DOI: 10.1002/asia.200700422

Nanoelectrocatalyst Based on High-Density Au/Pt Hybrid Nanoparticles Supported on a Silica Nanosphere

Shaojun Guo, Junfeng Zhai, Youxing Fang, Shaojun Dong, and Erkang Wang*[a]

Abstract: A high-efficiency nanoelectrocatalyst based on high-density Au/Pt hybrid nanoparticles supported on a silica nanosphere (Au-Pt/SiO_2) has been prepared by a facile wet chemical method. Scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy are employed to characterize the obtained Au-Pt/SiO_2. It was found that each hybrid nanosphere is composed of high-density small Au/Pt hybrid nanoparticles with rough surfaces. These small Au/Pt hybrid nanoparticles interconnect and form a porous nanostructure, which provides highly accessible activity sites, as required for high electrocatalytic activity. We suggest that the particular morphology of the Au-Pt/SiO_2 may be the reason for the high catalytic activity. Thus, this hybrid nanomaterial may find a potential application in fuel cells.

Keywords: electrochemistry · fuel cell · gold · nanostructures · X-ray absorption spectroscopy

Introduction

Electrocatalytic reactions are of vital importance in electrochemistry and play a key role in emerging technologies related to environmental and energy-related applications, such as fuel cells.[1–3] Considering the importance of the activity of the electrocatalysts used as cathodes and/or anodes for fuel cells, it is not surprising that intensive work has been done during the past decades to design new and improved electrocatalysts.[4–12] A high-efficiency electrocatalyst, which can complete not only the high-potential oxygen electrocatalytic reduction, but also the low-potential methanol electrocatalytic oxidation with high current density, is of great necessity. The development of nanotechnology provides new opportunities for searching or designing an effective nanomaterial that can accomplish the direct four-electron reduction of oxygen to water or electrocatalytic oxidation of methanol. Pt and Pt-based nanomaterials are still indispensable and are shown to be the most effective at present.[4–6,8–12] A significant amount of literature has reported the design of unsupported or supported Pt or alloy catalysts.[4–6,8–12,13–20] For example, Pt or Au/Pt alloy nanospheres have been designed by several groups as high-efficiency electrocatalysts.[7–19] Pt nanoparticles supported on carbon nanotubes (CNTs),[15,20] TiO_2,[21] and carbon[22,23] can also be employed as high-efficiency electrocatalysts for electrocatalytic oxidation of methanol. However, low Pt loading on supported materials greatly limits electrocatalytic performance. Considering the cost of materials, and also realizing a high-performance electrocatalyst, it is necessary to develop a cheaper and more effective hybrid nanomaterial, which is able not only to complete the direct four-electron reduction of oxygen, but also be useful for the methanol electrocatalytic oxidation with high efficiency.

In this paper, we have explored a facile, efficient, and economical route to obtain Au/Pt hybrid nanoparticles supported on silica nanospheres (Au-Pt/SiO_2). It is expected that this hybrid nanostructure will greatly increase the efficient surface-to-volume ratios of Pt. The rapid development of the fuel cell has inspired us to investigate the electrocatalytic properties of this novel hybrid nanomaterial for oxygen and methanol. It was found that the Au-Pt/SiO_2 mentioned here exhibited much higher electrocatalytic activity for oxygen reduction and methanol oxidation than approximately 6 nm Pt nanoparticles, suggesting that silica nanospheres as supporting materials can provide a high surface-to-volume ratio, and greatly increase the electrocatalytic activity of Pt. Several advantages associated with this hybrid

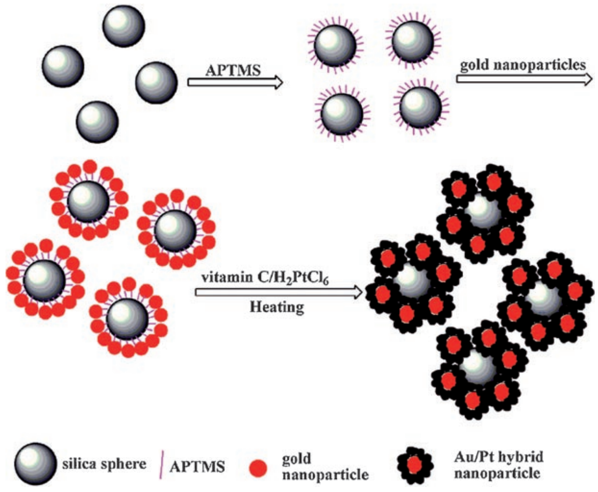
---

[a] S. Guo, J. Zhai, Y. Fang, Prof. S. Dong, Prof. E. Wang
State Key Laboratory of Electroanalytical Chemistry
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun 130022, Jilin (China)
and
Graduate School of the Chinese Academy of Sciences
Beijing, 100039 (China)
Fax: (+86)431-8568-9711
E-mail: ekwang@ciac.jl.cn

nanoelectrocatalyst should be noted. First, the immobilization of hybrid nanoparticles (Au/Pt) on the surface of silica for heterogeneous catalysis may avoid small nanoparticles aggregation, movement, and leaching in the electrocatalytic process.[5] Second, high-density small Au/Pt hybrid nanoparticles interconnect and form a porous nanostructure, which provides highly accessible activity sites. Third, the size of Au/Pt nanoparticles is less than 10 nm, which was reported to be of vital importance to a high electrocatalytic performance for oxygen reduction and methanol oxidation.

