Preparation and properties of antibacterial TiO$_2$@C/Ag core–shell composite

San-Xiang Tan$^1$, Shao-Zao Tan$^1$, Jing-Xing Chen$^1$, Ying-Liang Liu$^{1,2}$ and Ding-Sheng Yuan$^{1,2}$

$^1$ Department of Chemistry, Jinan University, Guangzhou 51063, People’s Republic of China
$^2$ Institute of Nanochemistry, Jinan University, Guangzhou 510632, People’s Republic of China

E-mail: tanshaozao@163.com and tydsh@jnu.edu.cn

Received 14 May 2009
Accepted for publication 9 July 2009
Published 25 August 2009
Online at stacks.iop.org/STAM/10/045002

Abstract
An environment-friendly hydrothermal method was used to prepare TiO$_2$@C core–shell composite using TiO$_2$ as core and sucrose as carbon source. TiO$_2$@C served as a support for the immobilization of Ag by impregnation in silver nitrate aqueous solution. The chemical structures and morphologies of TiO$_2$@C and TiO$_2$@C/Ag composite were characterized by x-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, energy dispersive x-ray spectroscopy and Brunauer–Emmett–Teller (BET) analysis. The antibacterial properties of the TiO$_2$@C/Ag core–shell composite against Escherichia coli ($E. coli$) and Staphylococcus aureus ($S. aureus$) were examined by the viable cell counting method. The results indicate that silver supported on the surface of TiO$_2$@C shows excellent antibacterial activity.

Keywords: hydrothermal method, core–shell structure, TiO$_2$@C, antibacterial activity

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Carbon materials have excellent chemical, mechanical and thermal stabilities and are therefore suitable for various applications [1–4]. Novel carbon materials as supports for antibacterial composites have been produced recently [1, 4]. Zhang et al [1] prepared silver-dispersed carbon aerogels (CAs) by direct immersion of organic aerogels in AgNO$_3$ aqueous solution followed by carbonization. Ag-dispersed CAs exhibit strong long-term antibacterial activity. Carbon monolith samples with a silver coating showed good antimicrobial activity against Escherichia coli, Staphylococcus aureus and Candida albicans [4]. Because of its specific shape, low silver attrition rate and good antibacterial activity, the impregnated monolith can be utilized as a personal disposable filter. Silver composites as antibacterial materials have become a hot research topic owing to the high efficiency and stability as well as broad spectrum of antimicrobial activities of silver [1, 4–7]. Nanomaterials with core–shell structure have been extensively studied because of their multifunctional properties and various applications, such as drug delivery [8] and increasing their solubility and stability [9, 10] and altering the emission properties of quantum dots [11, 12]. In addition to the above-mentioned characteristics, core–shell nano-oxides such as TiO$_2$@X and ZnO@X also have unique antibacterial properties that have attracted attention to this area in recent years [13–16]. It was found that the antibacterial activity of ZnO@C core–shell powders increases with increasing amount of ZnO and decreases with increasing carbonization temperature. The antibacterial activity towards S. aureus was found to be stronger than that towards E. coli. No activity of the carbon samples without ZnO was observed. The antibacterial activity was attributed to the generation of...
hydrogen peroxide from ZnO in core–shell powders [13].
Apatite-coated TiO$_2$ was also prepared and fixed on cotton
textiles by dip coating, and the antimicrobial properties of the
produced fabrics were then investigated [14]. The
findings suggest that the presence of apatite-coated TiO$_2$
induces antibacterial activity in the presence of black light
or visible light, suggesting a potential use in reducing the
risk of microorganism transmission for textile application.
However, the applications of the core–shell nano-oxides
were limited owing to their relatively poor antibacterial
activity. This activity can possibly be improved using silver
ions. TiO$_2$@C core–shell composite has wide applications in
photocatalysts [17, 18] and anode materials of lithium
batteries [19] owing to the excellent performance of TiO$_2$
and the unique structure of carbon. It also possesses some
antibacterial activity and can be used as a carrier for
antibacterial materials. However, to the best of our knowledge,
there have been few reports on its antibacterial activity.

