Powder Technology 217 (2012) 585–590

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Synthesis and catalytic activity of Au-supported porous TiO_2 nanospheres for CO oxidation

Jun Zhang [a,*], Xianghong Liu [b], Shurong Wang [b], Shihua Wu [b], Bingqiang Cao [a], Shaohua Zheng [a]

[a] *School of Materials Science and Engineering, University of Jinan, Jinan 250022, China*
[b] *Department of Chemistry, Nankai University, Tianjin 300071, China*

ARTICLE INFO

Article history:
Received 15 September 2011
Received in revised form 17 November 2011
Accepted 19 November 2011
Available online 26 November 2011

Keywords:
Gold
Porous TiO_2 nanospheres
Metal–support interaction
CO oxidation

ABSTRACT

Au-supported TiO_2 nanospheres catalyst was prepared by a simple *in-situ* solution reduction method using amino acid (lysine) as the capping agent. The catalyst was characterized by means of X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), N_2 adsorption–desorption, and X-ray photoelectron spectroscopy (XPS). Preliminary CO oxidation tests demonstrate that the Au-supported TiO_2 nanospheres showed high activity for CO conversion even at room temperature (conversion 78% at 20 °C) in comparison to pristine TiO_2. The enhanced catalyst performance is ascribed to the synergic interaction between the porous TiO_2 nanospheres and Au nanoparticles. The facile procedure reported in this work may provide potential for preparing other noble metal-supported catalyst.

1. Introduction

As one of the most important semiconductor metal oxides, titanium dioxide (TiO_2) has received extensive interests for various applications [1–6] including photocatalyst, pigment, solar cells, chemical gas sensor, and especially for low temperature CO oxidation due to its unique ability to supply oxygen species [7–9] and strong metal–oxide interface interaction when used as a support for noble metals [10–14]. Recently porous anatase TiO_2 nanospheres [15] with an open crystalline framework, high surface area and high porosity have attracted particular attention for applications such as environmental water treatment [16] and photocatalyst [17], lithium batteries [18,19] and dye-sensitized solar cells [20] due to their large surface area, highly porous framework and small crystallite size. Such anatase TiO_2 nanospheres may be also promising for low temperature CO oxidation due to their unique structural features, especially when used as a platform to load catalytic noble metals, which has been rarely reported.

On the other hand, Au-based catalysts have been proven to show exceptional catalytic activity for low temperature CO oxidation [21–24]. It is therefore very appealing to combine the high surface area of porous materials and the unique catalytic properties of noble metals to achieve an advanced hybrid catalyst, which should provide enhanced properties for many applications [25–29]. A number of approaches, including cooperative assembly [11], deposition method [28,30,31], in-situ reduction [32], using linker reagents such as silane [33,34] and $SnCl_2$ [35], and amino acid-capped Au colloidal method [36,37], have been established for the synthesis of Au-based catalyst. Despite the success of these methods, the complex synthesis and the use of toxic chemicals may hinder their further applications. Thus a simple one-step approach without using any toxic agents is of great significance for the synthesis and application of nanocomposite catalyst.

In this work, a novel catalyst of Au nanoparticles-supported porous anatase TiO_2 nanospheres was synthesized using a one-pot *in-situ* reduction method. Au nanoparticles are formed on reduction by $NaBH_4$ in the presence of lysine as the capping agent and simultaneously supported on TiO_2 nanospheres (see Fig. 1 for detailed procedure). The approach presented here is convenient, time-saving and user-friendly because no toxic organic agent is used and no pretreatment of the TiO_2 support is needed, hence simplifying the synthetic procedure. Low temperature CO oxidation tests demonstrate that the Au-loaded TiO_2 porous nanospheres show high activity for CO conversion even at room temperature (conversion 78% at 20 °C).

2. Experimental

2.1. Materials

Chemicals including tetrabutoxytitanium (TBT), ethylene glycol (EG), acetone, ethanol, lysine, and $NaBH_4$ were of analytical grade and purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). $HAuCl_4 \cdot 4H_2O$ was obtained from Yingdaxigui Chemical Reagent Company (Tianjin, China). Distilled water was used throughout the experiments.

---

* Corresponding author. Tel.: +86 0531 8973 6292.
E-mail address: zj1025@gmail.com (J. Zhang).

