

DOI: 10.13208/j.electrochem.131171

Artical ID:1006-3471(2014)04-0377-05

Cite this: *J. Electrochem.* 2014, 20(4): 377-381

Http://electrochem.xmu.edu.cn

Pt-TiO₂/Graphene 催化剂的氧还原和 甲醇氧化电催化性能研究

戚 利^{1,2,3}, 殷 璞^{1,2,3}, 涂文广¹, 吴兵兵^{1,2,3}, 王兆生⁵,
刘建国^{1,2,3,4*}, 顾 军^{1,3,4}, 邹志刚^{1,2,3,4}

(1. 南京大学物理学院环境材料与再生能源研究中心, 江苏 南京 210093; 2. 南京大学现代
工程与应用科学学院, 江苏 南京 210093; 3. 江苏省纳米技术重点实验室, 江苏 南京 210093;
4. 南京大学昆山创新研究院, 江苏 南京 210093; 5. 浙江省绍兴县永利新能源
研究院有限公司, 浙江 绍兴 312028)

摘要: 以二(2-羟基丙酸)二氢氧化二铵合钛(TBA)和氧化石墨烯(GO)为前驱体,通过水热法合成出不同TiO₂含量的TiO₂/Graphene(TiO₂/G)复合材料,随之用微波醇热法还原Pt前驱体可得Pt-TiO₂/G催化剂.实验结果表明,TiO₂可与Pt相互作用,添入适量TiO₂的Pt-TiO₂/G催化剂具有较高的氧还原电催化活性及甲醇氧化的电催化活性与稳定性.但TiO₂电导率偏低,过量TiO₂的添入反而使其电催化性能降低.

关键词: TiO₂; 石墨烯; 氧还原; 甲醇氧化

中图分类号: TM911.4

文献标识码: A

质子交换膜燃料电池(PEMFC)由于具有能量密度高、运行温度低、启动时间短和可靠性高等优点而备受关注^[1-5].但目前该燃料电池的阴极和阳极有效催化剂仍以昂贵的铂为主,严重限制了其在商业上的应用.因此,寻找优秀的催化剂载体材料,从而提高铂的利用率、降低铂载量是尤为重要的. TiO₂不仅在强酸碱环境有很好的稳定性,此前报道Pt-TiO₂/C等阴极催化剂有很好的氧还原电催化活性^[6-7],其阳极催化剂也可提高甲醇电催化活性与抗CO中毒能力^[8-9],但TiO₂的低电导率和低比表面限制了其作为催化剂载体的应用.

与其它碳材料相比,石墨烯有较大的理论比表面积(约2630 m²·g⁻¹)和较好的电子传导能力(约2×10⁵ cm²·V⁻¹·s⁻¹),是一种理想的燃料电池催化剂载体材料^[10-11].而石墨烯片层间存在的范德华力会使石墨烯发生团聚,降低催化剂的稳定性.本文通过水热法合成TiO₂/Graphene(TiO₂/G)复合载体.一方

面,通过TiO₂的抗氧化和抗腐蚀能力,可提高载体稳定性,同时也可防止石墨烯片层间的团聚;另一方面,石墨烯可改善TiO₂的低电导率和低比表面的缺点.电化学结果表明,适量TiO₂的加入可以使Pt-TiO₂/G催化剂具有比Pt-G催化剂更高的氧还原和甲醇氧化电催化活性.

1 实 验

1.1 样品制备

参照文献^[12],将40 mL水、20 mL乙二醇、100 mg氧化石墨烯(Hummers法^[10,13])和一定量的二(2-羟基丙酸)二氢氧化二铵合钛(TBA)搅拌混合0.5 h,转入高压反应釜,200 °C反应12 h.该样品过滤并冷冻干燥可得TiO₂/G样品,其中TBA是按TiO₂的质量分数计算确定的.同时根据投料比而计算得到的TiO₂的质量分数,将样品标记为G(0%),TiO₂/G₁(15%),TiO₂/G₂(25%),TiO₂/G₃(35%)和TiO₂/G₄(45%).再以TiO₂/G_x(或G)和H₂PtCl₆·6H₂O的乙二醇溶液为前

收稿日期: 2014-01-17, 修订日期: 2014-03-10 * 通讯作者, Tel: (86-25)83621219, E-mail: jiangnoliu@nju.edu.cn

国家自然科学基金项目(No. 21176111)、浙江省重大科技专项(No. 2012C11014)和绍兴县科技攻关计划项目(No. 2012506)资助

驱体,采用间歇微波法在载体上担载Pt(具体实验参照文献^[2]),获得Pt(20%,by mass)催化剂.