Results and Discussion

The whole preparation strategy is shown in Scheme 1. A three-step process was employed to synthesize the Au-Pt/SiO_2. First, silica nanospheres were synthesized by the method described by Stöber et al.[24] and functionalized with an NH_2 group. Second, amino-functionalized silica nanoparticles were mixed with gold nanoparticles to obtain a SiO_2/Au nanocomposite. Third, the Au-Pt/SiO_2 was obtained by heating the SiO_2/Au nanocomposite and a solution of H_2PtCl_6 in the presence of a reductant (vitamin C, VC). A detailed preparation process of Au-Pt/SiO_2 is shown in the Experimental Section.



Scheme 1. Procedure to design Au/Pt hybrid nanoparticles supported on a silica nanosphere.

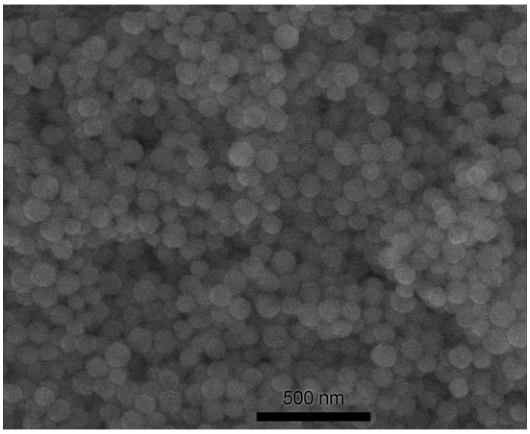


Figure 1. SEM image of silica nanospheres.

The structure and morphology of the resulting product were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1 shows the typical SEM image of the as-prepared silica nanosphere. Monodisperse nanospheres with a size of about 80 nm are observed in the resulting product. After the silica nanoparticles were modified by gold nanoparticles, a monodisperse silica/Au nanocomposite with a rough surface was obtained. The structural details are revealed in Figure 2. The inset of Figure 2 shows the TEM image of the silica/Au nanocomposite. It is observed that a great number of gold nanoparticles with a diameter of 3–6 nm are located on the

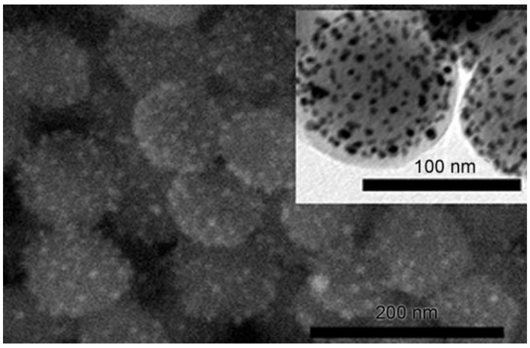


Figure 2. TEM image of the silica/Au nanocomposite.

Abstract in Chinese:

一个湿的化学方法被用于制备基于高密度的金/铂杂化纳米粒子载体于二氧化硅纳米球上的高效纳米电催化剂(Au-Pt/SiO_2)。运用扫描电子显微镜、透射电子显微镜、能量分散的 X 射线光谱以及 X 射线光电子能谱等技术表征所得的 Au-Pt/SiO_2。结果表明每个拥有粗糙表面的杂化纳米球是由高密度的小的金/铂杂化纳米粒子组成的。这些小的金/铂杂化纳米粒子相互交联并形成孔状的纳米结构，这就提供了高活性位置并有助于产生高电催化活性。对该 Au-Pt/SiO_2 应用于氧的电催化还原和甲醇的电催化氧化的研究表明，该新材料具有比~6 nm 铂纳米粒子更高的电催化活性。Au-Pt/SiO_2 提供更高的吸氢和脱氢峰表明 Au-Pt/SiO_2 拥有比~ 6 nm 铂纳米粒子更高的电活性比表面（两个样品中铂的固载量是一样的）。此外，氧还原电位达0.6 V，正于铂纳米粒子修饰的金电极约160 mV。旋转圆盘电极实验演示了 Au-Pt/SiO_2 在空气饱和的 0.5 M 硫酸溶液中呈现近四电子还原氧气到水。进一步，在 Au-Pt/SiO_2 上得到的甲醇氧化电流约三倍高于在铂纳米粒子修饰金电极得到的结果。我们认为，Au-Pt/SiO_2 特别的形貌是上面高催化活性的主要原因。这样，这个拥有高效率电催化性能的杂化纳米材料很可能在燃料电池领域发挥潜在的应用。