0032-5910/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.powtec.2011.11.027

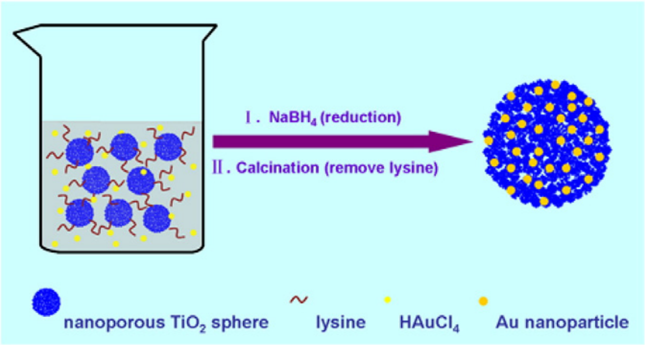

Fig. 1. Schematic preparation of the Au-supported TiO_2 nanospheres.

2.2. Synthesis

Anatase TiO_2 nanospheres were prepared according to the literature method [15,17,19]. In a typical synthesis, 2 mL TBT was added to 50 mL EG under magnetic stirring for 10 h, then the mixture was transferred into a solution containing 2.7 mL water and 170 mL acetone. After further stirring for an hour, the white precipitate (titania glycolate precursor) was centrifuged and washed with water and ethanol several times and dried at 80 °C. The as-obtained titania glycolate precursor was amorphous [15]. To obtain crystalline anatase TiO_2, 0.5 g of the amorphous precursor was dispersed into a mixture of 20 mL ethanol and 20 mL water. The suspension was sealed in a 50 mL Teflon-lined autoclave and heated at 170 °C for 12 h. After reaction, the white product (crystalline TiO_2 spheres) was collected by centrifugation and washed with water and ethanol several times, then dried at 80 °C.

Au-supported anatase TiO_2 nanospheres were synthesized using a one-pot procedure [36–40], where Au nanoparticles were formed in the presence of lysine and simultaneously supported on TiO_2 spheres. In a typical preparation, 0.3 g of as-prepared TiO_2 spheres was dispersed into 40 mL water under stirring, followed by adding 5 mL $HAuCl_4$ (0.01 M) and 5 mL lysine (0.01 M) aqueous solution. After sonication for 10 min, 5 mL fresh $NaBH_4$ (0.1 M) solution was added into the mixture. The reaction system was further sonicated for 10 min and stirred for another 10 min, followed by centrifugation and washing with water and ethanol for several times. The product with a purple color was obtained and dried at 80 °C.

2.3. Characterization

The products were characterized by means of powder X-ray diffraction (XRD, Rigaku D/max-2500, Cu kα, λ = 1.5418 Å), scanning electron microscope (SEM, Shimadzu SS-550, 15 kV), transmission electron microscope (TEM, Philips FEI Tecnai 20ST, 200 kV), X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD spectrometer, Al-Kα X-ray monochromator) and N_2 adsorption–desorption

