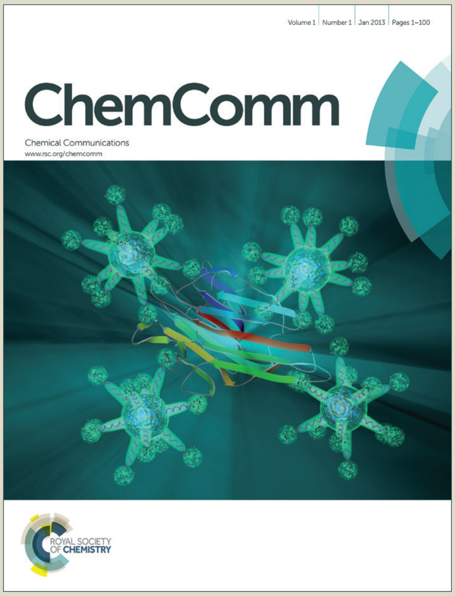
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ChemComm

COMMUNICATION

Fabrication of CeO_2 nanotube supported Pt catalyst encapsulated with silica for high and stable performance

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Chao Wan,[a, b] Dang-guo Cheng,[b,*] Fengqiu Chen,[a, b] and Xiaoli Zhan[b]

This communication describes the fabrication of Pt/CeO_2 nanotube@SiO_2 core–shell catalysts for the application of highly efficient water gas shift reaction, where the initial CO conversion is 30.2% at 250 °C. Pt/CeO_2 nanotube@SiO_2 core–shell catalysts is demonstrated outstanding thermal stability, even after accelerated aging under reaction conditions at 450 °C for 6 h, and the morphology is also unchanged after thermal treatment at 800 °C.

Noble metal nanoparticles (NPs) play great roles in many significant chemical reactions [1-3]. For example, Pt NPs have been extensively applied for water-gas-shift (WGS) reaction[4-6], hydrogenation [7] and electrocatalysis [8]. Usually noble metal NPs is supported on mesoporous materials with high surface areas to get a high dispersion [9]. Some metal oxides such as CeO_2 and ZrO_2 are also used as supports to obtain the proper interactions between catalytic metals and these oxides [10,11]. With this interaction, the performance of catalysts may be improved due to the oxygen and/or electron transfer between them [12-14]. Unfortunately, the supported catalysts with small noble metal particles size are usually unstable. These particles tend to sinter and grow into larger particles under the conditions of catalytic reactions, leading to loss of the superior properties of metal NPs [15]. Much effort has been devoted to overcome the problem of NPs migration and aggregation, which includes [16-18]: (1) exploitation of the strong metal–support interaction, (2) formation of multi-metallic alloys, and (3) addition of co-catalysts. Although these methods may improve the catalytic performance to some extent, they can not completely prevent migration and aggregation of NPs. Therefore, developing the methods to prevent the aggregation, sintering of metal NPs remains a challenging issue for the effective synthesis and utilization of noble metal NPs catalysts.

Recently, some other strategy, which can be named as encapsulation or core-shell structure, is used to prevent the aggregation of metal NPs. That is to encapsulate NPs in a thermally stable inorganic oxide layer (e.g., alumina, carbon, and zirconia). The outer shells can isolate the metal NPs and prevent the possibility of sintering during catalytic reactions at high temperatures. For example, Pt nanoparticles encapsulated in mesoporous CeO_2 were stable against thermal treatment at 700 °C [19]. Some approaches like chemical vapour deposition [20], molecular layer deposition [21] have been employed to synthesize the layer. Although the thickness of layer can be controlled effectively by these methods, otherwise leading to a decrease in catalytic performance, they often need to operate under wild or not moderate condition.

