

Insertion of Platinum Particles in Bacterial Cellulose Membranes from PtCl₄ and H₂PtCl₆ Precursors

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2 Insertion of Platinum Particles in Bacterial Cellulose Membranes from PtCl_4 and H_2PtCl_6 Precursors

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Summary: The Pt nanoparticles have been synthesized in situ using bacterial cellulose (BC) membranes as the matrix. The BC was immersed in a solution of PtCl_4 and H_2PtCl_6 as Pt(IV) precursors also in surfactant stabilized Multiwall Carbon Nanotubes (MWCNT) as carbon source. Then, the Pt(IV) was reduced by hydrogen gas. Two routes have been applied for the insertion Pt particles; in the first route the Pt particles were inserted before the insertion of MWCNT and in the second route the other way around was applied. The products of these two insertion routes for each precursor are designated as BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT, BC- $\text{Pt}_{\text{H}_2\text{PtCl}_6}$ -MWCNT for the first route and BC-MWCNT- $\text{Pt}_{\text{PtCl}_4}$, BC-MWCNT- $\text{Pt}_{\text{H}_2\text{PtCl}_6}$ for the second route, respectively. Both routes revealed that the Pt particles insertion in BC depends on the type of precursors and insertion routes, as seen from the morphology and Pt particles content. The first route produces Pt diameter of 26 nm while the second one 42 nm. The use of PtCl_4 in the first route resulted in higher content of Pt particles (50%) compared to H_2PtCl_6 (39%). On the other hand, the type of precursor did not give any significant effect to the content of Pt inserted; both gave 29% of Pt to the second route. The high Pt content observed on the BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT membrane surface is possible because PtCl_4 precursor forms $\text{H}_2[\text{PtCl}_4(\text{OH})_2]$ that initially can be bound via hydrogen bonding to the BC backbone. It is concluded that smaller size and high content of Pt particles have been obtained from PtCl_4 precursor, the distribution of Pt particles and MWCNT are almost homogenous in the BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT membrane derived from precursor PtCl_4 .

Keywords: bacterial cellulose; biopolymers; H_2PtCl_6 ; membranes; PtCl_4

Introduction

Platinum (Pt) is an interesting transition metal that has the highest catalytic activity among other metals,^[1] which puts its role as

a catalyst for several chemical reaction applications such as a fuel cell electrode.^[2] It is well known that nanosized Pt is more active than the macrosized one due to its higher surface active area.^[3] To prepare nanosize Pt materials, several methods have been applied such as colloidal process,^[4] reduction,^[5] using bacterial cellulose (BC) as hydrophilic matrix,^[6] microemulsion,^[7] sol-gel technique,^[8] sonochemical process,^[9] electrodeposition,^[10] and others. Among these methods, the preparation of Pt nanoparticle using BC matrix seems to be more interesting, since the BC fibers form three-dimensional networks in which their cavities or pores allow them to be used as reactors for nanometal deposition. BC can act as a reducing agent for several metal ions

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such as palladium(IV), silver(I) and gold(III).^[6] However for Pt(IV) ions additional reductors, such as NaBH₄ and formic acid have to be added to reduce the metal ion.^[11] The role of Pt particle as fuel cell catalyst needs to be supported by carbon materials which act as conductive materials due to their transfer electron ability. Most of the researchers use carbon in powder form or carbon paper to improve the catalytic activity of Pt metal.^[12,13] Other researches stated that Multiwall Carbon Nanotubes (MWCNT) showed the highest conductivity among other carbon materials,^[14,15] and the insertion of MWCNT in BC can lead to electrical current.^[16] The insertion of Pt particles together with MWCNT inside the BC could cause competition between the Pt particles and MWCNT and different types of Pt precursors affect the insertion process. According to Yang *et al.*^[11], the insertion of Pt particles into the BC matrix can be explained by a mass diffusion process. Pt precursor solution interacts with BC hydroxyl groups, and NaBH₄ as reducing agent is added to reduce the Pt precursors. However, information of the insertion of Pt and MWCNT particles with different insertion route methods are not yet available. In this method, shorter synthesis time requires to deposit Pt particles on the BC membrane compared to other methods.^[11] On the other hand, partly of the Pt particles loose from the BC membrane during the synthesis process is the weakness of this method. Therefore, the insertion of Pt particles from two different precursors (PtCl₄ and H₂PtCl₆) has been studied in this work via two different routes: Pt particles were inserted before MWCNT and the second route applied the other way around. The size and content of Pt particles inside the BC were measured using SEM-EDX technique.