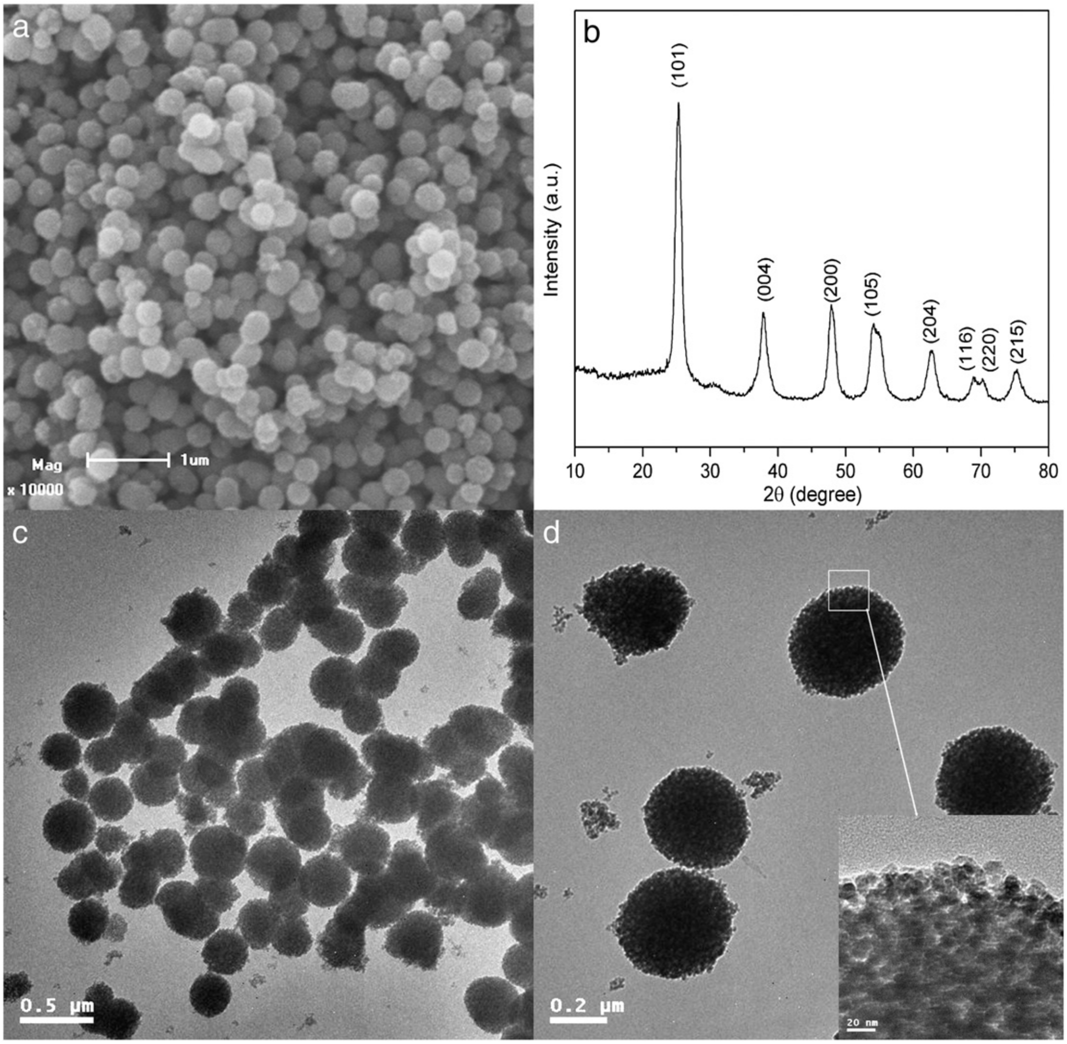

Fig. 2. (a) SEM image, (b) XRD pattern and (c, d) TEM images of the TiO_2 nanospheres (inset is the magnified part in panel d).

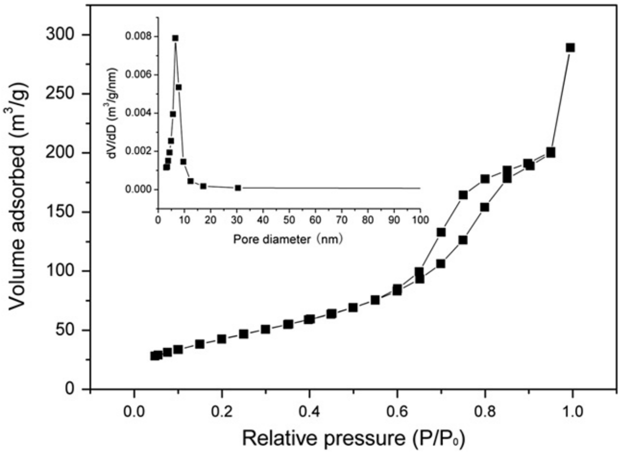

Fig. 3. N_2 adsorption–desorption isotherm and the pore size distribution (inset) of the porous TiO_2 nanospheres.

(Autosorb-1-C). The specific surface area and pore size distribution of the TiO_2 nanospheres were calculated by using the Brunauer–Emmett–Teller (BET) equation and the Barrett–Joyner–Halenda (BJH) method, respectively.

2.4. Catalytic activity for CO oxidation

Prior to test, the catalyst was annealed in air at 300 °C for 0.5 h to remove lysine. The catalytic activity of the Au-supported TiO_2 nanospheres was measured in a fixed-bed stainless-steel tubular reactor using 50 mg catalyst powder. The reaction gas contains 10% CO balanced with air at a total flow rate of 36.3 mL/min. The operation temperature was controlled with a thermocouple placed in the catalyst bed. After 30 min reaction, the effluent gases were analyzed online by a GC-900A gas chromatography with a thermal conductivity detector (TCD). The activity of catalyst was evaluated by the CO conversion.

3. Results and discussion

Amino acids and peptides on account of their non-toxicity and biocompatibility, which can serve as a promising substitute for conventional harsh reagents (e.g., cetyltrimethylammonium bromide and alkyl thiol) and organic solvents (e.g., toluene) [41], have been frequently employed to prepare advanced nanomaterials [38–44]. Our previous work has demonstrated that [39,40,45,46] lysine can be used to assemble noble metals onto α-Fe_2O_3 particles, one-dimensional and hierarchical ZnO structures to fabricate hybrid nanomaterials. The lysine-capped Au nanoparticles have a small size of 3–8 nm [39,40].