In this communication, we herein report a facile method for the synthesis of a thermally stable catalytic system consisting of Pt nanoparticles. CeO_2 nanotube, synthesized by hydrothermal synthesis method, is used as support due to its tubular morphology and high surface area [22]. And CeO_2 has exhibited superior catalytic activities for a wide variety of reactions [23-25]. The supported Pt catalysts will be encapsulated with a porous SiO_2 shell. This new system is referred to as Pt/CeO_2 nanotube@SiO_2 in our discussion. We used WGS as a probe reaction to explore the catalytic activities of the Pt/CeO_2 nanotube@SiO_2 catalysts. The preparation of Pt/CeO_2 nanotube@SiO_2 catalysts include four major procedures (Figure 1): (i) synthesis of Pt NPs with a high coverage of poly(vinyl pyrrolidone) (PVP); (ii) deposition of the Pt NPs onto a CeO_2 nanotube to generate Pt/CeO_2 nanotube; (iii) coating of SiO_2 with cetyltrimethylammonium bromide (CTAB) as a pore-generating agent; and (iv) calcination in air to generate a porous sheath of SiO_2. By using this approach, the porous SiO_2 coating provides physical and energy barrier to hinder further migration and agglomeration of individual Pt atoms or NPs at high temperature because of its weak interaction with metal oxide, and accordingly, under the protection of a silica shell, these nanoparticles are capable of preserving their initial nanostructures and modifying crystallinity simultaneously. Therefore, Pt/CeO_2 nanotube @SiO_2, with a relatively small particle size, maximize Pt/CeO_2 nanotube interfaces

---

[a] *Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China*
[b] *College of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China.*
** Corresponding author. E-mail address: dgcheng@zju.edu.cn (D.G. Cheng)*
Tel.: +86 571 87953382; Fax: +86 571 87951227

Electronic Supplementary Information (ESI) available: Details of sample preparation, activity tests, characterisation method, and some other results. See DOI: 10.1039/x0xx00000x

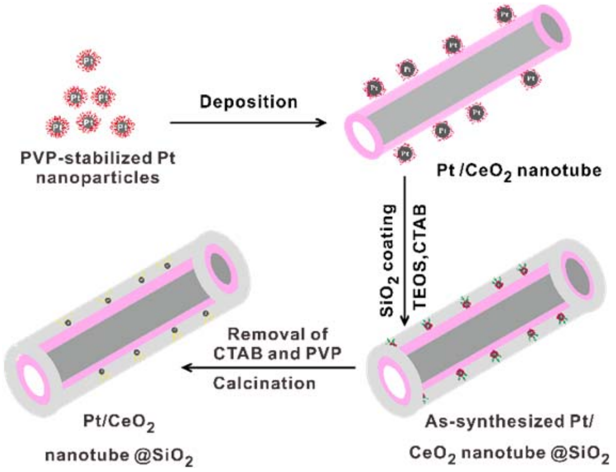


Figure 1. Preparation of the catalytic system based on Pt nanoparticles that are supported on CeO$_2$ nanotube and then covered by porous sheaths of SiO$_2$

and exhibit good stability up to 800 °C in an oxidative atmosphere such as air. In particular, sufficient thermal stability may serve as an excellent model for important high-temperature catalytic reactions.

Poly(vinyl pyrrolidone) (PVP) stabilized Pt NPs were prepared by using the polyol method [26]. TEM and HRTEM images of PVP-capped Pt, Pt/CeO$_2$ nanotube, and Pt/CeO$_2$ nanotube@SiO$_2$ are displayed in Figure 2. The PVP-capped Pt nanoparticles (Figure 2(A), (B)) disperses uniformly with an average particle size of around 3.1 nm, as reported in the literature[26]. In the case of the as-synthesized Pt/ CeO$_2$ nanotube, CeO$_2$ nanotube was immersed in a suspension of the Pt nanoparticles, which was diluted a 15-fold of the as-prepared Pt NPs with ethanol. As displayed in Figure 2(C), the Pt nanoparticles were uniformly dispersed on the surface of each CeO$_2$ nanotube, without significant aggregation. The Pt loading in the Pt/CeO$_2$ nanotube was 0.9 wt %, as determined by inductively coupled plasma mass spectrometry (ICP-MS) measurements. For comparison, some commercial CeO$_2$ (Aladdin, 99.9%) was purchased to prepare Pt/CeO$_2$. In this case, a 15-fold of the as-prepared Pt NPs with ethanol was deposited on CeO$_2$. Figure 2(D) shows TEM image of Pt/CeO$_2$, which indicates that Pt nanoparticles were also uniformly dispersed on the surface of CeO$_2$. The CeO$_2$ or CeO$_2$ nanotube supported Pt NPs was then encapsulated with SiO$_2$ shell by using a modified Stöber method [23], in which CTAB was served as a pore-generating agent. The TEM image in Figure 2(E) clearly demonstrates that an overview of the SiO$_2$-coated samples, revealing good uniformity for the SiO$_2$ layer covered both the CeO$_2$ nanotube and the Pt nanoparticles. The uniform thickness of SiO$_2$ shell was estimated to be about 5.4±0.9 nm. No isolated SiO$_2$ particles in the product were observed in both TEM and HRTEM analyses. XRD patterns (Figure 2(F)) reveal all distinctive peaks are ascribed to diffraction from crystalline CeO$_2$ (JCPDS 34-394) [27]. The peaks located at 2θ = 28.6°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.7°, and 79.1° can be indexed to (111), (200), (220), (311), (222), (400), (331), and (420) crystal planes of cubic fluorite-structured CeO$_2$. No noble metal Pt NPs diffraction peaks are observed in the XRD spectra, possibly because of the high dispersion of Pt NPs with low weight content on the CeO$_2$ nanotube support. Such phenomenon has also been found in previous reports [27,28]. The peak located at 2θ = 24.5° in Figure 2(F)c can be assigned to amorphous SiO$_2$.

