A convenient solvothermal route to ruthenium nanoparticles

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A convenient solvothermal route has been developed to prepare ruthenium nanoparticles, which have been characterized by X-ray diffraction, transmission electron microscopy and other techniques.

Nanoscale metal particles have been attracting much attention for their intriguing chemical and physical properties and potential applications.[1] A great effort has been directed towards preparing metal nanoparticles by many methods such as chemical reduction,[2] UV photolysis,[3] thermal decomposition,[4] metal vapor deposition,[5] electrochemical reduction,[6] sonochemical decomposition,[7] microwave irradiation[8] and the recently reported rapid expansion of supercritical fluid solutions (RESS).[9] Ruthenium metal is a useful catalyst.[10] The per-atom catalytic efficiency typically increases as the size of the metal particles decreases,[11] however, the reported methods of preparation often involve sophisticated equipment and rigid experimental conditions.[12] Here we report a simple and direct method of preparing ruthenium nanoparticles by solvothermal synthesis under mild conditions. The obtained ruthenium nanoparticles have been characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and BET surface area measurement.

The preparation was conducted by reaction of a dark-brown solution of $RuCl_3 \cdot xH_2O$ (0.5 g) in 10 ml of anhydrous ethanol or anhydrous methanol in a polyfluoroethylene-lined stainless steel bomb (20 ml capacity) under autogenous pressure. After heating at 175 °C for 24 h, a gray precipitate was filtered off, washed with alcohol and dried under vacuum. The FTIR spectra of the colorless filtrate revealed a band at 1660 cm^{-1}, indicating the oxidation of methanol to formaldehyde [eqn. (1)] or ethanol to acetaldehyde [eqn. (2)]. The filtrate was strongly acidic.

$$3\,CH_3OH + 2\,RuCl_3 \rightarrow 3\,CH_2O + 2\,Ru + 6\,HCl \qquad (1)$$

$$3\,C_2H_5OH + 2\,RuCl_3 \rightarrow 3\,CH_3CHO + 2\,Ru + 6\,HCl \qquad (2)$$

It has been reported that high valency Ru ions (VI or IV) can oxidize alcohols to aldehydes.[13] In this work, Ru(III) was directly reduced to Ru(0) in a one-pot reaction. Conclusive evidence of Ru metal formation comes from X-ray powder diffraction data. As shown in Fig. 1, the data for the gray powder can be indexed to *hcp* ruthenium metal. The lattice parameters were calculated to be $a = 2.709 \pm 0.002$ and $c = 4.278 \pm 0.005$ Å, in agreement with those of Ru metal reported in the JCPDS diffraction file.[14] No other lines were observed in the pattern. From the widths of the XRD peaks, the size of the Ru nanoparticles is estimated to be 6.4 nm from the Scherrer equation.[15]

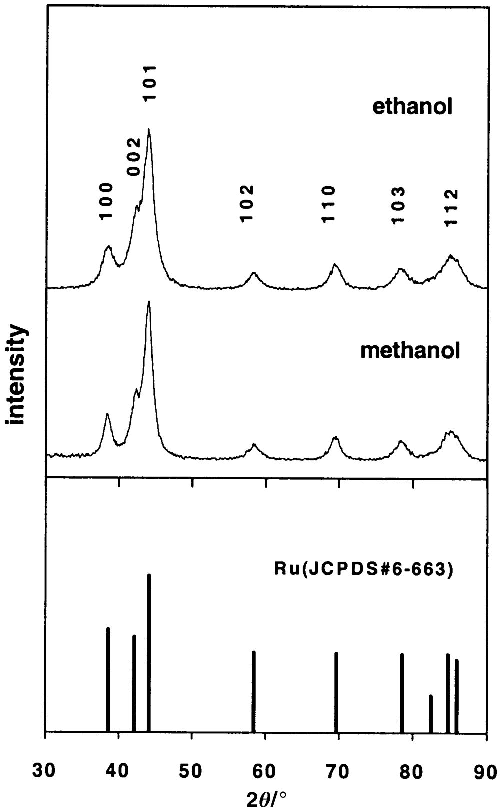

Fig. 1 X-ray powder diffraction pattern of Ru metal particles.

A TEM image of the Ru particles is shown in Fig. 2. It can be seen that the metal particles are agglomerated; some of them seem to be needle-like. The size of individual Ru particles is in the range 2–10 nm. This is a little larger than the product (1–3 nm) obtained by a vapor synthesis techniques.[12d]

A little oxygen was detected by XPS, which may come from absorbed H_2O on the surface of the particles. The binding energy of Ru $3d_{5/2}$ is 280.65 eV, which is slightly larger than that in bulk Ru metal (280.1 eV). This can be attributed to the small metal clusters of Ru.[16]

The surface area of the ruthenium powders was determined by a single-point nitrogen BET measurement but the efficiency of the degassing procedure is unknown, thus this surface area value may be a conservative estimate. The BET surface area of the nanoparticles is 11.4 $m^2\ g^{-1}$ and the average pore size diameter is 29 nm. The size of particles calculated from the data is 42 nm, much larger than that from TEM and XRD; this is due to the aggregation of the nanoparticles.