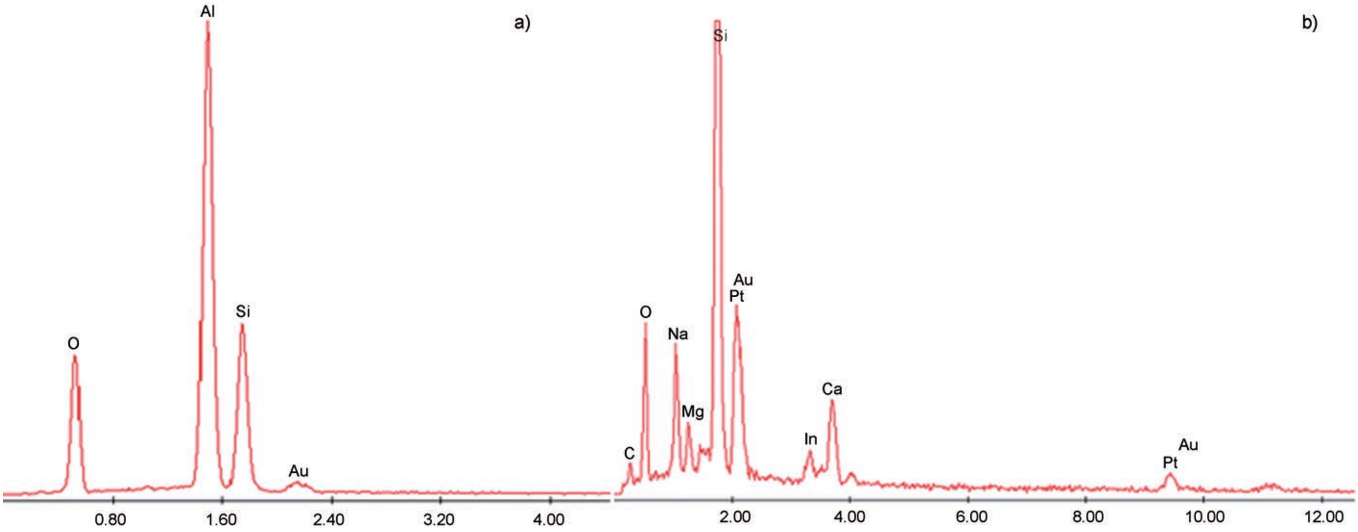


Figure 3. EDX images of the silica/Au nanocomposite (a) and the Au-Pt/SiO_2 (b).

surface of silica nanospheres. In order to prove the presence of gold, Figure 3a shows the energy-dispersive X-ray spectroscopy (EDX) spectrum of the SiO_2/Au nanocomposite. One main peak (Au) was observed (the other peaks originate from the Al glass substrate and silica), indicating that the SiO_2/Au nanocomposites were made up of metallic gold and silica. Figure 4a shows a typical SEM image of the Au-Pt/SiO_2, where numerous hybrid nanospheres are observed. In order to reveal the detailed structure of the Au-Pt/SiO_2, typical TEM images of the Au-Pt/SiO_2 at different magnifications are shown in Figure 4b and Figure 4c. From the magnified image (Figure 4c), it is observed that each hybrid nanosphere is composed of a high-density of small Au/Pt hybrid nanoparticles with a rough surface. These small Au/Pt hybrid nanoparticles with a diameter of 8–10 nm interconnect and form a porous nanostructure, which provides highly accessible activity sites necessary for high electrocatalytic activity. Furthermore, the chemical composition of Au-Pt/SiO_2 was determined by EDX (Figure 3b). The EDX spectrum with two main peaks (Au and Pt) was observed (other peaks originate from the ITO glass substrate and silica), indicating that the Au-Pt/SiO_2 was made up of metallic gold, platinum, and silica. To further confirm the existence of Au, Pt, and silica in the resulting hybrid nanospheres, X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface of the sample. XPS patterns of the resulting Au-Pt/SiO_2 show a significant Pt4f signal corresponding to the binding energy of metallic Pt (Figure 5a), a weak Au4f signal characteristic of metallic Au (Figure 5b), a weak N1s signal characteristic of NH_2 (Figure 5c), and a weak Si2p signal characteristic of silica (Figure 5D). The weak Au4f, N1s, and Si2p signals are probably a result of the fact that the thickness of most Pt shells on the surface of gold nanoparticles located on the top of the silica nanospheres exceeds the detection depth of the X-ray (ca. 10 nm).

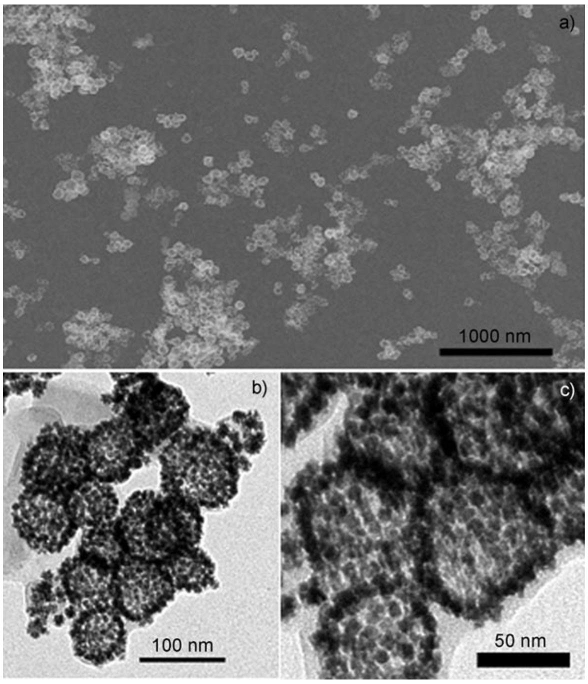


Figure 4. SEM (a) and TEM (b, c) images of the Au-Pt/SiO_2.