Experimental Part

Materials

Platinum tetrachloride (PtCl₄) and chloroplatinic acid hexahydrate (H₂PtCl₆·6

H₂O) were obtained from Sigma-Aldrich, while cetyltrimethylammonium bromide (CTAB) was from Merck. MWCNT with outer diameters of 8–15 nm, length ~50 μm and purity of >95% was purchased from He Ji Limited Company, Hongkong. Hydrogen gas (80% pure) was obtained from a local supplier. All the chemicals were used without further purification.

Preparation of BC

The BC gel was prepared from fermentation of coconut water in static culture using *Gluconacetobacter xylinus* according to literature reported.^[17] Before BC gels were immersed in aqueous Pt(IV) solution, they were cut to a size of 4 × 4 cm, then pressed to remove water and finally air dried at room temperature.

Preparation of MWCNT Dispersion

MWCNT was added to pure water to obtain a concentration of 0.1% w/w and CTAB was also added as cationic surfactant (0.1% w/w). The mixture was sonicated using ultrasonic bath (Bransonic® 2510E-DTH) to homogenize the MWCNT dispersion. This process took place at room temperature for 2 h.

Insertion of Pt and MWCNT in the BC

3 Membranes

The BC membrane was immersed in a solution containing 20 mM PtCl₄ and sonicated at room temperature for 2 h. The BC membrane was removed from the precursor solution, rinsed with deionized water and immersed in water with hydrogen gas bubbled to reduce the Pt(IV) ion. The hydrogen pressure was kept constant at 0.2 atm and the water solution was stirred at 500 rpm. The Pt-BC membrane was then removed from water, immersed in a MWCNT solution and sonicated at room temperature for another 2 h. This membrane was removed from the solution, rinsed with deionized water and then pressed to remove water and to obtain the dry composite membrane. The same procedure was carried out using H₂PtCl₆

precursor. Membrane derived from PtCl_4 precursor was designated as BC-Pt PtCl_4 -MWCNT while the one generated from H_2PtCl_6 precursor was designated as BC-Pt H_2PtCl_6 -MWCNT. The insertion of Pt particles after MWCNT insertion using similar method as above was designated as BC-MWCNT-Pt PtCl_4 and BC-MWCNT-Pt H_2PtCl_6 . The insertion of Pt particles and MWCNT in the BC matrix has been carried out in two different routes, which is illustrated schematically in Figure 1.

Scanning Electron Microscopy (SEM)

The morphology of BC, BC-Pt-MWCNT and BC-MWCNT-Pt membrane surfaces were observed using a SEM-EDX (JEOL, JSM-6510 LA). The membrane and composite membrane were coated with a thin layer of gold before analysis.

Elemental Analysis

Energy-dispersive X-ray spectroscopy (EDS, JEOL, JSM-6510 LA) was used for the elemental analysis of the BC-Pt-MWCNT and BC-MWCNT-Pt membrane surface. Before analysis, the composite membrane was coated with a thin layer of gold and the analysis was performed in conjunction with morphology analysis.

Results and Discussion

Qualitative Observation on the Insertion Process

BC is a gelly-like white sheet which turned to a semi-transparent membrane after being pressed and dried. After the immersion of BC gel into Pt precursor solution, the colour of BC gel changed to yellow. Indicating that the Pt(IV) solution has been trapped inside the BC membrane. The color of the BC membrane immersed in PtCl_4 solution was slightly yellow, while the one immersed in H_2PtCl_6 solution was darker yellow. This is due to the color of the precursor solutions; the yellow color of H_2PtCl_6 solution is darker than that of PtCl_4 solution, although both precursors have the same concentration. When the BC membrane was reduced by hydrogen gas, the yellow color changed to black indicated that the Pt(IV) ion had successfully been reduced and inserted into the BC fibers. Subsequently, no color change was observed when the membrane was immersed in a MWCNT solution. Conversely, when BC gel was first immersed in MWCNT solution, the colour of the BC gel turned to black and remained black after the immersion into the Pt precursor solution.