1.2 样品表征

使用透射电镜(FEI Tecnai20 FEG,工作电压200 kV)观察样品形貌.使用Rigaku D/MAX-Ultima II X射线衍射仪表征测试样品($\text{Cu K}\alpha$ 射线, $\lambda=0.15406\text{ nm}$,管压40 kV,管电流40 mA,扫描速率 $10^\circ\cdot\text{min}^{-1}$).在电化学工作站(PARSTAT 2273, Princeton Applied Research)上测试电极性能,三电极体系由工作电极(5 mg催化剂、200 μL Nafion溶液(5%,by mass)和1800 μL 乙醇混合,超声30 min,将20 μL 混合浆料滴于直径5 mm玻碳基底,烘干即可)、饱和甘汞参比电极和铂丝对电极组成.

2 结果与讨论

图1A是 TiO_2/G_2 和 $\text{Pt-TiO}_2/\text{G}_2$ 的XRD谱图.由图可见,纳米 TiO_2 晶型为典型的锐钛矿型.在 $\text{Pt-TiO}_2/\text{G}_2$ 的XRD谱图中,由于Pt的掺入导致 TiO_2 的衍射峰降低,其 $2\theta=40^\circ$ 的衍射峰对应于Pt的(111)晶面衍射峰.图2B是 TiO_2/G_2 的TEM照片,图2C和D是 $\text{Pt-TiO}_2/\text{G}_2$ 的TEM照片,可以看出3~4 nm粒径的Pt纳米颗粒分散在 TiO_2/G_2 载体上.

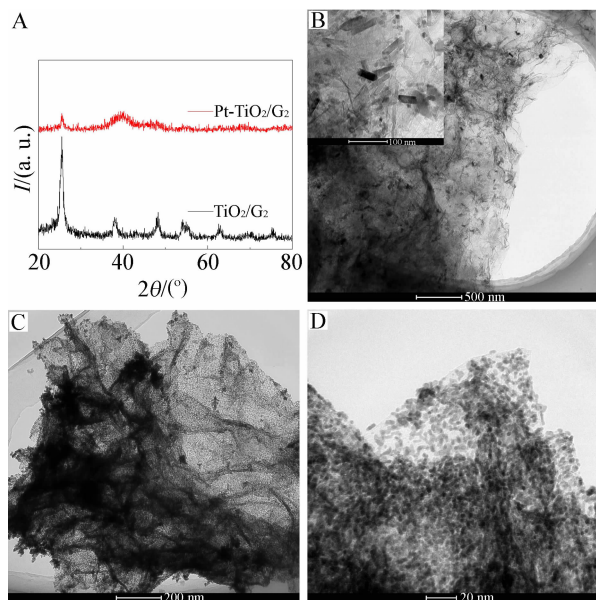


图1 A. TiO_2/G_2 和 $\text{Pt-TiO}_2/\text{G}_2$ 样品的XRD谱图;B. TiO_2/G_2 样品的TEM照片;C、D. $\text{Pt-TiO}_2/\text{G}_2$ 样品的TEM照片
Fig. 1 A. XRD patterns of TiO_2/G_2 and $\text{Pt-TiO}_2/\text{G}_2$; B. TEM image of TiO_2/G_2 ; C, D. TEM images of $\text{Pt-TiO}_2/\text{G}_2$

为研究催化剂的氧还原活性,在氧气饱和的 $0.5\text{ mol}\cdot\text{L}^{-1}\text{ H}_2\text{SO}_4$ 溶液中,利用旋转圆盘电极测定电极的氧还原极化曲线.如图2所示, TiO_2 含量不同,其电极的氧还原电催化活性存在明显差别.