The oxygen reduction reaction (ORR) is of indispensable importance in metal–air batteries, fuel cells, as well as in oxygen sensors.[27,28] It is also noted that the electroreduction of oxygen usually requires high current density, low overpotential, and nearly synchronous delivery of four electrons. In this study, we have obtained and characterized the Au/Pt hybrid nanoparticles supported on silica nanospheres. This hybrid nanostructure is expected to have a highly-efficient electrocatalytic performance. Therefore, the electrocatalytic activity of the hybrid nanostructure was first investigated for oxygen reduction. Figures 6c and 6d show the typical cyclic voltammograms (CVs) of oxygen reduction at the Au-Pt/SiO_2-modified gold electrode in a solution of H_2SO_4 (0.5 M)

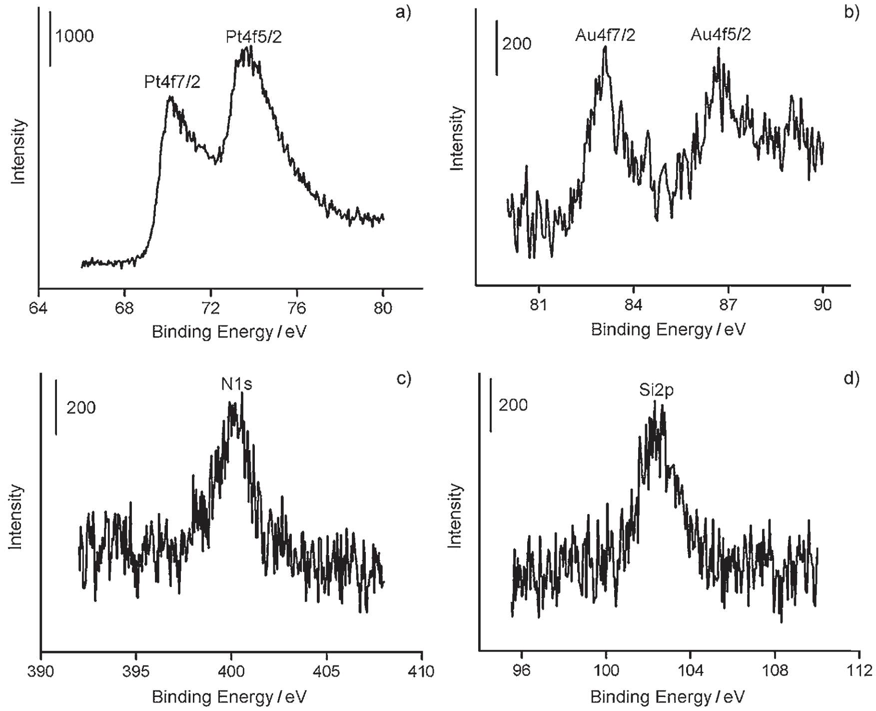


Figure 5. XPS spectra of the as-prepared Au-Pt/SiO_2: a) Pt4f, b) Au4f, c) N1s, and d) Si2p.

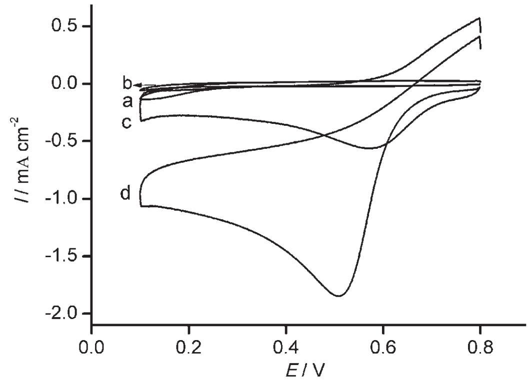


Figure 6. CVs of O_2 reduction at the bare gold electrode- (line a), silica/Au nanocomposite- (lines b and c), and Au-Pt/SiO_2- (line d) modified gold electrode in air-saturated (lines a, b, c) and O_2-saturated (line d) solutions of H_2SO_4 (0.5 M) at a scan rate of 50 mV s.$^{-1}$

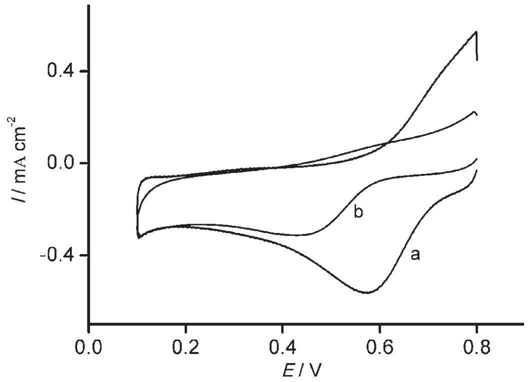


Figure 7. CVs of O_2 reduction at the Au-Pt/SiO_2- (line a) and approximately 6 nm Pt nanoparticle- (line b) modified gold electrode in an air-saturated solution of H_2SO_4 (0.5 M) at a scan rate of 50 mV s.$^{-1}$

