RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name RSCPublishing

ARTICLE

TiO_2 Hollow Spheres with Nanoporous Structures Fabricated by Anodization of Ti Particles

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Takashi Yanagishita, Masahiko Imaizumi, Kondo Toshiaki, and Hideki Masuda*

TiO_2 hollow spheres with nanoporous structures on their surfaces were prepared by the anodization of small Ti particles and the subsequent leaching of the residual metal. The geometrical structures of the TiO_2 porous layers could be controlled by changing the anodization conditions. Au-loaded TiO_2 hollow spheres were also obtained by depositing Au nanoparticles on the surface of the TiO_2 spheres. The obtained porous hollow spheres and metal loaded TiO_2 composite hollow spheres can be applied to various types of functional devices.

Introduction

There has been growing interest in the preparation of hollow spheres of metal oxides with nanoporous structures owing to their potential applications in various field. Among them, the formation of hollow spheres of TiO_2 is one of important challenge in applications of the photocatalysis, solar cells, and gas sensors.1-5) Although a number of methods for the preparation of TiO_2 hollow spheres have been developed, it is difficult to prepare porous hollow spheres with controlled geometrical structures on their surface.6-8) In our previous report, we described the fabrication of alumina hollow spheres with nanoporous structures on their surface by the anodization of small Al particles.9) In this process, the anodization of small close-packed Al particles in an acidic electrolyte yields a porous alumina layer on their surface, and the subsequent leaching of the residual Al using an etchant generates hollow spheres with an anodic porous alumina shell. One important advantage of such a process is that the geometrical structures of porous layers can be controlled by adjusting the anodization conditions. In the present report, we describe the preparation of TiO_2 hollow spheres with porous structures by the anodization of small Ti particles. Au-loaded TiO_2 hollow spheres were also fabricated by the chemical deposition of Au on the surface of the obtained TiO_2 hollow spheres. Due to their high specific surface area and transparency, the Au-loaded TiO_2 hollow spheres can be applied as a base material for surface-enhanced Raman scattering (SERS) measurement, in which the enhancement of the electric field of incident light on the Au nanoparticles can effectively enhance the obtained signals.10-14)

Experimental

For the preparation of TiO_2 porous spheres, Ti particles (average diameter: 92 μm, 99.5% purity) were used as a starting material. Prior to the anodization, the Ti particles were dipped in commercially available chemical etching solution (TCP-80; Mitsubishi Gas Chemical Co.) at 90 ºC for 1 min to remove the air-formed oxide layer on their surface. The Ti particles were anodized by a similar process to that reported previously.9) The Ti particles were packed in a holder, the bottom of which was equipped with a filter membrane with 100 nm pores to enable the circulation of the electrolyte, and then a Ti electrode was set on top of the packed Ti particles under an appropriate pressure to ensure the electrical interconnection between the particles. Pressure was usually applied by a mass of 5 kg/cm^2. The anodization of Ti particles was carried out using a mixture of 0.5 wt% HF and 1 M phosphoric acid solution at a constant voltage of 5 - 20 V.15) After the anodization, the TiO_2/Ti particles were could be separated easily because the particles were just in contact each other even after anodization. To form the hollow spheres, the residual Ti was dissolved in a saturated iodine methanol solution at 50 ºC for 24 h. For the preparation of Au-loaded TiO_2 hollow spheres, a deposition-precipitation method was adopted.16) TiO_2 hollow spheres were dipped in 5 mM $HAuCl_4$ aqueous solution, the pH of which was adjusted to 6 using 0.1 M NaOH solution, at 70 ºC for 5 h. After rinsing the hollow spheres in distilled water, the sample was heat-treated at 300 ºC for 3 h in air to form Au nanoparticles. The obtained sample was observed using a scanning electron microscope (SEM; JEOL JSM 6700F). SERS measurement was carried out using a Raman spectroscopic apparatus (JASCO NRS-2000) equipped with a He-Ne laser (λ= 633 nm) for excitation.