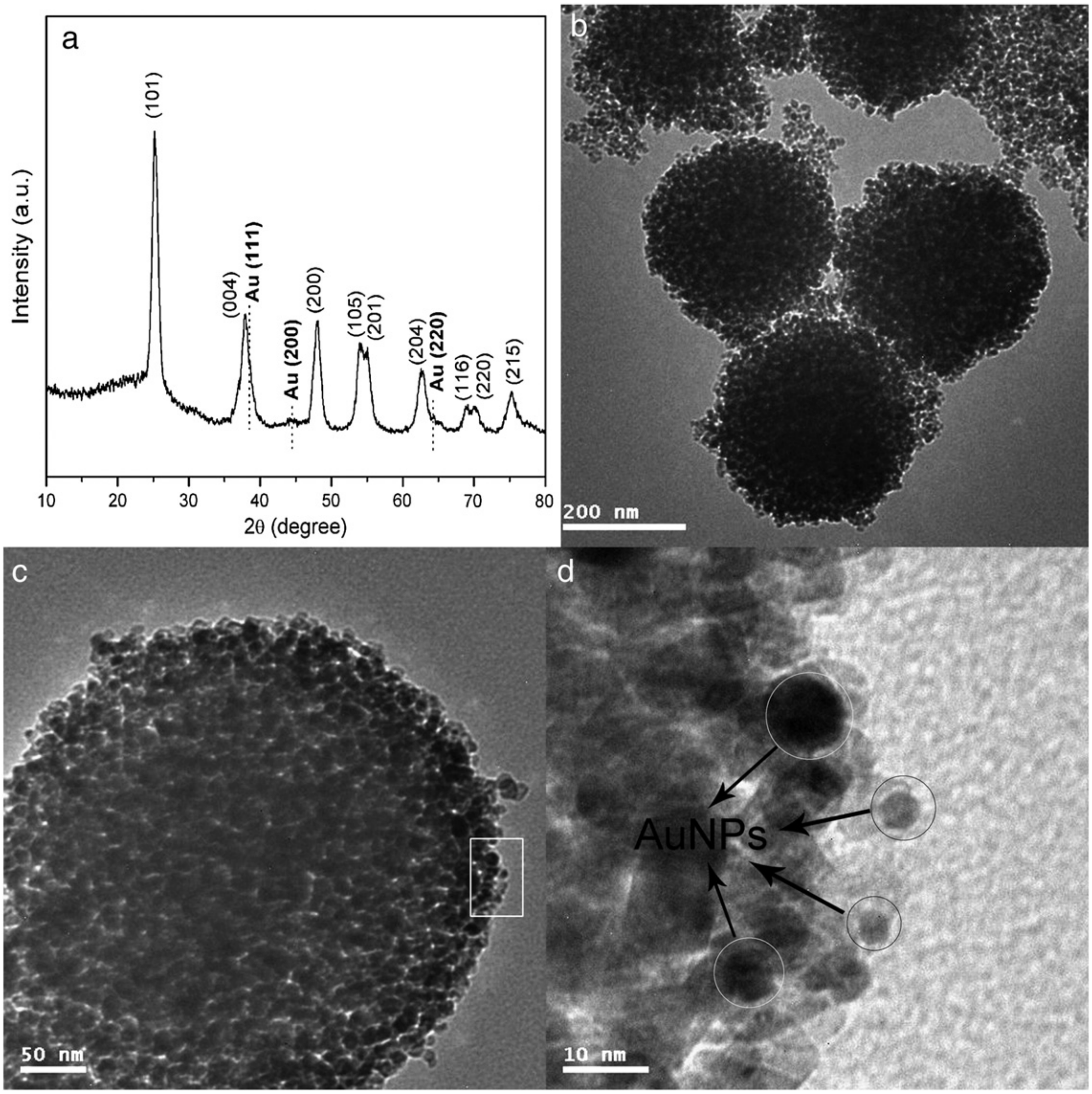

Fig. 4. (a) XRD pattern and (b–d) TEM images of Au-supported TiO_2 nanospheres.

Such lysine-capped Au nanoparticles could be useful for synthesizing Au-based catalyst for CO oxidation [36,37].