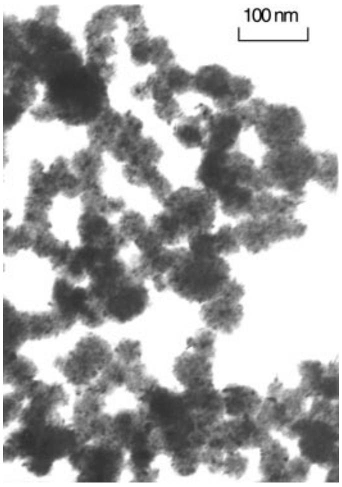

Fig. 2 TEM micrograph of Ru metal particles.

In summary, a convenient solvothermal route has been developed to produce nanoscale ruthenium particles, which may be used as a catalyst or precursor for other Ru-containing functional materials. Since hydrothermal reduction has been used to prepare fine metal powders of nickel and cobalt,[17] it should be possible to use the solvothermal method, by itself or in combination with chemical reduction, to prepare other metal nanoparticals. This work is in progress in our laboratory.

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References

1 (*a*) *Clusters and Colloids*, ed. D. Schmid, VCH Press, New York, 1994; (*b*) *Active Metals*, ed. A. Furstner, VCH, Weinheim and New York, 1996.
2 (*a*) J. Turkevich and G. Kim, *Science*, 1970, **169**, 873; (*b*) T. O. Ely, C. Pan, C. Amiens, B. Chaudret, F. Dassenoy, P. Lecante, M.-J. Casanove, A. Mosset, M. Respaud and J.-M. Broto, *J. Phys. Chem. B*, 2000, **104**, 695; (*c*) J. Schulz, *Chem. Eur. J.*, 2000, **6**, 618; (*d*) S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
3 K. Torigoe and K. Esumi, *Langmuir*, 1993, **9**, 1664.
4 (*a*) J. S. Bradley, E. W. Hill, C. Klein, B. Chaudret and A. Duteil, *Chem. Mater.*, 1993, **5**, 254; (*b*) D. S. Shephard, T. Maschmeyer, G. Sankar, J. M. Thomas, D. Ozkaya, B. F. G. Johnson, R. Raja, R. D. Oldroyd and R. G. Bell, *Chem. Eur. J.*, 1998, **4**, 1214.
5 (*a*) R. S. Bowles, J. J. Kolstad, J. M. Calo and R. P. Andres, *Surf. Sci.*, 1981, **106**, 117; (*b*) K. J. Klabunde, Y. X. Li and B. J. Tan, *Chem. Mater.*, 1991, **3**, 30.
6 M. T. Reetz and W. J. Heibig, *J. Am. Chem. Soc.*, 1994, **116**, 7401.
7 (*a*) K. S. Suslick, S.-B. Choe, A. A. Cichowlas and M. W. Grinstaff, *Nature* (*London*), 1991, **353**, 414; (*b*) K. S. Suslick, M. Fang and T. Hyeon, *J. Am. Chem. Soc.*, 1996, **118**, 11960.
8 W. Tu and H. Liu, *Chem. Mater.*, 2000, **12**, 564.
9 Y.-P. Sun, H. W. Rollins and R. Guduru, *Chem. Mater.*, 1999, **11**, 7.
10 Y. J. Zhu, Y. T. Qian, H. Huang, M. W. Zhang and L. Yang, *J. Mater. Sci. Lett.*, 1996, **15**, 1346.
11 D. L. Gin and J. H. Ding, *Chem. Mater.*, 2000, **12**, 22.
12 (*a*) W. Z. Zhou, J. M. Thomas, D. S. Shephard, B. F. G. Johnson, D. Ozkaya, T. Maschmeyer, R. G. Bell and Q. F. Ge, *Science*, 1998, **280**, 705; (*b*) J. M. Miller, B. Dunn, T. D. Tran and R. W. Pekala, *J. Electrochem. Soc.*, 1997, **144**, L309; (*c*) M. S. Nashner, A. I. Frenkel, D. L. Adler, J. R. Shapley and R. G. Nuzzo, *J. Am. Chem. Soc.*, 1997, **119**, 7760; (*d*) R. W. Devenish, T. Goulding, B. T. Heaton and R. Whyman, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 673.
13 E. L. Lebeau and T. J. Meyer, *Inorg. Chem.*, 1999, **38**, 2174.
14 JCPDS file no. 06-663.
15 H. P. Klig and L. E. Alexander, *X-Ray Diffraction Procedures*, John Wiley and Sons, New York, 1959.
16 G. K. Wertheim, *Z. Phys. B*, *Condens. Matter*, 1987, **66**, 53.
17 Y. D. Li, L. Q. Li, H. W. Liao and H. R. Wang, *J. Mater. Chem.*, 1999, **9**, 2675.