in the presence of air and saturated oxygen, respectively. In the presence of air, a remarkable catalytic reduction current occurs at 0.6 V (Figure 6c) at a scan rate of 50 mV s.$^{-1}$ A higher catalytic current for oxygen reduction is observed at 0.52 V in the presence of saturated oxygen (Figure 6d), whereas no catalytic reduction current can be observed at the bare ITO (Figure 6a), and the silica/Au nanocomposite-modified (Figure 6b) electrode in the potential range employed. To further reveal the high electrocatalytic performance of the obtained Au-Pt/SiO_2, the ORR of approximately 6 nm Pt nanoparticles was also investigated. Figure 7 shows the typical CVs of oxygen reduction at the Au-Pt/SiO_2- (a) and the 6 nm Pt nanoparticles- (b) modified gold electrode in a solution of H_2SO_4 (0.5 M) in the presence of air. The Au-Pt/SiO_2-modified gold electrode (Figure 7a) exhibits a more positive potential and higher current for oxygen reduction than that obtained from the 6 nm Pt nanoparticles (Figure 7b). Furthermore, the reduction potential (0.52 V) observed at the Au-Pt/SiO_2-modified electrode is significantly more positive than the other Pt-based electrode.[8b,d] For instance, our group studied the electrocatalytic reduction of oxygen at a Pt-coated Au particle, and observed the reduction of oxygen at about 0.1 V (Ag/AgCl).[8d] Crooks and co-workers reported that the dendrimer-encapsulated Pt nanoparticle-modified electrode shows the reduction peak at about 0.25 V.[8b] Comparing the results obtained at our electrode with those already reported reveals the present electrode to show a higher electrocatalytic activity. Furthermore, the Au-Pt/SiO_2 (Figure 8a) possesses a higher electroactive surface area than that of the 6 nm Pt nanoparticles (Figure 8b), as evidenced by the current associated with the hydrogen adsorption and desorption events. This is probably caused by the fact that the silica particle, as a 3D support, can supply high surface areas for the Au/Pt hybrid nanoparticles, thus leading to more accessible sites for molecular species.

In this study, we have shown that Au-Pt/SiO_2 exhibits a high catalytic current and low overpotential for the reduction of oxygen. The additional important index is the four-

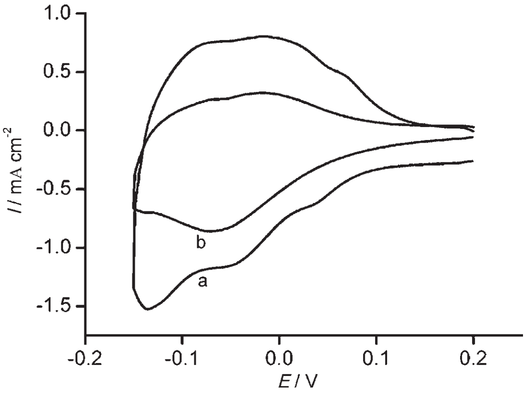


Figure 8. CVs of the Au-Pt/SiO_2-modified gold electrode in a N_2-purged solution of H_2SO_4 (0.5 M) at a scan rate of 50 mV s.$^{-1}$

electron electroreduction of oxygen to water, which is greatly pursued by scientists around the world in view of the important application in fuel cells. Thus, the ORR was also probed by RRDE experiments to demonstrate the ORR process of the Au-Pt/SiO_2, and to see which of the following two reactions [Eq. (1)] and [Eq. (2)] the Au-Pt/SiO_2 would catalyze:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

It is known that the $4e^-$ reduction of oxygen to H_2O is preferred for fuel cells since reduction to H_2O_2 has a lower potential and causes cell degradation. Herein, a rotating GC disk–platinum ring electrode was employed to determine the electron-transfer number (n) of oxygen reduction. Figure 9 shows the voltammetric curves for oxygen reduction recorded at the RRDE with the Au-Pt/SiO_2 films immobilized on the GC disk electrode. The disk potential was scanned from 0.75 to 0.15 V, whereas the ring potential was held at 1.0 V to oxidize the H_2O_2 generated by the O_2 reduction at the disk electrode. A large disk current was obtained whereas almost no ring current was observed, suggesting that the as-prepared hybrid electrocatalysts reduce O_2 predominantly by four electrons to H_2O. The collection efficiency (N) of the ring electrode obtained by reducing ferricyanide at the disk electrode was 0.139. From the ratio of the ring-disk current, the electron-transfer number (n) is calculated to be about 4 (3.92) according to the equation $n = 4 - 2(I_R/I_DN)$.[29]

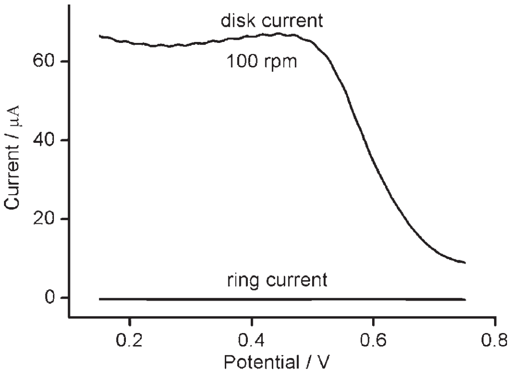


Figure 9. Current-potential curves for the reduction of air-saturated O_2 at a rotating platinum ring–GC electrode with Au-Pt/SiO_2 adsorbed on the disk electrode. The potential of the ring electrode was maintained at 1.0 V with a rotation rate of 100 rpm and a scan rate of 50 mV s.$^{-1}$ The supporting electrolyte was H_2SO_4 (0.5 M).