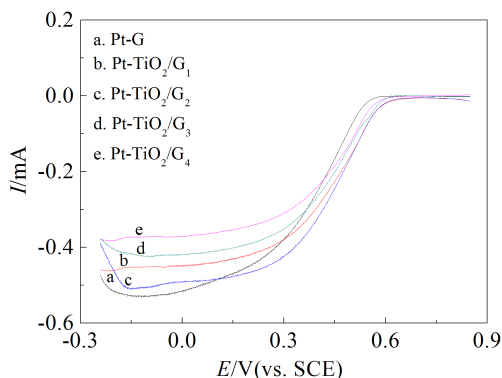


图2 Pt-G和 $\text{Pt-TiO}_2/\text{G}$ 电极在氧气饱和 $0.5\text{ mol}\cdot\text{L}^{-1}\text{ H}_2\text{SO}_4$ 溶液的氧还原极化曲线(扫描速率为 $5\text{ mV}\cdot\text{s}^{-1}$,圆盘电极旋转 $1000\text{ r}\cdot\text{min}^{-1}$)

Fig. 2 Polarization curves of oxygen reduction at Pt-G and $\text{Pt-TiO}_2/\text{G}$ catalysts in O_2 -saturated $0.5\text{ mol}\cdot\text{L}^{-1}\text{ H}_2\text{SO}_4$ solution (scan rate: $5\text{ mV}\cdot\text{s}^{-1}$, rotation speed: $1000\text{ r}\cdot\text{min}^{-1}$)

表1、2列出了各电极的氧还原起始电位(E_{onset})以及不同电位 E 下的氧还原电流(据图2).可以看出,其氧还原起始电位顺序: $\text{Pt-TiO}_2/\text{G}_2 = \text{Pt-TiO}_2/\text{G}_1 > \text{Pt-TiO}_2/\text{G}_3 = \text{Pt-TiO}_2/\text{G}_4 > \text{Pt-G}$,且 $\text{Pt-TiO}_2/\text{G}_2$ 氧还原起始电位相对于Pt-G正移了60 mV.在不同电位下,电极氧还原电流次序如下: $\text{Pt-TiO}_2/\text{G}_2 > \text{Pt-TiO}_2/\text{G}_1 > \text{Pt-TiO}_2/\text{G}_3 > \text{Pt-TiO}_2/\text{G}_4 > \text{Pt-G}$. TiO_2 可改变Pt电子结构,从而提高Pt电极的氧还原活性^[6],这也许是 $\text{Pt-TiO}_2/\text{G}_2$ 和 $\text{Pt-TiO}_2/\text{G}_1$ 电极活性较高的缘由.而 TiO_2 电导率低,其过多掺入导致电极电子转移能力变差^[14],故 $\text{Pt-TiO}_2/\text{G}_3$ 和 $\text{Pt-TiO}_2/\text{G}_4$ 电极氧还原性能相对降低.

表1 各电极的氧还原起始电位(E_{onset})

Tab. 1 Oxygen reduction onset potential (E_{onset}) of Pt-G and $\text{Pt-TiO}_2/\text{G}$ catalysts

	Pt-G	$\text{Pt-TiO}_2/\text{G}_1$	$\text{Pt-TiO}_2/\text{G}_2$	$\text{Pt-TiO}_2/\text{G}_3$	$\text{Pt-TiO}_2/\text{G}_4$
$E_{\text{onset}}/\text{V}$	0.58	0.64	0.64	0.61	0.61

表2 各电极不同电位(*E*)下的氧还原电流

Tab. 2 Oxygen reduction current at different potentials (*E*)
determined from ORR curves

<i>E</i> /V	<i>I</i> /mA				
	Pt-G	Pt-TiO ₂ /G ₁	Pt-TiO ₂ /G ₂	Pt-TiO ₂ /G ₃	Pt-TiO ₂ /G ₄
0.55	0.014	0.667	0.068	0.057	0.039
0.50	0.075	0.152	0.156	1.123	0.116
0.45	0.165	0.226	0.244	0.200	0.184
0.40	0.250	0.292	0.322	0.264	0.238