TiO$_2$ has three crystalline phases: anatase, rutile and
brookite. Thermodynamically, rutile is the most stable form.
Anatase has attracted much attention owing to its application
in photovoltaic cells [20] and photocatalysts [21] and for its
antimicrobial properties [22]. In this study, we synthesized
TiO$_2$@C core–shell composite using TiO$_2$ as the core
and sucrose carbonization as the shell via a simple hydrothermal
method. Sucrose is a cheap and environment-friendly
carbon precursor [23]. Silver-supported TiO$_2$@C core–shell
composite was obtained by direct immersion of TiO$_2$@C
in AgNO$_3$ aqueous solution. The chemical structures and
morphologies of TiO$_2$@C and TiO$_2$@C/Ag composite were
investigated, and the antibacterial activities of TiO$_2$@C/Ag
composite were examined by the viable cell counting method.

2. Experimental details

2.1. Synthesis of TiO$_2$@C/Ag core–shell composite

All chemical reagents were of analytical-grade purity and
used as received. A certain amount of commercial TiO$_2$
(P25, Degussa, Germany) and 15.0 g of sucrose were dispersed
in 40 ml of distilled water, then added to a 60-ml stainless
steel autoclave. The autoclave was maintained at 600°C
for 16 h to complete the reaction and then allowed to cool
to room temperature. A dark precipitate was collected and
washed with distilled water and absolute ethanol, and then
dried in vacuum at 60°C for 6 h. To deposit silver on the
TiO$_2$@C surface, we used the synthesized TiO$_2$@C as a
support for the immobilization of silver. Silver was deposited
by impregnation in the AgNO$_3$ aqueous solution with different
concentrations for 15 min under ultrasonic agitation. TiO$_2$@C
containing silver is labeled here as TiO$_2$@C/Ag.

2.2. Characterization of TiO$_2$@C and TiO$_2$@C/Ag

The structure of as-prepared samples was analyzed with an
MSAL-XD2 x-ray diffractometer (CuK$_\alpha$, 40 kV, 20 mA, $\lambda = 1.5406$ Å). The morphologies were observed using a Philips
Tecnai-10 transmission electron microscope (TEM) at an
accelerating voltage of 100 kV. The functional groups on the
surface of TiO$_2$@C were detected through Fourier transform
infrared (FTIR) absorption spectra recorded with a Nicolet
6700 spectrometer. The specific surface area was measured
using a Micromeritics TriStar 3000 analyzer. The chemical
composition of the as-prepared TiO$_2$@C/Ag composite was
analyzed with an Oxford Inca 350 energy dispersive x-ray
spectroscope (EDS).

2.3. TiO$_2$@C/Ag for tests of antibacterial activity

For antibacterial tests, E. coli (ATCC25922) and S. aureus
(ATCC6538) were selected as indicators, following the
method of viable cell counts [24, 25]. All glassware and
materials were sterilized in an autoclave at 120°C for 25 min
prior to the experiments. A set of test tubes containing 0.1 mg
(against E. coli) or 0.2 mg (against S. aureus) of the samples
were weighed. Each sample was dispersed in 10 ml of the 0.9
wt.% saline water containing about 10$^5$ colony forming units
(cfu) ml$^{-1}$ of E. coli or S. aureus, and then shaken at 37°C
for 6 h. One milliliter of the treated solution was obtained
from the test tube at the prescribed time, centrifuged and
diluted with distilled water to a certain volume. To ensure
that the grown bacterial colonies could be counted easily
and correctly, tenfold dilution was applied. The final diluted
solution was plated on agar in triplicate, and then the obtained
plates were cultivated at 37°C for 24 h. The number of
bacterial colonies on each plate was counted and the obtained
values were averaged to obtain the final data.