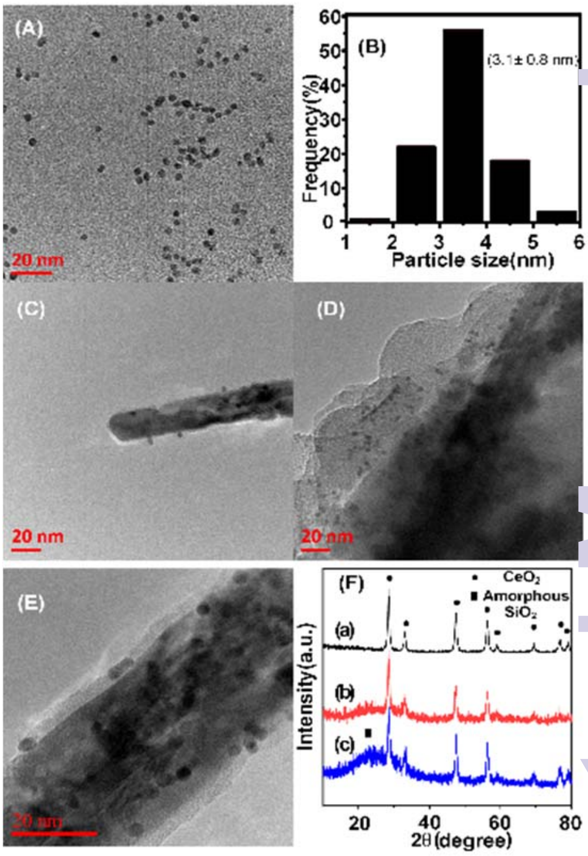


Figure 2. (A) TEM image of PVP-stabilized Pt nanoparticles synthesized using the polyol method; (B) size distribution of the Pt NPs; (C) TEM image of the Pt/CeO$_2$ nanotube sample prepared by immersing the calcined CeO$_2$ nanotube in a suspension of the Pt NPs; (D) TEM image of Pt/CeO$_2$ sample prepared by immersing the calcined CeO$_2$ in a suspension of the Pt NPs; (E) TEM image of SiO$_2$-protected Pt/CeO$_2$ nanotube (Pt/CeO$_2$ nanotube @SiO$_2$); (F) XRD patterns of (a) CeO$_2$ nanotube, (b) Pt/CeO$_2$ nanotube, (c) Pt/CeO$_2$ nanotube @SiO$_2$

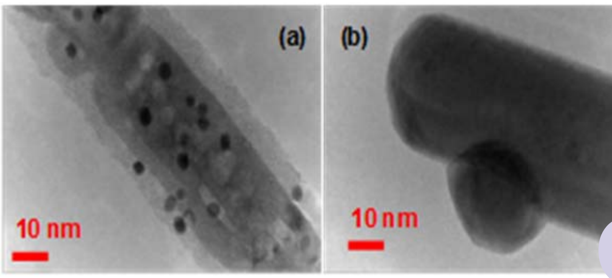


Figure 3. TEM images showing thermal stability of (a) the SiO$_2$-protected Pt/CeO$_2$ nanotube calcined at 800 °C in air for 2 h; (b) the Pt/CeO$_2$ nanotube calcined at 800 °C in air for 2 h