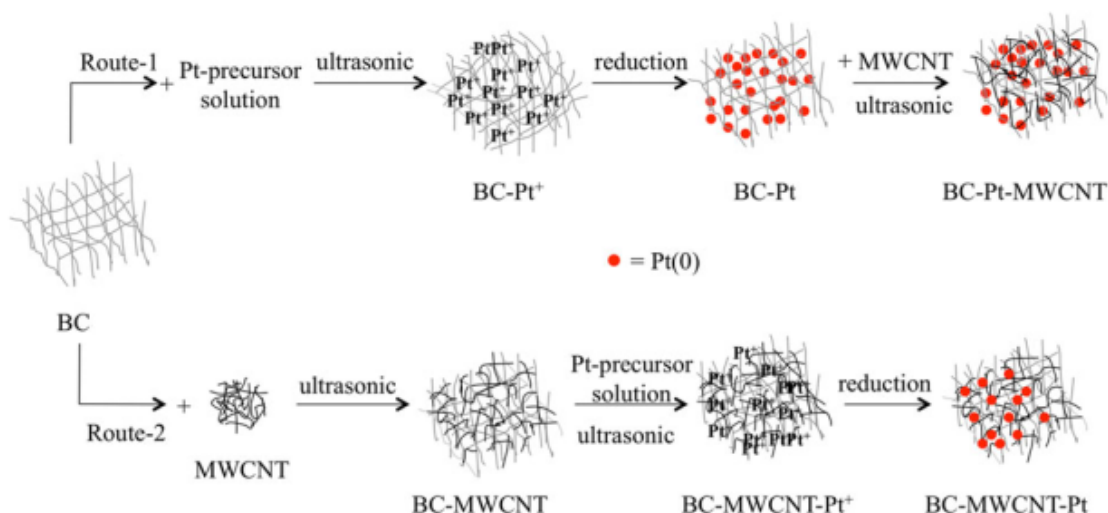


Figure 1.

Schematic illustration of the insertion of Pt particles and MWCNT in BC matrix via two routes: (1) the Pt particles inserted before MWCNT; (2) the Pt particles inserted after MWCNT.

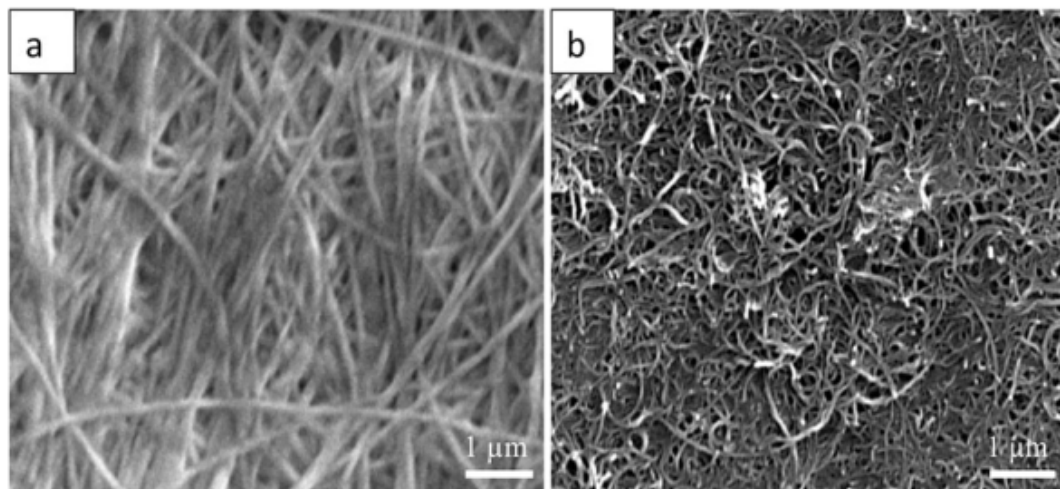


Figure 2.
SEM images of (a) BC membrane (b) BC-MWCNT membrane.

