoh, A. Wagawa, A. Kondo, H. Yoshimura, Nano Lett. 5 (2005) 991.
[5] J. Zhang, N. Coombs, E. Kumacheva, Y. Lin, E.H. Sargent, Adv. Mater. 14 (2002) 1756.
[6] R. Zanella, E.V. Bsiuk, P. Santiago, V.A. Basiuk, E. Mireles, I. Puente-Lee, J.M. Saniger, J. Phys. Chem., B 109 (2005) 16290.
[7] A. Sarkar, S. Kapoor, G. Yashwant, H.G. Salunke, T. Mukherjee, J. Phys. Chem., B 109 (2005) 7203.
[8] J. He, T. Kunitake, T. Watanabe, Chem. Comm. (2005) 795.
[9] S.K. Pillalmarri, F.D. Blum, A.T. Tokuhiro, M.F. Bertino, Chem. Mater. 17 (2005) 5941.
[10] H. Dong, E. Fey, A. Grandelman, W.E. Jones Jr., Chem. Mater. 18 (2006) 2008.
[11] H. Li, R. Wang, Q. Hong, L. Chen, Z. Zhong, Y. Koltypin, J. Calderon-Moreno, A. Gedanken, Langmuir 20 (2004) 8352.
[12] J. Yang, J.Y. Lee, T.C. Deivaraj, H.-P. Too, J. Colloid Interface Sci. 271 (2004) 308.
[13] S. Gao, J. Zhang, Y.-F. Zhu, C.-M. Che, N. J. Chem. 24 (2000) 739.
[14] G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lakaze, F. Fièvet-Vincent, F. Fièvet, Chem. Mater. 15 (2003) 486.
[15] N. Chakroune, G. Viau, S. Ammar, L. Poul, D. Veautier, M.M. Chehimi, C. Mangeney, F. Villain, F. Fièvet, Langmuir 21 (2005) 6788.
[16] L. Qiu, F. Liu, L. Zhao, W. Y., J. Yao, Langmuir 22 (2006) 4480.