The SiO_2 shell contains CTAB in the as-prepared Pt/CeO_2 nanotube@SiO_2 sample and the Pt nanoparticles were surrounded by PVP. These organic species in the as-prepared Pt/CeO_2 nanotube@SiO_2 was calcined in air at 450 °C to produce porous SiO_2 layer [23,26]. The TEM image and particle size analyses of the calcined Pt/CeO_2 nanotube@SiO_2 demonstrated that the Pt nanoparticles prevented from aggregating and maintained small sizes with an average size of (3.1±0.8) nm, as shown in Figure 3. It was worth noting that the Pt nanoparticles remained a morphological unchanged upon calcination at temperatures up to 800 °C (Figure 3 a). However, in sharp contrast, the Pt NPs were observed to agglomerate in the absence of SiO_2 shell at 800 °C (Figure 3b), the Pt nanoparticles aggregated extensively to form particles larger than 20 nm in size. These results reveal that the porous SiO_2 sheath could offer an effective physical and energy barrier to prevent the migration of Pt atoms and/or NPs during calcination, thus enabling the Pt NPs to get sinter-resistant capacity. Even if Pt/CeO_2 nanotube@SiO_2 was put in a reducing gas environment such as hydrogen, this new catalytic system also exhibits good resistance against sintering (ESI, Figure S1). Moreover, TEM images of Pt/CeO_2@SiO_2 show that SiO_2 layer can also prohibit the aggregation of Pt NPs over CeO_2 at high temperature (ESI, Figure S2).

We investigated the activity of the prepared catalysts by employing the WGS as a model reaction, as shown in Figure 4. One can see that CeO_2 nanotube supported Pt catalysts show an initial CO conversion of 30.2% at 250 °C, which is higher than those of CeO_2 supported, regardless of the absence or presence of SiO_2 layer. The higher activity of Pt/CeO_2 nanotube catalysts is most likely attributed to their high surface area (ESI, Table S1), which increases the contact interface between the metal nanoparticles and transition metal oxide supports. The nano-effect of CeO_2 nanotube may also exist. After 6 h aging treatment at 450 °C, the Pt NPs catalysts without SiO_2 layer exhibit a severe deactivation, no matter what supports. For example, CO conversion on Pt/CeO_2 decreases from 14.7% to 4.8%. TEM image of the spent Pt/CeO_2 nanotube@SiO_2 catalyst reveals that the particle size did not change after the stability test (ESI, Figure S3). This indicates that the SiO_2 encapsulation can enhance the thermal stability of noble metal nanoparticles under the condition of chemical reaction. The calculated turnover frequency (TOF) of the developed Pt/CeO_2 nanotube@SiO_2 is 0.48 s^{-1}, which is much higher than some reported Pt catalysts (ESI, Table S1).

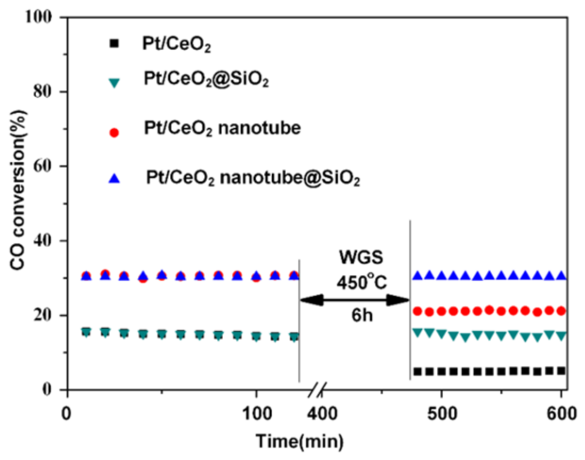


Figure 4. CO oxidation activity during WGS reaction at 250°C. Reaction conditions: catalyst weight, 0.05g, total flow rate, 80 ml/min: 1.0 vol % CO, 3.0 vol % H_2O, diluted in Ar, 1 atm for all catalysts

Moreover, since the Pt NPs was coated by a layer of SiO_2, the mass transfer limitation during the reaction should be considered. In this work, we used CTAB to generate the pore in SiO_2 layer. It was reported that the pore size formed by this method is 4.5 nm[29,30], which is much bigger than that of CO and H_2O (0.376nm and 0.4nm, respectively). To further investigate the effect of the SiO_2 layer on mass transfer, Weisz-Prater criterion for internal diffusion and Mears' criterion for external diffusion were employed [31,32]. The calculated Weisz-Prater criterion is 0.06, which are less than 0.3. This indicates that the reaction is not influenced by internal diffusion. For the external diffusion, it is also can be neglected because the Mears' criterion is estimated to 0.04, which is much lower than 0.15. Therefore, the mass transfer limitation of the layer can be ignored for WGS reaction.