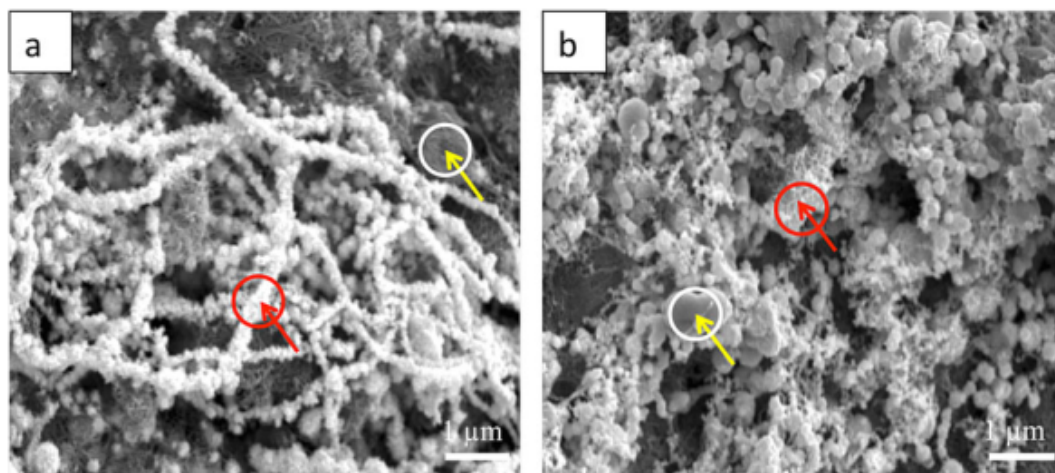
Effects of MWCNT on the Morphology of BC Membrane

To understand more clearly the insertion of Pt particles, the SEM analysis has been done. Naturally, the BC membrane contains cellulose fibers with an average fiber diameter of 40–100 nm. The three-dimensional network of BC fibers are interconnected each other producing cavities or pores with diameters between 20–80 nm. These cavities act as a matrix for the inserted metal nanoparticles. The pore size of BC membrane became smaller after MWCNT insertion, because MWCNT network covered the BC membrane surface and hence, reduced the cavities of BC.

Figure 2 shows SEM images of BC and BC membrane which has been immersed in MWCNT solution (BC-MWCNT).

Effects of PtCl_4 Precursor on the Size and Content of Pt Particles in BC Membrane

Figure 3 shows the morphology of BC membranes containing Pt particles from PtCl_4 precursor and MWCNT. It can be seen that the insertion of Pt particles (from PtCl_4 precursor) and MWCNT with different insertion routes in BC membranes provides different morphologies. When the Pt particles were inserted before MWCNT (the resulting membrane was designated as BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT membrane), the Pt



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Figure 3.
SEM images of (a) BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT membrane (b) BC-MWCNT- $\text{Pt}_{\text{PtCl}_4}$ membrane using PtCl_4 as precursor. (Pt particles: red circles and arrows; MWCNT: white circles and arrows).

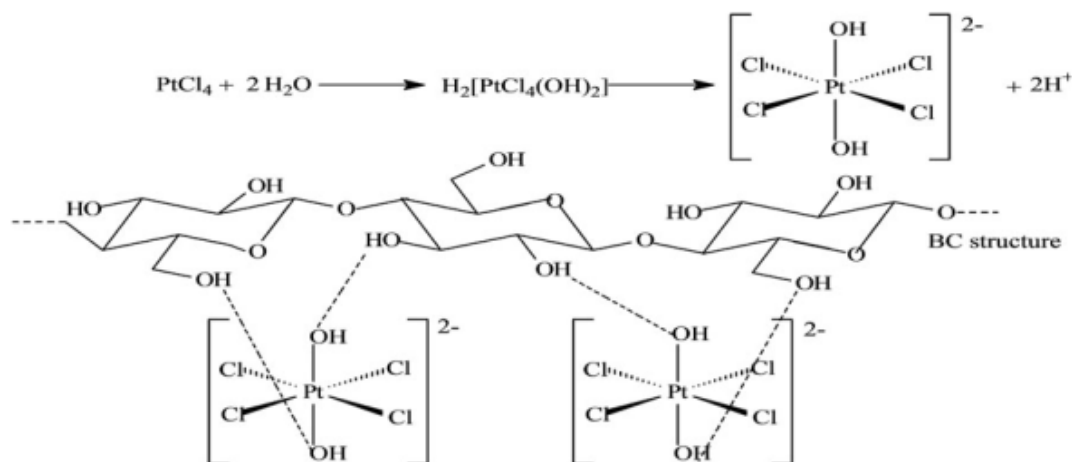


Figure 4.

Schematic illustration of the hydrogen bonds between the PtCl_4 precursor solution and BC.

particles (shown by red circles in Figure 3) are distributed almost homogenous on the membrane surface. When MWCNT (shown by white circle) was inserted later on, the Pt particles move to the MWCNT surface and the resulting Pt particle size is 26 nm on average. Meanwhile, when the Pt particles were inserted after MWCNT (BC-MWCNT- $\text{Pt}_{\text{PtCl}_4}$ membrane), the Pt particles form agglomerations and the average Pt particle size is larger (i.e. 42 nm) compared to that of the previous route.