Results and Discussion

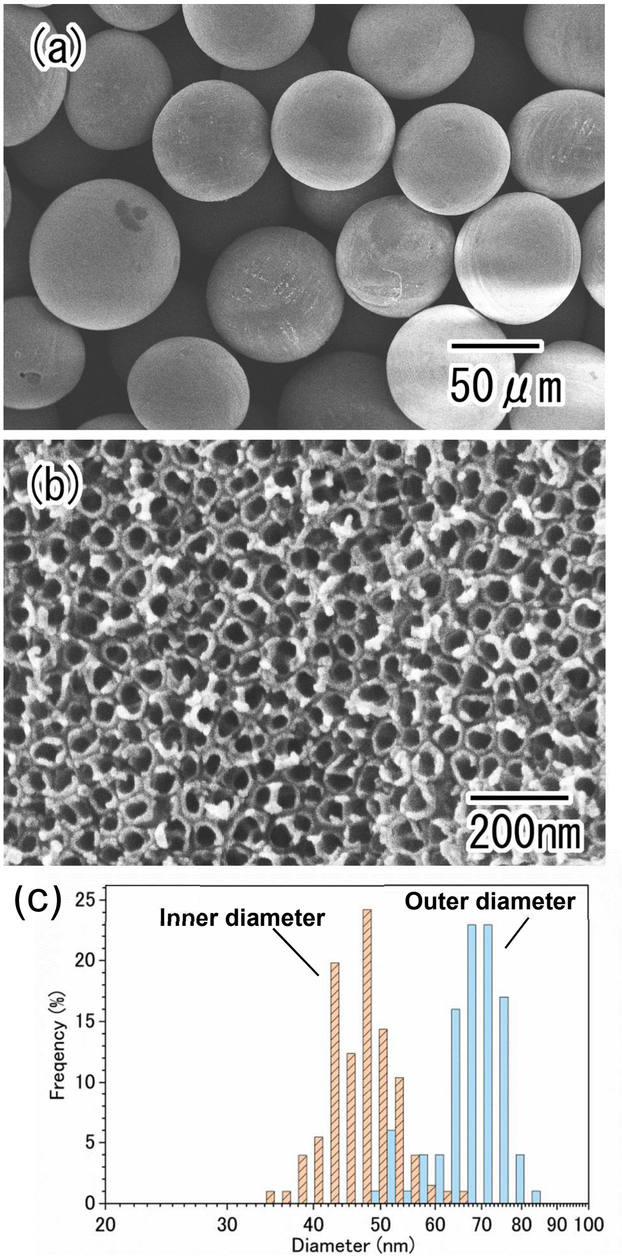


Figure 1. SEM images of Ti particles after anodization: (a) low-magnification, (b) high-magnification views, and (c) distributions of inner diameter and outer diameter of TiO_2 tubes.

Figure 1 shows SEM images of the Ti particles after anodization at a constant voltage of 10 V for 18 h. From the low-magnification image shown in Fig. 1a, the formation of the porous layer on the surface of the Ti particles can be confirmed. From the high-magnification image shown in Fig. 1b, it was observed that nanoporous structures composed of TiO_2 nanotubes were formed on the surface of the Ti particles. Figure 1c shows the distributions of inner diameter and outer diameter of TiO_2 nanotubes. For the size analysis, the diameters of 300 tubes were measured form SEM observation. From the results in Fig. 1c, the average inner and outer diameters of TiO_2 nanotubes were 49 and 67nm, respectively. From this result, average hole period of the TiO_2 porous layer was evaluated to be 67 nm, because the average hole period is equal to the average outer diameter of TiO_2 nanotubes.

Figure 2 shows an optical microscope image and SEM images of the TiO_2 hollow spheres after the leaching of the residual metal. In the close-packed structures of Ti particles, an oxide layer was not formed at the contact part of the Ti particles because this part did not touch to the electrolyte and producing the non-oxidized areas on the particles. The residual Ti could be dissolved selectively using the non-oxidized areas. As shown in the optical microscope image in Fig. 2a, transparent TiO_2 hollow spheres were observed. The spherical structures could be maintained even after the removal of the inner residual metal. The rainbow color of the spheres originated from the interference of the incident light at the shells, reflecting the high refractive index of TiO_2. In the low-magnification SEM image shown in Fig. 2b, micron-size openings, which