Recently, direct methanol fuel cells (DMFCs) have been intensely pursued because of their numerous advantages including high energy density, the ease of handling a liquid, low operating temperatures, and their possible applications to micro fuel cells.[30,31] The performance of fuel cells, such as DMFCs, is known to be strongly dependent on the electrocatalytic materials used. Accordingly, for the best DMFC performance, it is essential to develop a good electrocatalytic nanomaterial for exploring the performance of the methanol electrocatalytic oxidation. The electrocatalytic properties of the Au-Pt/SiO_2 hybrid nanostructure toward the methanol oxidation reaction were tested and compared with approximately 6 nm Pt nanoparticles and a bare Pt electrode in a solution of H_2SO_4. A gold plate electrode with a diameter of 2 mm was used. From the CV in Figure 10d, the Au-Pt/SiO_2- modified gold electrode shows a catalytic behavior for the electrooxidation of methanol by the appearance of an oxidation current in the positive potential region. The onset potentials are around 0.3 V (vs. Ag/AgCl). The peak current at about 0.69 V (vs. Ag/AgCl) in the forward scan is attributed to methanol electrooxidation on the hybrid electrocatalysts.[32] This peak current (with the same Pt loadings for two samples tested) is about 3 times higher than that obtained from the 6 nm Pt nanoparticles (Figure 10c) and much higher than that obtained from the bare Pt electrode (Figure 10e). This significant improvement in the catalytic performance can probably be attributed to a particular mor-

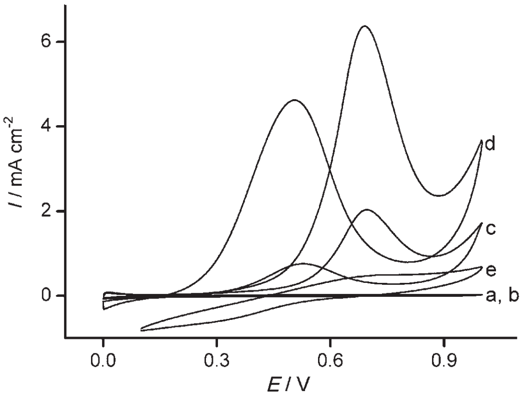


Figure 10. CVs of methanol oxidation at the silica/Au nanocomposite-modified gold electrode (line a), bare gold electrode (line b), approximately 6nm Pt nanoparticles- (line c), Au-Pt/SiO_2- (line d)-modified gold electrode, and bare Pt electrode (line e) in a solution of H_2SO_4 (0.5 M) containing methanol (1 M). Scan rate is 50 mV s.$^{-1}$

phology of the Au-Pt/SiO_2 designed here. In the reverse scan, an oxidation peak is observed at around 0.50 V, which is probably associated with the removal of the residual carbon species formed in the forward scan.[33] In comparison, methanol electrocatalytic oxidation was also investigated on silica/Au nanocomposite-modified gold electrode (Figure 10b) and bare gold electrode (Figure 10a). No oxidation peaks of methanol are observed, indicating that the electrocatalytic current observed in Figure 10d can most likely be ascribed to the high electrocatalytic activity of the Au-Pt/SiO_2 with a high surface-to-volume ratio.

Considering the particular structure of the Au-Pt/SiO_2, three important factors could be responsible for the high electrocatalytic activity mentioned above. First, the Au/Pt hybrid nanostructure was supported on 3D silica nanoparticles. Silica particles, as a 3D support, can supply high surface areas for Au/Pt hybrid nanoparticles, leading to more accessible sites for molecular species. Second, the Au-Pt/SiO_2 itself provides a higher efficient active surface than the Au/Pt bimetallic nanosphere obtained by Zhang and co-workers[34] because of its particular structure (that is, a porous nanostructure with spacings between the Pt nanoparticles on the Au-Pt/SiO_2-modified electrode). Third, the size of Au/Pt nanoparticles is less than 10 nm, which was reported to be of vital importance to a high electrocatalytic performance for oxygen reduction and methanol oxidation.

Conclusions

In summary, by taking advantage of the recent advances in nanotechnology, we demonstrate a novel and highly-efficient nanoelectrocatalyst based on Au/Pt hybrid nanoparticles supported on a silica nanosphere. It is found that the hybrid nanomaterial exhibits higher electrocatalytic activity than the approximately 6 nm Pt nanoparticle, and the bare Pt electrode. The potential for oxygen reduction reaches 0.6 V, which is about 160 mV higher than that obtained on the Pt nanoparticle-modified gold electrode. RRDE voltammetry demonstrates that the Au-Pt/SiO_2 can catalyze an almost four-electron reduction of O_2 to H_2O in an air-saturated solution of H_2SO_4 (0.5 M). Furthermore, the current for methanol oxidation obtained in the Au-Pt/SiO_2-modified gold electrode is about 3 times higher than that obtained on the Pt nanoparticle-modified electrode. It is expected that this hybrid nanomaterial with high-efficiency electrocatalytic performance will be useful for application in fuel cells.