The method of insertion routes also affects the distribution of MWCNT in the membrane. When the MWCNT was inserted at the second stage, the MWCNT was distributed homogeneously on the membrane surface. Conversely, when the MWCNT was inserted before the Pt particles, the distribution of MWCNT is not homogeneous due to the agglomeration formed on the membrane surface.

Based on the SEM and EDX data, it can be seen that the Pt particles content of the first route is higher than the second route.

Around 50% of Pt particles were on the BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT membrane surface. This is due to the ability of MWCNT to attract Pt particles from the cavity of BC. The high Pt content observed on the BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT membrane surface is possible because PtCl_4 precursor forms $\text{H}_2[\text{PtCl}_4(\text{OH})_2]$ ^[18] that initially can be bound to the BC backbone via hydrogen bond as shown in Figure 4. However after reduction process, no more hydrogen bonding occurred and the MWCNT was able to move Pt particles from the BC membrane surface.

The Pt particles content (mass %) from two different routes are tabulated in Table 1. Table 1 shows that the insertion routes also give effect to the MWCNT content.

Effects of H_2PtCl_6 Precursor on the Size and Content of Pt Particles in BC Membrane

Figure 5 shows the morphology of composite membranes containing Pt particles

Table 1.

The elemental composition of membrane surface derived from PtCl_4 precursor.

Route	Membrane code	Elements [mass %]				Average of Pt [mass %]	Average of Pt size [nm]
		C	O	Cl	Pt		
1	BC- $\text{Pt}_{\text{PtCl}_4}$ -MWCNT	35.72	11.71	1.14	51.43	50.63	26
		36.99	12.11	1.08	49.82		
2	BC-MWCNT- $\text{Pt}_{\text{PtCl}_4}$	46.03	21.26	3.30	29.41	28.73	42
		47.31	20.78	3.86	28.05		

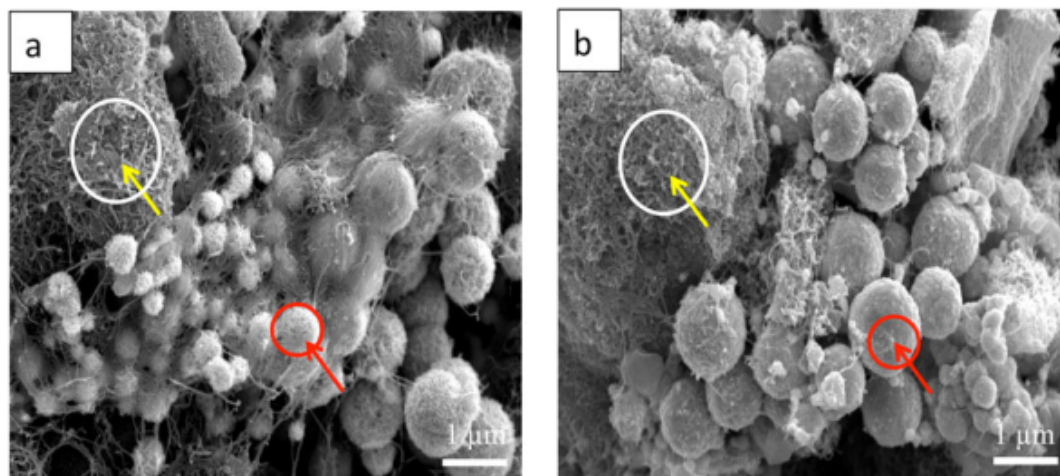


Figure 5. SEM images of (a) BC-Pt_{H₂PtCl₆}-MWCNT membrane (b) BC-MWCNT-Pt_{H₂PtCl₆} membrane using H₂PtCl₆ as precursor. (Pt particles: red circles and arrows; MWCNT: white circles and arrows).

from H₂PtCl₆ precursor and MWCNT. The elemental analysis of all components (mass %) of BC-Pt_{H₂PtCl₆}-MWCNT and BC-MWCNT-Pt_{H₂PtCl₆} membranes are shown in Table 2. However, when the second route was applied, the average Pt content was found to be similar to the BC-MWCNT-Pt_{PtCl₄} membrane.