3. Results and discussion

3.1. Characterization of structure and morphology

Commercial TiO$_2$ powder with the particle diameter of
30–40 nm was used as a core in our experiment. Reaction
time and temperature are critical for the preparation of
carbon materials. The reaction system was maintained at
500–700°C for 12–20 h and an optimized synthesis condition
was identified at 600°C for 16 h. The as-prepared products
under the optimum synthesis condition were characterized by
x-ray diffraction (XRD). Figure 1(a) shows the XRD patterns of
P25 and TiO$_2$@C samples synthesized under different
gravimetric ratios of sucrose/TiO$_2$, illustrating that P25 and
TiO$_2$@C series products are composed of anatase and rutile. It
is well known that Degussa P25 is a mixture of anatase (70%)
and rutile (30%) and has a surface area of 50 m$^2$ g$^{-1}$ [26]. The
two phases of TiO$_2$ were confirmed from the XRD pattern
shown in figure 1(a), curve 1. The intensity of anatase peaks
in all TiO$_2$@C samples was lower than that in the case of P25.
This indicates that some anatase transformed into rutile
upon calcination. Furthermore, the anatase peaks strengthened
and the rutile peaks weakened with increasing ratio of
sucrose/TiO$_2$, indicating that the carbon layer suppressed the
phase transformation from anatase to rutile. With the increase
in the sucrose/TiO$_2$ ratio, the carbon shell became thicker
and the anatase TiO$_2$ phase became more stable. It is known
that the phase transformation of anatase to rutile occurs at
approximately 600°C [27], but by coating anatase TiO$_2$ with
carbon, the temperature of crystal transformation becomes
higher. Similar results were reported by Tsumura et al. [28] and Shanmugam et al. [17]. Figure 1(b) shows the XRD patterns of TiO$_2$@C/Ag prepared at different concentrations of AgNO$_3$ aqueous solution. TiO$_2$@C (sucrose/TiO$_2$ = 28) was immersed in 0.01, 0.02 and 0.05 mol l$^{-1}$ AgNO$_3$ solution for 15 min under ultrasonic agitation. The thus produced samples were denoted as TCA-1, TCA-2 and TCA-3 (T from TiO$_2$, C-carbon and A-Ag), respectively. The weak diffraction peaks of silver crystal in curves 2–4 of figure 1(b) indicate that a redox reaction between Ag$^+$ and reductive carbon occurred during the adsorption [1]. Three characteristic peaks are observed at 2θ values of 38.1°, 44.2° and 64.5°, respectively, corresponding to the (111), (200) and (220) crystalline planes of Ag crystal. As shown in the XRD pattern, TiO$_2$ is mainly present in the form of anatase existing in the TiO$_2$@C sample (sucrose/TiO$_2$ = 28/1) and all the TiO$_2$@C/Ag samples. The amount of deposited silver depends on the initial concentration of Ag$^+$ as well as the surface area, pore structure and quantity of acidic functional groups that can act as initial active sites for adsorption [4, 29]. Yue et al. [29] explained that there are two types of reaction that might occur during Ag$^+$ adsorption: (i) an ion-exchange reaction between silver ions and surface carboxylic groups and (ii) redox adsorption, which is confirmed by XRD. The XRD patterns indicate that some silver ions were reduced to silver crystals.

Figure 2 shows TEM images of the TiO$_2$@C and TCA-3 samples obtained under the optimum synthesis condition. Figure 2(a) is a low-magnification TEM image of TiO$_2$@C (sucrose/TiO$_2$ = 28); it reveals TiO$_2$ nanoparticles wrapped in a carbon film. A core–shell TiO$_2$@C structure is shown in detail in a high-magnification TEM image (figure 2(b)); the thickness of the carbon shell is approximately 20 nm. Figure 2(c) shows a high-magnification TEM image of TCA-3. The silver particles in TCA-3 are round and are dispersed separately on the surface of the carbon shell.