Experimental Section

Chemicals

Tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH), trisodium citrate, vitamin C (VC), $HAuCl_4{\cdot}4H_2O$, $H_2PtCl_6{\cdot}6H_2O$, H_2SO_4, methanol, and ethanol were purchased from Beijing Chemical Factory (Beijing, China) and used as received without further purification. (3-Aminopropyl)trimethoxysilane (APTMS) and nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols, and water) was purchased from Aldrich and used as received. Water used throughout the experiments was purified with the millipore system.

Apparatus

An XL30 ESEM scanning electron microscope equipped with an energy-dispersive X-ray analyzer was used to determine the morphology and composition of products. Transmission electron microscope (TEM) measurements were made on a HITACHI H-8100 EM with an accelerating voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on a carbon-coated copper grid and dried at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. The XPS sample was dropped on an Al substrate. Cyclic voltammetric experiments were performed with a CHI 832 electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including a Ag/AgCl (saturated KCl) electrode as a reference electrode (applying to all electrochemical experiments), a platinum wire as a counterelectrode, and a bare or modified gold electrode as a working electrode. The working electrode was a gold disk with a diameter of about 2 mm, polished with Al_2O_3 paste, and washed ultrasonically in millipore water. An EG&G PARC Model 366 bi-potentiostat was used for rotating ring-disk electrode (RRDE) experiments. A rotating glassy carbon (GC, 5 mm) disk-platinum ring electrode was also used as a working electrode. The collection efficiency (N) of the ring electrode obtained by reducing ferricyanide at a disk electrode was 0.139.

Preparation of Silica/Au Nanocomposite

All glassware used in the following procedures was cleaned in a bath of freshly prepared 3:1 HCl/HNO_3 (aqua regia) and rinsed thoroughly in milli-Q grade water prior to use. Silica nanoparticles with a diameter of about 80 nm were prepared as described by Stöber et al.[24] Briefly, ammonium hydroxide (1.7 mL; 25–28%) was added to dry ethanol (50 mL) with TEOS (1.5 mL) and water (1 mL) then added to the ethanol solution under vigorous magnetic stirring. After 3 h, additional TEOS (1 mL) was added. Silica nanospheres were obtained after stirring for 12 h. Finally, APTMS (0.4 mL) was added for 6 h. The APTMS-functionalized silica nanoparticles were purified by centrifugation and redispersion in water (40 mL). Colloidal gold nanoparticles were prepared according to the reported literature.[25] SiO_2/Au nanocomposites were synthesized by the following approach. Mainly, the APTMS-functionalized silica nanoparticles (2 mL) dispersed in water were placed in a flask (100 mL), and the prepared gold colloid (40 mL) was added. After stirring for several minutes, the red-colored SiO_2/Au nanocomposites were obtained. The purified SiO_2/Au nanocomposites (6.98 mM, calculated by using the silicon atom) were redispersed and sonicated in water (80 mL) until required.

Preparation of Au/Pt Hybrid Nanomaterial Supported on a Silica Nanosphere

The prepared SiO_2/Au nanocomposites (80 mL) were heated to boil. Then, H_2PtCl_6 (2 mL, 1%) and citrate (3 mL, 1%) were added to the solution, followed by the addition of VC (2 mL, 0.1 M). After heating for 30 min, the Au-Pt/SiO_2 (2.41 mM, calculated by using the Pt atom) was obtained. The resulting solution was centrifuged four times and redispersed in water (16 mL). The Au-Pt/SiO_2 was stable in the aqueous solution after storing for one day.

Synthesis of Pt Nanoparticles (ca. 6 nm)

The Pt nanoparticles were synthesized according to the literature.[26] Briefly, an aqueous solution of H_2PtCl_6 (1 mL, 1%) was added to water (100 mL), and heated to boiling. Aging of the solution of H_2PtCl_6 was not necessary in this synthetic procedure. Then, an aqueous solution of sodium citrate (3 mL, 1%) was added rapidly, and the mixture was kept at a boiling temperature for ca. 30 min. The diameter of the Pt nanoparticles was about 6 nm (data not shown) as characterized by using TEM.

Electrocatalytic Experiment

The electrode was loaded with hybrid nanomaterials or Pt nanoparticles (5 μL, the same Pt loadings for two samples tested, 2.35 μg). Electrocatalytic oxygen reduction measurements were carried out in a solution of H_2SO_4 (0.5 M) in the presence of air or saturated oxygen at the scan rate of 50 mV s.$^{-1}$ Methanol electrocatalytic oxidation measurements were carried out in a solution of H_2SO_4 (0.5 M) containing methanol (1 M) at the scan rate of 50 mV s.$^{-1}$ For the RRDE voltammetry experiment, a solution of Au-Pt/SiO_2 (10 μL) was dropped on the GC electrode (5 mm) and allowed to dry at room temperature. Then, nafion (5 μL , 0.2 %) was placed on the surface of the Au-Pt/SiO_2-modified GC electrode.

Acknowledgements

This work was supported by the National Science Foundation of China (Nos. 20575063, 20575064, 20675076, and 20427003).

---

[1] K. Kinoshita, Electrochemical Oxygen Technology, Wiley, New York, **1992**.

[2] F. Matsumoto, S. Uesugi, N. Koura, T. Okajima, T. Ohsaka, *J. Electroanal. Chem.* **2001**, *505*, 150.