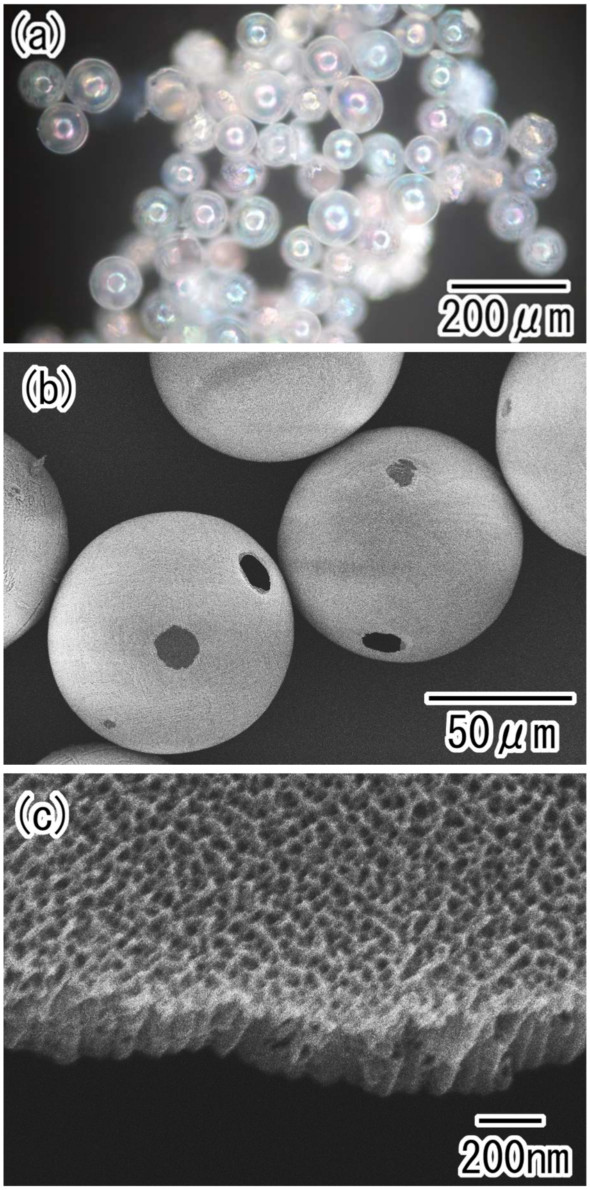


Figure 2. TiO_2 hollow spheres composed of porous TiO_2 shells obtained by leaching of the inner Ti: (a) optical microscope image, (b) low-magnification SEM image, and (c) enlarged SEM image.

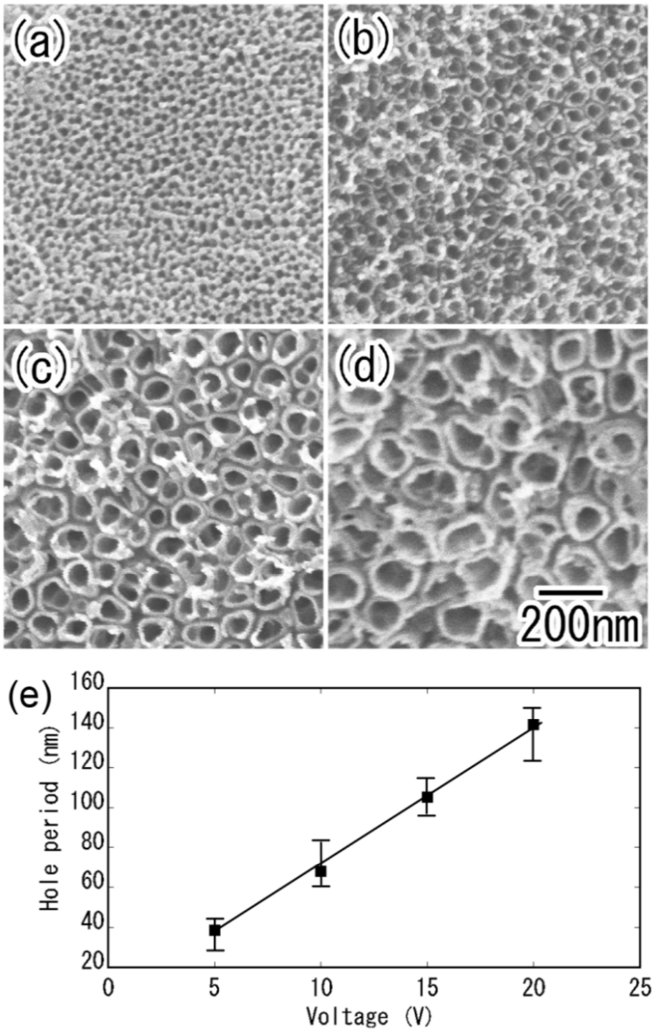


Figure 3. SEM images of TiO_2 hollow spheres fabricated with different anodization voltages: (a) 5, (b) 10, (c) 15, and (d) 20 V. (e) Relationship between hole interval in porous TiO_2 layer and anodization voltage.