Fig. 2a displays the SEM images of the hydrothermally produced TiO_2 nanospheres with a diameter of 200–400 nm. According to the XRD analysis (Fig. 2b), these TiO_2 nanospheres are highly crystalline. The well-resolved diffraction peaks can be well indexed to the anatase structure (JCPDS No. 21-1272), which is a highly active phase for application in catalysis. Details of the anatase TiO_2 nanospheres have been examined by TEM (Fig. 2c and d). It is observed that these spheres have a rough surface and loose structure being composed of numerous nanocrystallites (inset of Fig. 2d). The interspaces between the abundant nanocrystallites endow the spheres with a highly porous structure, which should be very promising for catalyst application. According to the N_2 adsorption–desorption analysis (Fig. 3), the TiO_2 nanospheres have a large Brunauer–Emmett–Teller (BET) surface area of 163.3 m^2/g. The N_2 adsorption–desorption isotherm confirms that the TiO_2 nanospheres have a mesoporous structure. The Barrett–Joyner–Halenda (BJH) pore size distribution (inset of Fig. 3) obtained from the isotherm indicates a pore size in the range of 4–30 nm.

The composition and phase of the Au-supported TiO_2 spheres have been identified by XRD (Fig. 4a). From the XRD pattern, only weak diffraction peaks for Au (200) at 44.6° and (220) at 64.7° can be observed, however, the peak for Au (111) at 38.3° is not visible due to overlapping by TiO_2 (004) peak at 37.9°. The TEM images of the Au-supported TiO_2 spheres are shown in Fig. 4(c–d). However, under low magnifications (Fig. 4b and d), the Au nanoparticles cannot be clearly distinguished out against the TiO_2 matrix; because the large amount of TiO_2 nanocrystals might mask the supported Au nanoparticles. In Fig. 4d of high magnification (magnified area of the square in Fig. 4c), Au nanoparticles with a round contour and size of 3–10 nm are observed to be anchored on TiO_2 nanocrystals.

To further confirm the existence of Au on TiO_2 spheres, XPS analysis was performed. Fig. 5a exhibits the wide XPS spectrum of Au-supported TiO_2 catalyst, which clearly shows the signals for Au 4f and Ti 2p. Fig. 5b and c displays the high-resolution spectra for Au 4f and Ti 2p, respectively. The binding energies at 83.0 and 86.7 eV are attributed to Au $4f_{7/2}$ and Au $4f_{5/2}$ of metallic gold. Interestingly, it is noted that the binding energy of Au $4f_{7/2}$ shows a significant negative shift (ca. 1 eV) compared to 84.0 eV of bulk Au. Such a negative shift has been ascribed to the interaction between Au and support, which is believed to play an important role in the catalyst activity [10–14,36,47]. Considering the porous feature of TiO_2 nanospheres, some Au nanoparticles may form in the interior of the spheres on addition of reducing $NaBH_4$, because $HAuCl_4$ precursor could penetrate into the interspaces among the TiO_2 nanocrystallites. The Au nanoparticles formed therein could thus closely contact the TiO_2 matrix, which may result in the strong metal–support interaction [12,36]. To further prove the hypothesis of the metal–support interaction, we have also performed XPS analysis on pure TiO_2 nanospheres. Fig. 5d displays the XPS spectra of pure TiO_2, revealing two signals at 458.2 eV for Ti $2p_{3/2}$ and 463.8 eV for Ti $2p_{1/2}$. In comparison to the XPS data of Au-supported TiO_2 (Fig. 5c), the Ti $2p_{3/2}$ shows a positive shift after loading of Au nanoparticles, which