图3是各电极在0.5 mol·L⁻¹ H₂SO₄溶液的循环伏安曲线. 从图中可以看出,TiO₂含量增加,电极中石墨烯含量相对减少,其双电层电容呈下降趋势. 而其氢的吸-脱附峰出现于0.24~0.10 V之间,若氢单层吸附于电极表面,单层吸附电量0.21 mC·cm⁻²,据氢欠电位沉积计算电极电化学比表面(ECSA),其顺序如下:Pt-TiO₂/G₂ (96 m²·g⁻¹)> Pt-TiO₂/G₃ (86 m²·g⁻¹)> Pt-TiO₂/G₁ (78 m²·g⁻¹)> Pt-TiO₂/G₄ (63 m²·g⁻¹)> Pt-G (31 m²·g⁻¹). 其中,Pt-TiO₂/G₂电极有最大的电化学比表面,是Pt-G电极的3.1倍. 这归因于TiO₂与Pt之间的协同作用^[7,15],TiO₂的添入可增加电极电化学活性表面. TiO₂电导率低,其过量反而会降低电极电化学比表面.

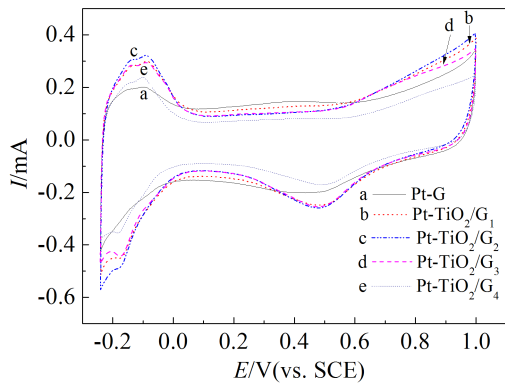


图3 Pt-G和Pt-TiO₂/G电极在氮气饱和0.5 mol·L⁻¹ H₂SO₄溶液的循环伏安曲线,扫描速率20 mV·s⁻¹

Fig. 3 Cyclic voltammograms of Pt-G and Pt-TiO₂/G catalysts in N₂ saturated 0.5 mol·L⁻¹ H₂SO₄ solution with a scan rate of 20 mV·s⁻¹

图4是不同电极在氮气饱和的0.5 mol·L⁻¹

H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH 溶液中的循环伏安曲线. 由图可见,正向扫描时在0.61 V左右出现甲醇的第一次氧化峰,负向扫描在0.20 V左右有甲醇的第二次氧化峰—即甲醇第一次氧化中间产物继续氧化. 其正向扫描时甲醇的起始氧化电位与峰电流分别按如下顺序:Pt-G(0.37 V)> Pt-TiO₂/G₄(0.31 V)> Pt-TiO₂/G₁= Pt-TiO₂/G₃ (0.28 V)> Pt-TiO₂/G₂(0.20 V)和Pt-TiO₂/G₂(3.01 mA)> Pt-TiO₂/G₃(2.89 mA)> Pt-TiO₂/G₁(2.59 mA)> Pt-TiO₂/G₄(2.25 mA)> Pt-G (1.30 mA). 其中Pt-TiO₂/G₂电极的甲醇起始氧化电位相对于Pt-G负移了0.17 V,并且其氧化峰电流是Pt-G的2.3倍. TiO₂改变Pt电子结构^[16],减弱Pt-TiO₂/G电极对CO等中间产物吸附力,从而提高其甲醇电催化性能. 另外,TiO₂表面富有的-OH基团促进甲醇及中间产物的氧化,体现双功能机理^[17]. 添加过量同样降低其甲醇的电催化氧化活性.

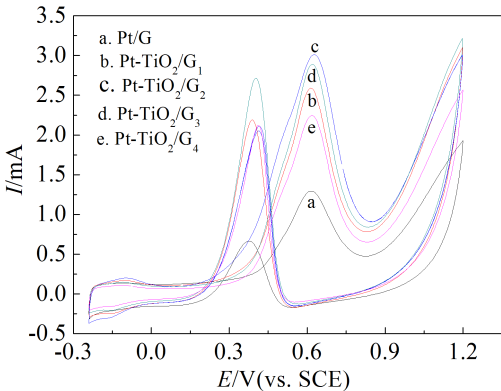


图4 Pt-G和Pt-TiO₂/G电极在氮气饱和的0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH溶液的循环伏安曲线,扫描速率20 mV·s⁻¹

Fig. 4 Cyclic voltammograms of Pt-G and Pt-TiO₂/G catalysts in N₂ saturated 0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH solution with a scan rate of 20 mV·s⁻¹