In summary, we have demonstrated a sinter-resistant catalytic system based on CeO_2 nanotube-supported Pt NPs encapsulated by a porous SiO_2 shell. The catalytic activity of core–shell catalysts in WGS reaction was higher than that of conventional catalysts due to the increased interfacial area between Pt nanoparticles and supports. The porous SiO_2 shell could offer a physical and energy barrier to prevent the Pt nanoparticles migration in the surface of CeO_2 nanotube, which leads to the excellent sinter-resist capacity of the catalysts. This work demonstrates that the isolation of metal particles by suitable encapsulation indeed keeps their thermal stability. The synthetic strategy presented herein should be extendible to other catalytic systems with different compositions.

The financial support by the National Natural Science Foundation of China (21176211, 21376209), Zhejiang Provincial Natural Science Foundation (LZ13B060004), Program for Zhejiang Leading Team of S&T Innovation (2013TD07), is gratefully acknowledged.

Notes and references

1 L. D. Shao, X. Huang, D. Teschner, and W. Zhang, *ACS Catal.*, 201 , **4(7)**, 2369.

2 W. N. Zhang, G. Lu, C. L. Cui, Y. Y. Liu, S. Z. Li, W. J. Yan, C. Xing, R. Chi, Y. H. Yang, and F. W. Huo, *Adv.Mater.*, 2014, **26**, 4056.

3 V. Evangelista, B. Acosta, S. Miridonov, E. Smolentseva, S. Fuente and A. Simakov, *Appl. Catal. B: Environ.*, 2015, **166–167**, 518.

4 D. Tibiletti, A. Goguet, F. C. Meunier, J. P. Breen, and R. Bu ch, *Chem. Commun.*, 2004, 1636.

5 A. M. Duarte de Fariasa, P. Bargiela, M. da G. C. Rocha, and M. Fraga, *J. Catal.*, 2008, **260**, 93.

6 (a) M. Cargnello, M. Grzelczak, B. Rodríguez-González, Syrgiannis, K. Bakhmutsky, V. L. Parola, L. M. Liz-Marzán, R. Gorte, M. Prato, and P. Fornasiero, *J. Am. Chem. Soc.*, 2012, **13** 11760; (b) Q. Fu, H. Saltsburg, and M. Flytzani-Stephanopoulos *Science*, 2003, **301**, 935.

7 (a) X. Yang, X. Yu, L. Z. Long, T. J. Wang, L. L. Ma, L. P. Wu, Y. Bai, X. J. Li, and S. J. Liao, *Chem. Commun.*, 2014, **50**, 2794; (b) S. W. Li, T. Boucheron, A. Tuel, D. Farrusseng, and F. Meunier, *Chem. Commun.*, 2014, **50**, 1824.

8 H. Z. Guo, X. Liu, C. D. Bai, Y. Z. Chen, L. Wang, M. S. Zheng, Q. F. Dong, and D. L. Peng, *ChemSusChem*, 2015, **8**, 486.

9 (a) Q. Yuan, Z. Zhou, J. Zhuang and X. Wang, *Chem. Commun.*, 2010, **46**, 1491; (b) Y. Q. Dai, B. Lim, Y. Yang, C. M. Cobley, W. Y. Li, E.C. Cho, B. Grayson, P. T. Fanson, C. T. Campbell, Y. M. Sun, and Y. N. Xia, *Angew. Chem. Int. Ed.*, 2010, **49**, 8165; (c) L. V. Mattos, G. Jacobs, B. H. Davis and F. B. Noronha, *Chem. Rev.*, 2012, **112**, 4094.

10 N. Zhang, and Y. J. Xu, *Chem. Mater.*, 2013, **25(9)**, 1979.

11 C. J. Karwacki, P. Ganesh, P. R. C. Kent, W. O. Gordon, G. W. Peterson, J. J. Niu, and Y. Gogotsi, *J. Mater. Chem. A*, 2013, **1**, 6051.