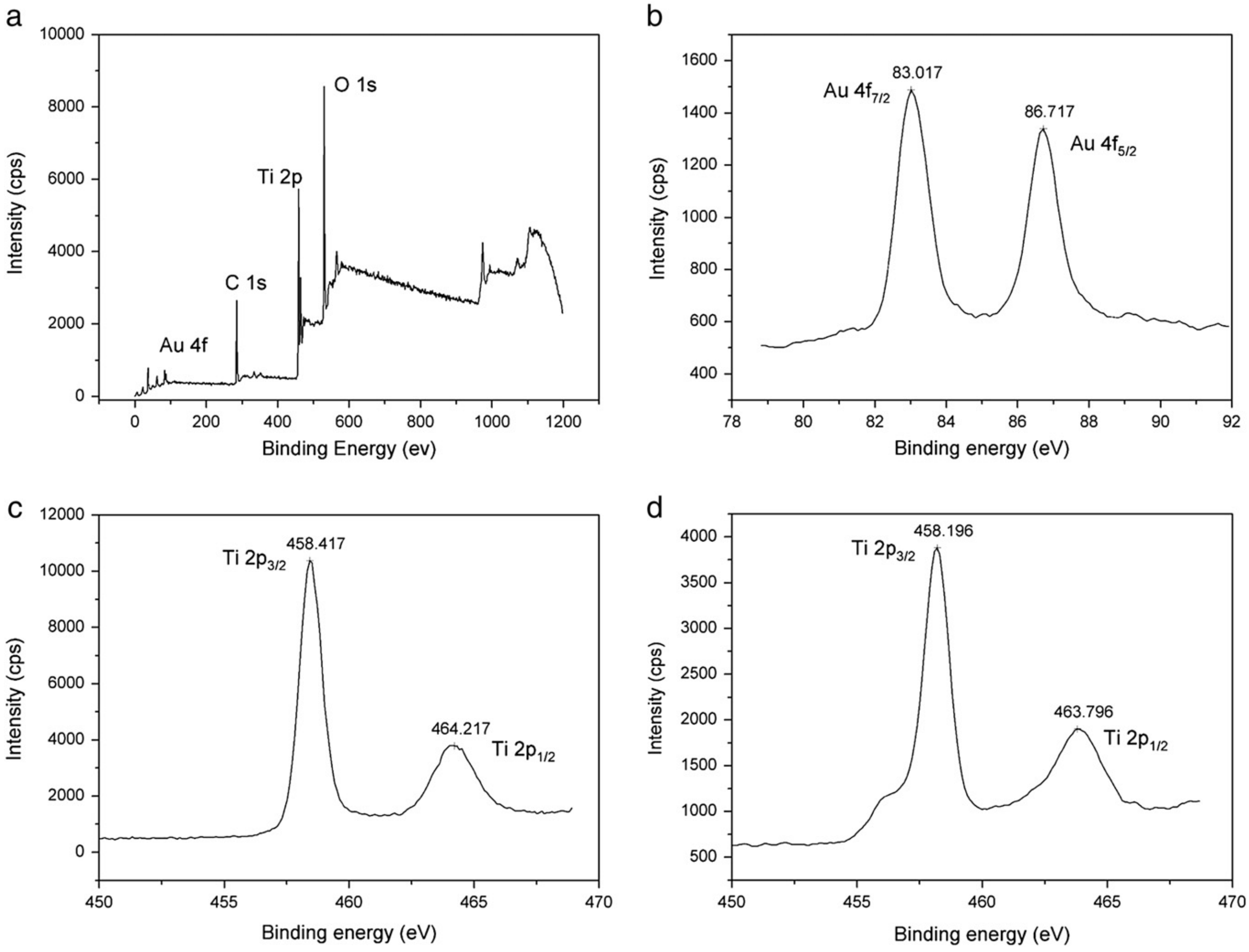

Fig. 5. Wide XPS spectrum (a) and high-resolution XPS spectra for Au 4f (b) and Ti 2p (c) of Au-supported TiO_2 nanospheres, and Ti 2p (d) of pure TiO_2 nanospheres.

provides another proof for the metal–support interaction. According to the XPS test, the mass content of Au nanoparticles in the catalyst is 5.11%.

Au-supported TiO_2 catalyst has been extensively studied for photocatalysis and low temperature CO oxidation. In this work we have preliminarily tested the catalytic activity of the prepared Au-supported TiO_2 nanospheres using CO oxidation as a probe reaction. The catalyst performances for CO oxidation are shown in Fig. 6. It can be seen that the Au-supported TiO_2 (Fig. 6a) exhibits significantly enhanced catalytic activity with a high CO conversion of 78% even at room temperature (20 °C), whereas the pure TiO_2 nanospheres only become active at a temperature above 180 °C (Fig. 6c). The catalytic activity of the Au-supported TiO_2 nanospheres was also re-examined after the first-run of test. The repeated test result is displayed in Fig. 6b, revealing a good repeatability and stability of the Au-supported TiO_2 nanospheres catalyst. Note that the 100% CO conversion is reached at 110 °C for the second-run of test, which is a bit lower than that (120 °C) in the first-run.

It is apparent that the TiO_2 nanospheres show a significantly improved catalytic activity after loading Au nanoparticles. Consequently, the enhanced catalytic performance might be ascribed to the following reasons. First, as demonstrated by TEM and other works, the TiO_2 nanospheres have a porous framework and consist of numerous TiO_2 nanocrystals. The unique structural features should provide a large active surface area and make the inner interspaces in the nanospheres accessible to CO molecules, thus improving the reaction efficiency. A second reason should be the strong metal–support interaction, which is confirmed by our XPS analysis. Many previous works have clearly demonstrated that the metal–support interaction plays an important role in enhancing the catalyst properties.