Pt-G和Pt-TiO₂/G电极的计时电流(*I*-*t*)曲线如图5所示. 其起始脉冲高电流主要源于双电层充电,此外甲醇氧化生成的中间产物(CO_{ads}和CHO_{ads}) 在电极表面积累,导致其中毒,电流随时间的推移迅速衰减. 随后中间产物达到吸附和脱附平衡,其氧化电流最后趋于稳定. 1200 s后,各电极甲醇氧化电流顺序如下:Pt-TiO₂/G₂(0.23 mA)> Pt-TiO₂/G₃ (0.17 mA)> Pt-TiO₂/G₁(0.14 mA)> Pt-TiO₂/G₄(0.07 mA)> Pt-G (0.04 mA). TiO₂在酸性氧化环境有极

好的稳定性,其表面-OH基团能增强Pt电极的抗中毒能力^[9],Pt-TiO₂/G电极有更好的甲醇氧化稳定性。

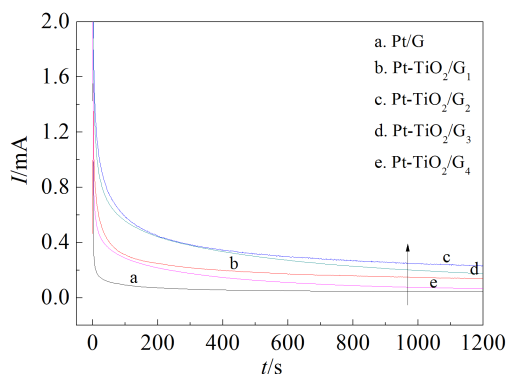


图5 Pt-G和Pt-TiO₂/G电极在氮气饱和0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH溶液中的计时电流 (*I*-*t*) 曲线, 电压为0.6 V

Fig. 5 Chronoamperograms of Pt-G and Pt/TiO₂-G catalysts in N₂ saturated 0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH solution recorded at 0.6 V

3 结 论

通过水热法合成TiO₂/G载体,一方面TiO₂可阻碍石墨烯片层间的团聚,增加了载体的稳定性,另一方面石墨烯可提高载体电导率和比表面。对于Pt-TiO₂/G催化剂,3~4 nm粒径的Pt颗粒分散在载体上,与Pt-G电极相比,添加适量TiO₂使Pt-TiO₂/G电极有更高的氧还原活性(活性比表面96 m²·g⁻¹),其甲醇氧化也有更高的电催化活性和稳定性(1200 s计时安培稳定电流0.23 mA)。但TiO₂电导率低,过量添加反而导致电催化性能下降,故适量的TiO₂/G可作为Pt催化剂的极佳载体材料。

参考文献(References):