The size of Pt particles obtained from H₂PtCl₆ precursor seems to be larger than those obtained from PtCl₄. This is shown from SEM image in Figure 5. Moreover, the particle size distribution does not influence by the insertion routes. The larger size of Pt particles was observed due to the agglomeration of Pt on the BC-Pt_{H₂PtCl₆}-MWCNT membrane surface. From EDX data the Pt content was found 38.74% for route-1 and 28.95% for route-2. The tendency to find low Pt content from route-2 is similar to both precursors. The average size of Pt particles derived from H₂PtCl₆ is significantly larger compared to

Pt from PtCl₄ precursor and depend on the insertion route type.

Conclusion

Pt particles and MWCNT insertion in BC have been successfully carried out by immersing BC membrane into aqueous solutions containing Pt precursors and MWCNT. The BC-Pt_{PtCl₄}-MWCNT membrane derived from PtCl₄ precursor shows that the resulting Pt particles size is relatively small (26 nm) and the Pt particles content is high (50%) compared to the other precursor. Besides that, this precursor also leads to homogeneous distribution of Pt particles and MWCNT in the BC-Pt_{PtCl₄}-MWCNT membranes. This result suggests that the PtCl₄ precursor can be proposed as a precursor to produce Pt nanoparticles in the BC matrix. The sequence of insertion affects the

Table 2.

The elemental composition of membrane surface derived from H₂PtCl₆ precursor.

Route	Membrane code	Elements [mass %]				Average of Pt [mass %]	Average of Pt size [nm]
		C	O	Cl	Pt		
1	BC-Pt _{H₂PtCl₆} -MWCNT	44.87	11.32	4.06	39.75	38.74	801
		50.89	7.77	3.61	37.73		
2	BC-MWCNT-Pt _{H₂PtCl₆}	49.76	20.01	1.71	28.51	28.97	850
		62.18	7.78	0.60	29.43		

distribution of Pt particles and MWCNT. The insertion of Pt prior to the MWCNT results in a more homogeneous distribution of Pt particles.

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- [1] D. H. Lim, W. D. Lee, H. I. Lee, *Catal. Surv. Asia* **2008**, 12, 310.
- [2] S. M. Haile, *Acta Mater.* **2003**, 51, 5981.
- [3] K. Bergamaski, A. L. N. Pinheiro, E. Teixeira-Neto, F. C. Nart, *J. Phys. Chem. B* **2006**, 110, 19271.
- [4] M. P. Pileni, *Langmuir* **1997**, 13, 3266.
- [5] S. H. Wu, D.-H. Chen, *J. Colloid Interface Sci.* **2003**, 259, 282.
- [6] B. R. Evans, H. M. O'Neil, V. P. Malyvanh, I. Lee, J. Woodward, *Biosens. Bioelectron.* **2003**, 18, 917.
- [7] M. S. Dominguez, M. Boutonnet, C. Solans, *J. Nanopart. Res.* **2009**, 11, 1823.
- [8] H. B. Suffredini, G. R. Salazar-Banda, L. A. Avaca, *J. Sol-Gel Sci. Technol.* **2009**, 49, 131.
- [9] C. A. Angelucci, M. D. Silva, F. C. Nart, *Electrochim. Acta* **2007**, 52, 7293.
- [10] J. M. Sieben, M. M. E. Duarte, C. E. Mayer, *J. Appl. Electrochem.* **2008**, 38, 483.
- [11] J. Yang, D. Sun, J. Li, X. Yang, J. Yu, Q. Hao, W. Liu, J. Liu, Z. Zou, J. Gu, *Electrochim. Acta* **2009**, 54, 6300.
- [12] E. Antolini, *Appl. Catal. B.* **2009**, 88, 1.
- [13] W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, Q. Xin, *Carbon* **2002**, 40, 791.
- [14] W. Li, C. Liang, J. Qiu, H. Lia, W. Zhou, G. Sun, Q. Xin, *React. Kinet. Catal. Lett.* **2004**, 82, 235.
- [15] W. Li, C. Liang, W. Zhou, J. Qiu, Z. Zhou, G. Sun, Q. Xin, *J. Phys. Chem. B* **2003**, 107, 6292.
- [16] S. H. Yoon, H. J. Jin, M. C. Kook, Y. R. Pyun, *Biomacromolecules* **2006**, 7, 1280.
- [17] C. Radiman, G. Yuliani, *Polym. Int.* **2008**, 57, 502.
- [18] W. C. Fernelius, in : "Inorganic Syntheses", 1st ed. vol. II, McGraw-Hill Book Company, New York **1946**, p. 247.

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