corresponded to the non-oxidized parts, were observed on the surface of each hollow sphere. Inner residual Ti could be completely dissolved by etching treatment regardless of the number of micro-size openings. From the high-magnification SEM image shown in Fig. 2c, uniform-size straight holes grew perpendicular to the surface. The thickness of the TiO_2 hollow spheres was ca. 500 nm. From XRD analysis, it was confirmed that the obtained TiO_2 hollow spheres were amorphous.

Figure 3 shows TiO_2 hollow spheres with different hole intervals obtained by varying the anodization voltage between 5 and 20 V. One of advantages of the present process is the controllability of the geometrical structures on the surface of the obtained TiO_2 hollow spheres. From the surface SEM images, it can be observed that the hole interval of the porous structures was dependent on the anodization voltage. Figure 3e summarizes the relationship between the hole interval and the anodization voltage. From this figure, it was confirmed that the hole interval of the porous structures had an almost linear relationship with the anodization voltage.

Figure 4 shows TiO_2 hollow spheres with different thicknesses of the porous layer. The samples were prepared

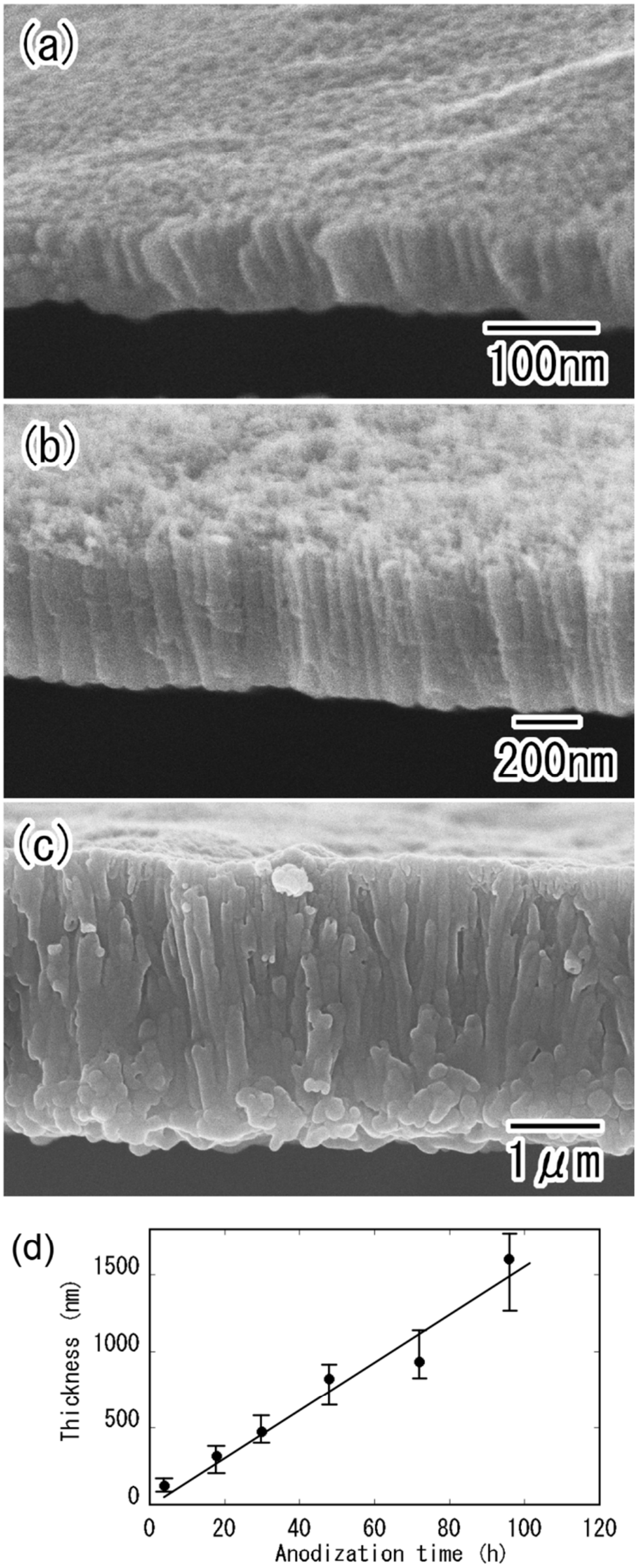


Figure 4. (a)-(c) Cross-sectional SEM images of TiO_2 hollow spheres formed with different anodization times. (d) Relationship between thickness of porous TiO_2 layer in hollow spheres and anodization time.