4. Conclusions

In summary, a one-pot straightforward procedure is developed to immobilize Au nanoparticles onto porous TiO_2 nanospheres to obtain a unique Au-supported TiO_2 nanospheres catalyst, where Au nanoparticles are formed in the presence of a green lysine capping agent and simultaneously supported on TiO_2 support. In the synthesis the TiO_2 nanospheres can be directly used as the support without any pretreatment by linker reagents. The Au-supported TiO_2 nanospheres possess a strong metal–support interaction as proved by the XPS data, which potentially provides the catalyst with a high activity for CO oxidation, with a CO conversion of 78% even at room temperature. It is expected that this facile synthetic strategy can also be used to produce other noble metal-supported nanomaterials for advanced application.

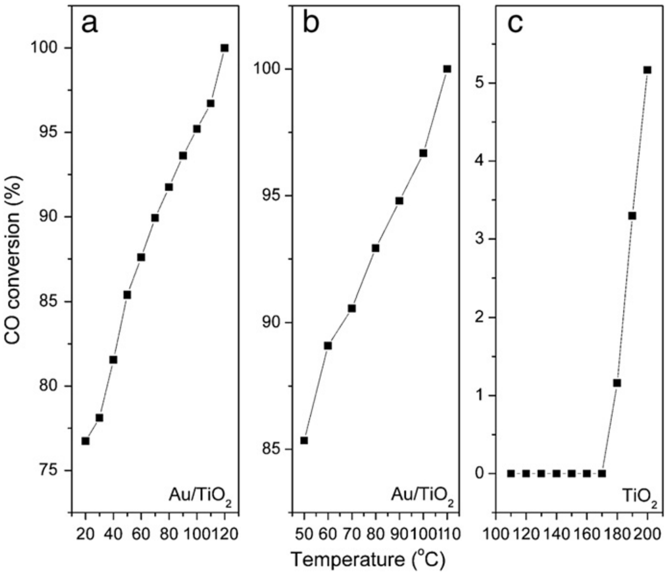

Fig. 6. Catalytic activity test of (a) first-run and (b) second-run of the Au-supported and (c) pure TiO_2 catalyst for CO oxidation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20871071) and the Applied Basic Research Programs of Science and Technology Commission Foundation of Tianjin (Nos. 09JCYBJC03600 and 10JCYBJC03900).