12 (a) S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170; (b) G. Dutta, U. V. Waghmare, T. Baidya, and M. S. Hegde, *Chem. Mater.*, 2007, **19**, 6430; (c)X.-B. Zhang, J.-M. Yan, S. Han, H. Shioyama, and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 2778; (d) J. Guzman, S. Carrettin, J. C. Fierro-Gonzalez, Y. Hao, B. C. Gates, and A. Corma, *Angew. Chem. Int. Ed.*, 2005, **44**, 4778.

13 G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K. C. Prince, V. Matolin, K. M. Neyman, and J. Libuda, *Nat. Mater.* 2011, **10**, 310.

14 A. Caballero, J. P. Holgado, V. M. Gonzalez-DelaCruz, S. E. Habas, T. Herranz, and M. Salmeron, *Chem. Commun.*, 2010, **46**, 1097.

15 (a) J. Lu, B. Fu, M. C. Kung, G. Xiao, J. W. Elam, H. H. Kung and P. C. Stair, *Science*, 2012, **335**, 1205; (b) W. C. Li, M. Comotti and F. Schüth, *J. Catal.*, 2006, **237**, 190; (c) M. Cargnello, J. J. Delgado Jaén, J. C. Hernández Garrido, K. Bakhmutsky, T. Montini, J. J. Calvino Gámez, R. J. Gorte, and P. Fornasiero, *Science*, 2012, **337**, 713.

16 (a) J. Li, Q. L. Zhu, and Q. Xu, *Chem. Commun.*, 2014, **50**, 5899; (b) K. Zhao, B. Qiao, J. Wang, Y. Zhang and T. Zhang, *Chem. Commun.*, 2011, **47**, 1779; (c) S. H. Joo, J. Y. Park, C.-K. Tsung, Y. Yamada, P. D. Yang, and G. A. Somorjai, *Nat. Mater.,* 2009, **8**, 126.

17 P. M. Arnal, M. Comotti and F. Schüth, *Angew. Chem., Int. Ed.*, 2006, **45**, 8224.

18 M. Cargnello, N. L. Wieder, T. Montini, R. J. Gorte and P. Fornasiero, *J. Am. Chem. Soc.*, 2010, **132**, 1402.

19 C. X. Zhang, S. R. Li, T. Wang, G. W. Wu, X. B. Ma and J. L. Gong, *Chem. Commun.*, 2013, **49**, 10647.

20 M. M. Forde, L. Kesavan, M. I. bin Saiman, Q. He, N. Dimitratos, J. A. Lopez-Sanchez, R. L. Jenkins, S. H. Taylor, C. J. Kiely, and G. J. Hutchings, *ACS Nano*, 2014, **8(1)**, 957.

21 Z. Y. Shang, R. L. Patel, B. W. Evanko and X. H. Liang, *Chem. Commun.*, 2013, **49**, 10067.

22 Y. J. Feng, L. L. Liu, and X. D. Wang, *J. Mater. Chem.*, 2011, **21**, 15442.

23 H.-P. Zhou, H.-S. Wu, J. Shen, A.-X. Yin, L.-D. Sun and C.-H. Yan, *J. Am. Chem. Soc.*, 2010, **132**, 4998.

24 C. M. Y. Yeung and S. C. Tsang, *J. Phys. Chem. C*, 2009, **113**, 6074.

25 C. M. Y. Yeung, K. M. K. Yu, Q. J. Fu, D. Thompsett, M. I. Petch and S. C. Tsang, *J. Am. Chem. Soc.*, 2005, **127**, 18010.

26 P. Lu, C. T. Campbell, and Y. N. Xia, *Nano Lett.,* 2013, **13**, 4957.

27 P. Bera, K. C. Patil, V. Jayaram, G. N. Subbanna, and M. S. Hegd , *J. Catal.*, 2000, **196**, 293.

28 W. J. Shen, and Y. Matsumura,*Phys. Chem. Chem. Phys.*, 2000, 1519.

29 Y. Wang, Y. P. Zhai, D. Pierre, and M. Flytzani-Stephanopoul . *Appl. Catal. B: Environ.*, 2012, **127**, 342.

30 B. Liu, H. Y. Xu, and Z. H. Zhang, *Catal. Commun.*, 2012, **2** . 159.

31 H. S. Fogler, *Elements of Chemical Reaction Engineering*, 3rd ed., Prentice-Hall, Englewood Cliffs, NJ 1999.

32 S. Mukherjee, and M. A. Vannice, *J. Catal.*, 2006, **243**, 108.