Figure 3 shows the isotherms of the nitrogen adsorption–desorption measurements of the TiO$_2$@C and TCA-3 samples. By the Brunauer–Deming–Deming–Teller (BDDT) method, both of them were found to yield a type-I nitrogen isotherm with an H4 hysteresis loop, which indicates a micropore structure and single-molecule chemical adsorption [30]. Micropores in the sample are mainly distributed on the surface of the carbon film. However, in the desorption branch, a clear hysteresis loop at the relative pressure of 0.45 indicates the presence of mesopores. Mesoporous structure is also supported by TEM observations. These results illustrate that the pore structure in TiO$_2$@C and TCA-3 samples consists of micropores and mesopores. The surface areas, pore diameters and pore volumes were calculated from the isotherms and are summarized in table 1. The pore size distributions were measured on the basis of the Barrett–Joyner–Halenda (BJH) adsorption isotherms. The $S_{BET}$ surface areas of TiO$_2$@C and TCA-3 samples are higher than that of P25. This result indicates that coating TiO$_2$ with carbon can considerably increase the surface area of pure TiO$_2$. Thus, the TiO$_2$@C core–shell structure is advantageous for loading silver. Compared with those of the TiO$_2$@C sample, the $S_{BET}$ and $V_{mic}$ of the TCA-3 sample were markedly lower. This is due to the blockage of pores by silver particles, as shown in figure 2(c). The result is similar to that reported for Ag/CAS [1].

The functional groups of the TiO$_2$ and TiO$_2$@C materials were characterized by FTIR transmittance, as shown in figure 4. Figure 4(a) shows a broad band around 3440 cm$^{-1}$ and another around 1640 cm$^{-1}$, which are attributed to the surface-adsorbed H$_2$O and the $\cdot$OH group of TiO$_2$ [31]. A broad band in the range of 400–900 cm$^{-1}$ is ascribed to the stretching vibration of the Ti–O bond. The IR spectrum of TiO$_2$@C dried under vacuum is shown in figure 4(b). The strong characteristic peak at 3434 cm$^{-1}$ is assigned to the stretching vibration of the O–H bond at the carbon surface, and the peaks at 2919 and 2847 cm$^{-1}$ originate from the stretching vibration of C–H bonds. The peak at 1389 cm$^{-1}$ corresponds to the C–O stretching [32]. Compared with that shown in figure 4(a), the additional peak at 1740 cm$^{-1}$ is due to the stretching vibration of the carboxyl group C=O. The weakening of the peak at around 1640 cm$^{-1}$ indicates the loss of H$_2$O adsorbed on the TiO$_2$@C surface under vacuum. Furthermore, owing to the carbon shell on the TiO$_2$
core, the stretching vibration of the Ti–O bond becomes visibly weak. The FTIR spectrum reveals many functional groups on the surface of the TiO$_2$@C composite. The retained functional groups provide a potential avenue to load other functional groups, molecules, ions or nanoparticles [33]. In our experiment, sucrose acts not only as a cheap and environment-friendly carbon source, but also retains many hydrophilic functional groups, such as $\text{OH}$ and $\text{C=O}$, on the carbon surface after calcination.

The elemental content in TCA samples was measured by EDS. The loadings of silver onto TCA-1, TCA-2 and TCA-3 samples were 0.81, 1.52 and 1.72 wt.%, respectively. The silver content in the TiO$_2$@C composite increased with the increase in the initial AgNO$_3$ concentration.

### 3.2. Antibacterial properties

TiO$_2$@C/Ag could be a good antibacterial material. Table 2 lists the antibacterial activity of different samples against *E. coli* and *S. aureus* after 6 h of contact. The sample...
concentration was 10.0 mg l⁻¹ against *E. coli* and 20.0 mg l⁻¹ against *S. aureus*. The commercial carbon black (C) has no antibacterial activity because of the increase in the number of viable bacterial colonies after 6 h of contact. TiO₂@C exhibits weak antibacterial activity as shown in the decrease in the number of viable bacterial colonies, which could be attributed to the antimicrobial properties of TiO₂. TiO₂, particularly anatase TiO₂, has an excellent photocatalytic performance. It can generate strong oxidizing power under certain conditions. After carbon-coated TiO₂ suspensions are irradiated and activated, reactive oxygen species such as OH, O₂⁻, and H₂O₂ might be generated on the irradiated TiO₂ surface; those species might attack and decompose polyunsaturated phospholipids in bacteria [34]. However, three materials, TiO₂@C/Ag (TCA-1, TCA-2 and TCA-3), showed excellent antibacterial activity, and the number of viable colonies of bacteria visibly decreased. It is clear that the antibacterial activity increased with the increase in silver content. As for TCA-2 and TCA-3 samples, all the *E. coli* and more than 99.99% of the *S. aureus* bacteria were killed within 6 h of contact. Moreover, TCAs exhibit higher activity against *E. coli* than against *S. aureus* under the same test conditions.