References

[1] U. Diebold, Surface Science Reports 48 (2003) 53–229.
[2] K. Zakrzewska, Thin Solid Films 391 (2001) 229–238.
[3] T.L. Thompson, J.T. Yates, Chemical Reviews 106 (2006) 4428–4453.
[4] X. Chen, S.S. Mao, Chemical Reviews 107 (2007) 2891–2959.
[5] D. Yang, H. Liu, Z. Zheng, Y. Yuan, J. Zhao, E.R. Waclawik, X. Ke, H. Zhu, Journal of the American Chemical Society 131 (2009) 17885–17893.
[6] D. Yang, Z. Zheng, H. Liu, H. Zhu, X. Ke, Y. Xu, D. Wu, Y. Sun, Journal of Physical Chemistry C 112 (2008) 16275–16280.
[7] V. Mendez, V. Caps, S. Daniele, Chemical Communications (2009) 3116–3118.
[8] B.K. Min, C.M. Friend, Chemical Reviews 107 (2007) 2709–2724.
[9] M.C. Kung, R.J. Davis, H.H. Kung, Journal of Physical Chemistry C 111 (2007) 11767–11775.
[10] Q. Fu, T. Wagner, Surface Science Reports 62 (2007) 431–498.
[11] N.F. Zheng, G.D. Stucky, Journal of the American Chemical Society 128 (2006) 14278–14280.
[12] B.H. Wu, H. Zhang, C. Chen, S.C. Lin, N.F. Zheng, Nano Research 2 (2009) 975–983.
[13] M. Haruta, CATTECH 6 (2002) 102–115.
[14] M. Comotti, W.C. Li, B. Spliethoff, F. Schuth, Journal of the American Chemical Society 128 (2006) 917–924.
[15] X.C. Jiang, T. Herricks, Y.N. Xia, Advanced Materials 15 (2003) 1205–1209.
[16] D. Yang, Z. Zheng, Y. Yuan, H. Liu, E.R. Waclawik, X. Ke, M. Xie, H. Zhu, Physical Chemistry Chemical Physics 12 (2009) 1271–1277.
[17] L.S. Zhong, J.S. Hu, L.J. Wan, W.G. Song, Chemical Communications (2008) 1184–1186.
[18] Y.G. Guo, Y.S. Hu, J. Maier, Chemical Communications (2006) 2783–2785.
[19] F.-F. Cao, X.-L. Wu, S. Xin, Y.-G. Guo, L.-J. Wan, Journal of Physical Chemistry C (2010), doi:10.1021/jp103218u.
[20] D.H. Chen, F.Z. Huang, Y.B. Cheng, R.A. Caruso, Advanced Materials 21 (2009) 2206–2211.
[21] M. Haruta, M. Date, Applied Catalysis A: General 222 (2001) 427–437.
[22] A.S.K. Hashmi, G.J. Hutchings, Angewandte Chemie. International Edition 45 (2006) 7896–7936.
[23] R. Sardar, A.M. Funston, P. Mulvaney, R.W. Murray, Langmuir 25 (2009) 13840–13851.
[24] C. Della Pina, E. Falletta, L. Prati, M. Rossi, Chemical Society Reviews 37 (2008) 2077–2095.
[25] X.Y. Liu, A.Q. Wang, X.D. Wang, C.Y. Mou, T. Zhang, Chemical Communications (2008) 3187–3189.
[26] C.M. Yang, M. Kalwei, F. Schuth, K.J. Chao, Applied Catalysis A: General 254 (2003) 289–296.
[27] Z.J. Wang, Y.B. Xie, C.J. Liu, Journal of Physical Chemistry C 112 (2008) 19818–19824.
[28] F.M. Cui, Z.L. Hua, C.Y. Wei, J.Q. Li, Z. Gao, J.L. Shi, Journal of Materials Chemistry 19 (2009) 7632–7637.
[29] C.Y. Ma, Z. Mu, J.J. Li, Y.G. Jin, J. Cheng, G.Q. Lu, Z.P. Hao, S.Z. Qiao, Journal of the American Chemical Society 132 (2010) 2608–2613.
[30] M.A. Elmoula, E. Panaitescu, M. Phan, D. Yin, C. Richter, L.H. Lewis, L. Menon, Journal of Materials Chemistry 19 (2009) 4483–4487.
[31] C. Hubert, A. Denicourt-Nowicki, P. Beaunier, A. Roucoux, Green Chemistry (2010), doi:10.1039/c004079g.
[32] Y. Xie, K.L. Ding, Z.M. Liu, R.T. Tao, Z.Y. Sun, H.Y. Zhang, G.M. An, Journal of the American Chemical Society 131 (2009) 6648–6649.
[33] S.J. Guo, S.J. Dong, E.K. Wang, Journal of Physical Chemistry C 113 (2009) 5485–5492.
[34] D. Wen, S.J. Guo, J.F. Zhai, L. Deng, W. Ren, S.J. Dong, Journal of Physical Chemistry C 113 (2009) 13023–13028.
[35] L.S. Zhong, J.S. Hu, Z.M. Cui, L.J. Wan, W.G. Song, Chemistry of Materials 19 (2007) 4557–4562.
[36] Z.Y. Zhong, J.Y. Lin, S.P. Teh, J. Teo, F.M. Dautzenberg, Advanced Functional Materials 17 (2007) 1402–1408.
[37] Z. Zhong, J. Ho, J. Teo, S. Shen, A. Gedanken, Chemistry of Materials 19 (2007) 4776–4782.
[38] P.R. Selvakannan, S. Mandal, S. Phadtare, R. Pasricha, M. Sastry, Langmuir 19 (2003) 3545–3549.
[39] J. Zhang, X.H. Liu, X.Z. Guo, S.H. Wu, S.R. Wang, Chemistry—A European Journal 16 (2010) 8108–8116.
[40] X.H. Liu, J. Zhang, X.Z. Guo, S.H. Wu, S.R. Wang, Nanoscale 2 (2010) 1178–1184.

[41] J. Wang, X. Sun, Y. Yang, H. Huang, Y. Lee, O. Tan, L. Vayssieres, Nanotechnology 17 (2006) 4995.

[42] M.B. Dickerson, K.H. Sandhage, R.R. Naik, Chemical Reviews 108 (2008) 4935–4978.

[43] C.L. Chen, P.J. Zhang, N.L. Rosi, Journal of the American Chemical Society 130 (2008) 13555–13557.

[44] X.Y. Fu, Y. Wang, L.X. Huang, Y.L. Sha, L.L. Gui, L.H. Lai, Y.Q. Tang, Advanced Materials 15 (2003) 902–906.

[45] X.H. Liu, J. Zhang, L.W. Wang, T.L. Yang, X.Z. Guo, S.H. Wu, S.R. Wang, Journal of Materials Chemistry 21 (2011) 349–356.

[46] J. Zhang, X. Liu, L. Wang, T. Yang, X. Guo, S. Wu, S. Wang, S. Zhang, Journal of Physical Chemistry C 115 (2011) 5352–5357.

[47] Y. Liu, L.F. Chen, J.C. Hu, J.L. Li, R. Richards, Journal of Physical Chemistry C 114 (2010) 1641–1645.