[3] E. Frackowiak, G. Lota, T. Cacciaguerra, F. Béguin, *Electrochem. Commun.* **2006**, *8*, 129.

[4] X. Teng, S. Maksimuk, S. Frommer, H. Yang, *Chem. Mater.* **2007**, *19*, 36.

[5] Z. Chen, M. Waje, W. Li, Y. Yan, *Angew. Chem.* **2007**, *119*, 4138; *Angew. Chem. Int. Ed.* **2007**, *46*, 4060.

[6] H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan, C. L. Bai, *Angew. Chem.* **2004**, *116*, 1566; *Angew. Chem. Int. Ed.* **2004**, *43*, 1540.

[7] M. H. Shao, K. Sasaki, R. R. Adzic, *J. Am. Chem. Soc.* **2006**, *128*, 3526.

[8] a) C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, *J. Am. Chem. Soc.* **2007**, *129*, 6974; b) H. Ye, R. M. Crooks, *J. Am. Chem. Soc.* **2005**, *127*, 4930; c) M. Zhao, R. M. Crooks, *Adv. Mater.* **1999**, *11*, 217; d) Y. D. Jin, Y. Shen, S. J. Dong, *J. Phys. Chem. B* **2004**, *108*, 8142; e) S. Guo, Y. Fang, S. Dong, E. Wang, *J. Phys. Chem. C* **2007**, *111*, 17104.

[9] S. Maksimuk, S. Yang, Z. Peng, H. Yang, *J. Am. Chem. Soc.* **2007**, *129*, 8684.

[10] H. Ye, R. M. Crooks, *J. Am. Chem. Soc.* **2005**, *127*, 4930.

[11] Y. Jin, Y. Shen, S. Dong, *J. Phys. Chem. B* **2004**, *108*, 8142.

[12] H. P. Liang, Y. G. Guo, H. M. Zhang, J. S. Hu, L. J. Wan, C. L. Bai, *Chem. Commun.* **2004**, 1496.

[13] L. Wang, S. J. Guo, L. J. Huang, S. J. Dong, *Electrochem. Commun.* **2007**, *9*, 827.

[14] Q. Huang, H. Yang, Y. Tang, T. Lu, D. L. Akins, *Electrochem. Commun.* **2006**, *8*, 1220.

[15] Y. Zhao, L. Fan, H. Zhong, Y. Li, S. Yang, *Adv. Funct. Mater.* **2007**, *17*, 1537.

[16] N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, *Science* **2007**, *316*, 732.

[17] G. Schmid, A. Lehnert, J. Malm, J. Bovin, *Angew. Chem.* **1991**, *103*, 852; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 874.

[18] L. Cao, L. Tong, P. Diao, T. Zhu, Z. Liu, *Chem. Mater.* **2004**, *16*, 3239.

[19] Y. Lou, M. M. Maye, L. Han, J. Luo, C. Zhong, *Chem. Commun.* **2001**, 473.

[20] J. Cao, C. Du, S. C. Wang, P. Mercier, X. Zhang, H. Yang, D. L. Akins, *Electrochem. Commun.* **2007**, *9*, 735.

[21] K. W. Park, S. B. Han, J. M. Lee, *Electrochem. Commun.* **2007**, *9*, 1578.

[22] Y. Song, Y. Li, X. Xia, *Electrochem. Commun.* **2007**, *9*, 201.

[23] C. Xu, L. Cheng, P. Shen, Y. Liu, *Electrochem. Commun.* **2007**, *9*, 997.

[24] W. Stöber, A. Fink, *J. Colloid Interface Sci.* **1968**, *26*, 62.

[25] K. C. Grabar, K. J. Allison, B. E. Baker, R. M. Bright, K. R. Brown, R. G. Freeman, A. P. Fox, C. D. Keating, M. D. Musick, M. J. Natan, *Langmuir* **1996**, *12*, 2353.

[26] M. Huang, Y. Jin, H. Jiang, X. Sun, H. Chen, B. Liu, E. Wang, S. Dong, *J. Phys. Chem. B* **2005**, *109*, 15264.

[27] N. Wakabayashi, M. Takeichi, H. Uchida, M. Watanabe, *J. Phys. Chem. B* **2005**, *109*, 5836.

[28] D. Zhang, D. H. Chi, T. Okajima, T. Ohsaka, *Electrochim. Acta* **2007**, *52*, 5400.

[29] S. Liu, J. Xu, H. Ran, D. Li, *Inorg. Chim. Acta* **2000**, *306*, 87.

[30] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E. S. Smotkin, T. E. Mallouk, *Science* **1998**, *280*, 1735.

[31] T. Hyeon, S. Han, Y. E. Sung, K. W. Park, Y. W. Kim, *Angew. Chem.* **2003**, *115*, 4488; *Angew. Chem. Int. Ed.* **2003**, *42*, 4352.

[32] J. S. Yu, S. Kanf, S. B. Yoon, G. Chai, *J. Am. Chem. Soc.* **2002**, *124*, 9382.

[33] T. Yajima, H. Uchida, M. Watanabe, *J. Phys. Chem. B* **2004**, *108*, 2654.

[34] L. Lu, G. Sun, S. Xi, H. Wang, H. Zhang, *Langmuir* **2003**, *19*, 3074.

Received: December 27, 2007