with anodization times of 4, 30, and 96 h. From the SEM images, it can be confirmed that the thickness of the porous layer increased with the anodization time, showing a good linear relationship (Fig. 4d).

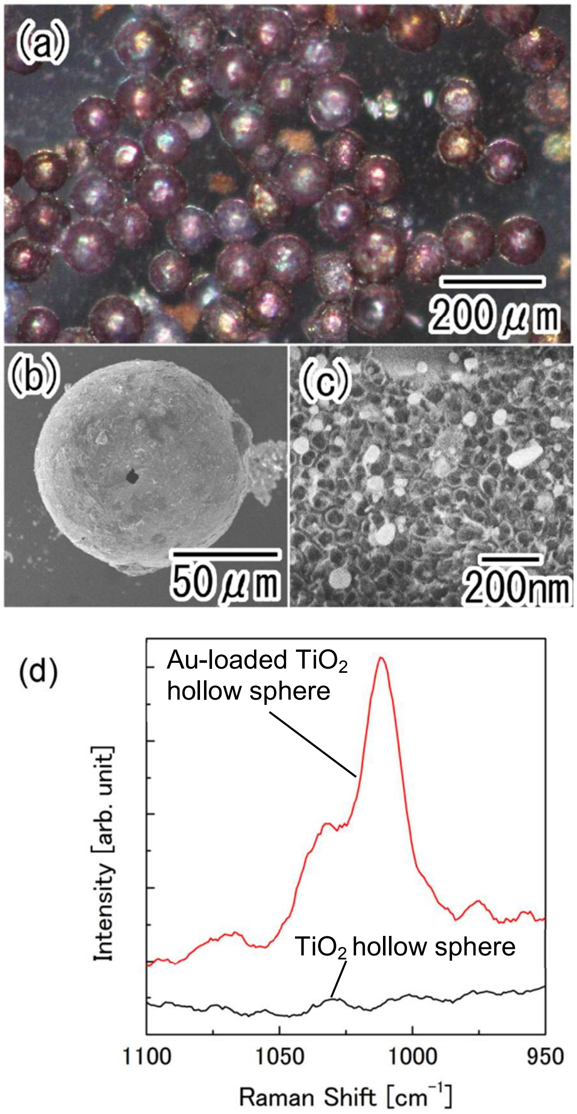


Figure 5. (a) Optical microscope image of Au/TiO_2 composite hollow spheres. (b), (c) SEM images of composite hollow spheres. (d) SERS spectra of pyridine molecules.

Figure 5 shows an optical microscope and SEM images of Au-loaded TiO_2 hollow spheres. From the optical microscope image shown in Fig. 5a, a reddish color was observed in the Au-loaded TiO_2 spheres, which originated from the localized surface plasmon resonance in the Au nanoparticles formed in the holes of the hollow spheres. From the SEM images of the Au-loaded spheres shown in Figs. 5b and 5c, the deposition of Au nanoparticles in the holes of the TiO_2 spheres was confirmed. These Au nanoparticles were formed by the reduction of $HAuCl_4$ to Au through the heat treatment at 300 ºC. The spherical shape of the hollow spheres was maintained even after the heat treatment. From the SEM observation, it was confirmed that the average diameter and relative standard deviation of Au nanoparticles were 78 nm and 45.8%, respectively. Figure 5d shows a typical SERS spectrum obtained using the Au-loaded spheres. The SERS spectra were obtained after dipping the spheres in a solution of pyridine (1.23 M) followed by drying in air. While no peak was observed in the spectrum of the TiO_2 hollow spheres without Au, in the case of the Au-loaded spheres, the two clear peaks were observed at 1014 and 1040 cm^{-1} in the spectrum of the Au-loaded spheres, corresponding to the ring breathing mode and the symmetric triangular ring deformation mode of pyridine. This is because that Raman scattering of pyridine molecule was enhanced by a localized surface plasmon of Au nanoparticles formed on the TiO_2 hollow spheres. This result means that the Au-loaded TiO_2 spheres can be used as a base material for SERS measurement. The assembled Au-loaded TiO_2 spheres will be useful as a highly efficient platform for SERS measurement due to their high specific surface area and high transparency.