- [1] Helmolt R V, Eberle U. Fuel cell vehicles: Status 2007[J]. Journal of Power Sources, 2007, 165(2): 833-843.
- [2] Xin Y C, Liu J G, Jie X, et al. Preparation and electrochemical characterization of nitrogen doped graphene by microwave as supporting materials for fuel cell catalysts[J]. Electrochimica Acta, 2012, 60: 354-358.
- [3] Liu W M, Xie Y, Liu J G, et al. Experimental study of proton exchange membrane fuel cells using Nafion 212 and Nafion 211 for portable application at ambient pressure and temperature conditions[J]. International Journal of Hydrogen Energy, 2012, 37(5): 4673-4677.
- [4] Ye J L, Liu J G, Zou Z G, et al. Preparation of Pt supported on WO₃-C with enhanced catalytic activity by microwave-pyrolysis method[J]. Journal of Power Sources, 2010, 195(9): 2633-2637.
- [5] Wu B B, Li B, Liu W M, et al. The performance improvement of membrane and electrode assembly in open-cathode proton exchange membrane fuel cell[J]. International Journal of Hydrogen Energy, 2013, 38(25): 10978-10984.
- [6] Tiido K, Alexeyeva N, Couillard M, et al. Graphene-TiO₂ composite supported Pt electrocatalyst for oxygen reduction reaction[J]. Electrochimica Acta, 2013, 107: 509-517.
- [7] Liu X, Chen J, Liu G, et al. Enhanced long-term durability of proton exchange membrane fuel cell cathode by employing Pt/TiO₂/C catalysts[J]. Journal of Power Sources, 2010, 195(13): 4098-4103.
- [8] Xia B Y, Wu H B, Chen J S, et al. Formation of Pt-TiO₂-rGO 3-phase junctions with significantly enhanced electro-activity for methanol oxidation[J]. Physical Chemistry Chemical Physics, 2012, 14(2): 473-476.
- [9] Fan Y, Yang Z J, Huang P, et al. Pt/TiO₂-C with hetero interfaces as enhanced catalyst for methanol electrooxidation[J]. Electrochimica Acta, 2013, 105: 157-161.
- [10] Xin Y C, Liu J G, Zhou Y, et al. Preparation and characterization of Pt supported on graphene with enhanced electrocatalytic activity in fuel cell[J]. Journal of Power Sources, 2011, 196(3): 1012-1018.
- [11] Geim A K, Novoselov K S. The rise of graphene[J]. Nature Materials, 2007, 6(3): 183-191.
- [12] Tu W G, Zhou Y, Liu Q, et al. An *in situ* simultaneous reduction-hydrolysis technique for fabrication of TiO₂-Graphene 2D sandwich-like hybrid nanosheets: graphene-promoted selectivity of photocatalytic-driven hydrogenation and coupling of CO₂ into methane and ethane[J]. Advanced Functional Materials, 2013, 23(14): 1743-1749.
- [13] Hummers W S, Offeman R E. Preparation of graphitic oxide[J]. Journal of the American Chemical Society, 1958, 80(6): 1339.
- [14] Montero-Ocampo C, Vargas Garcia J, Arce Estrada E. Comparison of TiO₂ and TiO₂-CNT as cathode catalyst supports for ORR[J]. International Journal of Electrochemical Science, 2013, 8(12): 1278-1280.
- [15] Shim J, Lee C R, Lee H K, et al. Electrochemical characteristics of Pt-WO₃/C and Pt-TiO₂/C electrocatalysts in a polymer electrolyte fuel cell[J]. Journal of Power Sources, 2001, 102(1/2): 172-177.
- [16] Zhao X, Zhu J B, Liang L, et al. Enhanced activity of Pt nano-crystals supported on a novel TiO₂@N-doped C

nano-composite for methanol oxidation reaction[J]. Journal of Materials Chemistry, 2012, 22(37): 19718-19725.

[17] Qu Y T, Gao Y Z, Kong F D, et al. Pt-rGO-TiO₂

nanocomposite by UV-photoreduction method as promising electrocatalyst for methanol oxidation[J]. International Journal of Hydrogen Energy, 2013, 38(28): 12310-12317.

Preparation of Pt-TiO₂/Graphene Composites with High Catalytic Activity towards Methanol Oxidation and Oxygen Reduction Reaction

QI Li^{1,2,3}, YIN Ying^{1,2,3}, TU Wen-guang¹, WU Bing-bing^{1,2,3}, WANG Zhao-sheng⁵,
LIU Jian-guo^{1,2,3,4*}, GU Jun^{1,3,4}, ZOU Zhi-gang^{1,2,3,4}

(1. *Eco-materials and Renewable Energy Research Center, Nanjing University, Nanjing 210093, China;*

2. *College of Engineering and Applied sciences, Nanjing University, Nanjing 210093, China;*

3. *Jiangsu Key Laboratory for Nano Technology, Nanjing University, Nanjing 210093, China;*

4. *Kunshan Innovation Institute of Nanjing University, Nanjing 210093, China;*

5. *Yong Li New Technology Research Institute Company Limited, Shaoxing 312028, Zhejiang, China)*

Abstract: A series of graphene-supported TiO₂ nanoparticles (TiO₂/G) with different TiO₂ contents were prepared by a facile hydrothermal method, and then the Pt-TiO₂/G catalysts were successfully prepared by reducing Pt-precursor with microwave technique. Compared with Pt-G catalysts, the catalytic performance toward oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) of Pt-TiO₂/G catalysts was improved due to the addition of TiO₂. However, the excessive TiO₂ would lead to a poor catalytic performance of Pt-TiO₂/G catalysts because of the low electrical conductivity of TiO₂.

Key words: TiO₂; graphene; oxygen reduction reaction; methanol oxidation