Silver ions are highly toxic to microorganisms and have a strong biocidal effect on many bacterial species. Silver nanoparticles also have inhibitory and bactericidal effects [35]. However, the actual bactericidal mechanism of silver nanoparticles is yet unknown. Some researchers support the idea that silver species release Ag⁺ ions, which interact with the thiol groups in bacterial proteins, affecting the replication of DNA [36]. In our experiment, there are two forms of silver existing in the samples of TCAs. One is silver ion obtained by an ion-exchange reaction, the other is silver metal that is formed by a redox adsorption. Therefore, it could be concluded that silver particles in the TiO₂@C composite were gradually oxidized into silver oxide and then released silver ions into the solution [37]. It may be reasonably presumed that such pore structures and functional groups of the TiO₂@C composite will prolong the release time of Ag⁺ ions and preserve the sustained antibacterial behavior. Because the cell wall is thicker in *S. aureus* than in *E. coli* [38], the antibacterial efficiency of TCAs is lower for *S. aureus* than for *E. coli*.

| Sample          | Ag content in samples (wt.%) | Number of viable colonies of bacteria (cfu ml⁻¹)          |
|-----------------|------------------------------|----------------------------------------------------------|
| C               | 0                            | 4.63 × 10⁶, 3.37 × 10⁵                                     |
| TiO₂@C          | 0.8                          | 3.72 × 10⁴, 5.18 × 10⁴                                    |
| TCA-1           | 0.8                          | 6, 1.45 × 10²                                            |
| TCA-2           | 1.5                          | 0, 35                                                   |
| TCA-3           | 1.7                          | 0, 9                                                   |

*Sample concentration: 10.0 mg l⁻¹ against *E. coli*, 20.0 mg l⁻¹ against *S. aureus*; initial numbers of viable colonies of bacteria: *E. coli*, 3.61 × 10⁷ cfu ml⁻¹, *S. aureus*, 2.15 × 10⁷ cfu ml⁻¹; contact time: 6 h.

### 4. Conclusions

TiO₂@C core–shell composite was successfully synthesized via a simple hydrothermal route. TiO₂@C/Ag composite obtained by impregnation of TiO₂@C in AgNO₃ aqueous solution was used to kill *E. coli* and *S. aureus*. The silver content of the TiO₂@C material can be controlled by adjusting the initial AgNO₃ concentration. The characterization by TEM, BET and FTIR techniques shows that TiO₂@C is an excellent carrier for the loading and adsorption of silver on the surface owing to the carbon layer that has a high BET surface area, porous structure and hydrophilic functional groups. TiO₂@C/Ag displays excellent antibacterial activity that increases with increasing silver content of the samples. Furthermore, the antibacterial activity towards *E. coli* was stronger than that towards *S. aureus*. Such core–shell structure composite could have promising applications as antibacterial materials for micro-biocides and water treatment.

### Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (Grant Nos. 20676049 and 20876067), Foundation of Enterprise-University-Research Institute Cooperation of Guangdong Province, Ministry of Education of China (Grant No. 2007B090400105) and Young Teacher Fund of Jinan University (51208023).