Conclusions

TiO_2 hollow spheres composed of nanoporous shells were obtained by the anodization of small Ti particles in a F^--containing electrolyte and the subsequent leaching of the residual Ti. The geometrical structures of the porous layers, i.e., the hole intervals and hole depths, could be controlled by adjusting the anodization conditions. The present process is simple and allows the high-throughput preparation of TiO_2 hollow spheres with controlled nanoporous structures. Au-loaded TiO_2 hollow spheres were also obtained by depositing Au nanoparticles in the holes of TiO_2, and could be applied as a base material for SERS measurement. The TiO_2 porous hollow spheres and metal loaded hollow spheres obtained by the present process are expected to be used in various application fields requiring the controlled geometrical nanostructures with a large surface area.

Notes and references

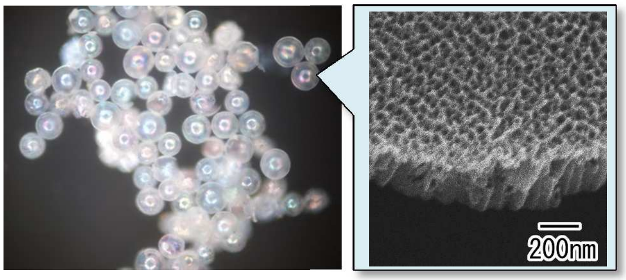
Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minamiosawa, Hachioji, Tokyo 192-0397, Japan
*Corresponding author. TEL: +81-42-677-2843
E-Mail: masuda-hideki@tmu.ac.jp

References

1) B. O'Regan and M. Grätzel, *Nature*, 1991, 353, 737.
2) A. Fujishima, K. Hashimoto, and T. Watanabe, *TiO_2 Photocatalysis*, GKC Inc., Tokyo, 1999.
3) Y. Yeh, T. Tseng, and D. Chang, *J. Am. Ceram. Soc.*, 1990, 73, 1992.
4) A. M. Azad, L. B. Younkman, S. A. Akbar, and M. A. Alim, *J. Am. Ceram. Soc.*, 1994, 77, 481.
5) J. E. Wijinhoven and W. L. Vos, *Science*, 1998, 281, 802.
6) S. Eiden-Assmann, J. Widoniak, and G. Maret, *Chem. Mater.*, 2004, 16, 6.
7) W. H. Suh, A. R. Jang, Y. Suh, and K. S. Suslick, *Adv. Mater.*, 2006, 18, 1832.
8) Y. Zeng, X. Wang, H. Wang, Y. Dong, Y. Ma, and J. Yao, *Chem. Commun.*, 2010, 46, 4312.
9) T. Yanagishita, S. Kimura, K. Nishio and H. Masuda, *Appl. Phys. Express*, 2008, 1, 084001.
10) P. J. Schuck, D. P. Fromm, A. Sundaramurthy, G. S. Kino, and W. E. Moerner, *Phys. Rev. Lett.*, 2005, 94, 017402.
11) H. Wang, C. S. Levin, and N. J. Halas, *J. Am. Chem. Soc.*, 2005, 127, 14992.
12) J. F. li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fun, W. Zhang, Z. Y. Zhou, D. Y. Wu, B. Ren, Z. L.

Wang, and Z. Q. Tian, *Nature*, 2010, 464, 392.
13) T. Kondo, F. Matsumoto, K. Nishio, and H. Masuda, *Chem. Lett.*, 2008, 37, 466.
14) T. Kondo, K. Nishio, and H. Masuda, *Appl. Phys. Express*, 2009, 2, 032001.
15) A. Ghicov, H. Tsuchiya, J. M. Macak, and P. Schmuki, *Electrochem. Commun.*, *2005, 7, 505*.
16) M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, *J. Catal.*, 1989, 115, 301.

Graphical abstract



TiO_2 hollow spheres with nanoporous structures were prepared by anodization of small Ti particles. The geometrical structures of TiO_2 porous layers could be controlled by adjusting the anodization conditions.