### References

[1] Zhang S T, Fu R W, Wu D C, Xu W, Ye Q W and Chen Z L 2004 *Carbon* 42 3209
[2] Yuan D S, Tan S Z, Liu Y L, Zeng J H, Hu F P, Wang X and Shen P K 2008 *Carbon* 46 531
[3] Xiao S J, Li Y F and Huang C Z 2007 *Chem. Lett.* 36 798
[4] Vukčević M, Kalijadis A, Dimitrijević-Branković S, Lašević Z and Laušević M 2008 *Sci. Technol. Adv. Mater.* 9 010006
[5] Zhang S T, Wu D C, Wan L, Tan H B and Fu R W 2006 *J. Appl. Polym. Sci.* 102 1030
[6] Damm C, Münstedt H and Rösch A 2008 *Mater. Chem. Phys.* 108 61
[7] Xu K, Wang J X, Kang X L and Chen J F 2009 *Mater. Lett.* 63 31
[8] Zhu Y, Shi J, Shen W, Dong X, Feng J, Ruan M and Li Y 2005 *Angew. Chem., Int. Ed. Engl.* 44 5083
[9] Chan Y, Zimmer J P, Strøm M, Steckel J S, Jain R K and Bawendi M G 2004 *Adv. Mater.* 16 2092
[10] Liu S, Zhang Z and Han M 2005 *Anal. Chem.* 77 2595
[11] Fleischhaker F and Zentel R 2005 *Chem. Mater.* 17 1346
[12] Song J H, Atay T, Shi S, Urabe H and Nurmikko A V 2005 *Nano Lett.* 5 1557
[13] Yamamoto O, Nakakoshi K, Sasamoto T, Nakagawa H and Miura K 2001 *Carbon* 39 1643
[14] Kangwansupanonkon W, Louruengtana V, Surassmo and Rukanonchaichai U 2009 *Nanomed. Nanotechnol. Biol. Med.* 5 240
[15] Wang H et al 2009 *J. Mater. Sci.: Mater. Med.* 20 11
[16] Chen W J, Tsai P J and Chen Y C 2008 *Small* 4 485
[17] Shanmugam S, Gabashvili A, Jacob D S, Yu J C and Gedanken A 2006 *Chem. Mater.* 18 2275
[18] Zhang L X, Liu P and Su Z X 2006 *J. Mol. Catal. A: Chem.* 248 189
[19] Fu L J, Liu H, Zhang H P, Li C, Zhang T, Wu Y P and Wu H Q 2006 J. Power Sources 159 219
[20] Fujishima A, Rao T N and Tryk D A 2000 J. Photochem. Photobiol. C 1 1
[21] Gratzel M 2001 Nature 414 338
[22] Fu G, Vary P S and Lin C-T 2005 J. Phys. Chem. B 109 8889
[23] Yuan D S, Chen J X, Zeng J H and Tan S X 2008 Electrochem. Commun. 10 1067
[24] Tan S Z, Ouyang Y S, Zhang L L, Chen Y B and Liu Y L 2008 Mater. Lett. 62 2122
[25] Garza M R, Olguín M T, Sosa I G, Alcántura D and Fuentes G R 2000 Micropor. Mesopor. Mater. 39 431
[26] 1990 Degussa Technical Bulletin Pigment Report vol 56 p 13
[27] Inagaki M, Hirose Y, Matsunaga T, Tsumura T and Toyoda M 2003 Carbon 41 2619
[28] Tsumura T, Kojitani N, Izumu I, Iwashita N, Toyoda M and Inagaki M 2002 J. Mater. Chem. 12 1391
[29] Yue Z R, Jiang W, Wang L, Toghiani H, Gardner S D and Pittman C U Jr 1999 Carbon 37 1607
[30] Sing K S W, Everrett D H, Haul R A W, Moscou L, Pierotti R A, Rouquérol J and Siemieniewska T 1985 Pure Appl. Chem. 57 603
[31] Ding Z, Lu G Q and Greenfield P F 2000 J. Phys. Chem. B 104 4815
[32] Cheng C H, Lehmann J, Thies J E, Burton S D and Engelhard M H 2006 Org. Geochem. 37 1477
[33] Bond A M, Miao W J and Raston C L 2000 Langmuir 16 6004
[34] Maness P C, Smolinski S, Blake D M, Huang Z, Wolfrum E J and Jacoby W A 1999 Appl. Environ. Microbiol. 65 4094
[35] Shrivastava S, Bera T, Roy A, Singh G, Ramachandrarao P and Dash D 2007 Nanotechnology 18 225103
[36] Marini M, De Niederhausern N, Iseppi R, Bondi M, Sabia C, Toselli M and Pilati F 2007 Biomacromolecules 8 1246
[37] Baker C, Pradhan A, Pakstis L, Pochan-Darrin J and Shah S I 2005 J. Nanosci. Nanotechnol. 5 244
[38] Zhao D F, Zhou J and Liu N 2006 Appl. Clay Sci. 33 161