

Cite this: *Chem. Commun.*, 2012, **48**, 2600–2602

www.rsc.org/chemcomm

## COMMUNICATION

## Highly efficient catalysts for Co(II/III) redox couples in dye-sensitized solar cells

Liang Wang,<sup>a</sup> Eric Wei-Guang Diao,<sup>b</sup> Mingxing Wu,<sup>a</sup> Hsueh-Pei Lu<sup>b</sup> and Tingli Ma<sup>\*a</sup>

Received 26th November 2011, Accepted 10th January 2012

DOI: 10.1039/c2cc17389a

**We developed several low-cost catalysts with high catalytic activity, which were used as counter electrodes in dye-sensitized solar cells (DSCs). They showed higher efficiencies than that of Pt. The efficiencies were improved by 18–42% for the DSCs composed of active carbon, niobium dioxide, ordered mesoporous carbon and commercial titanium carbide.**

In the past two decades, the dye-sensitized solar cell (DSC) has been widely investigated by researchers from all over the world due to its high efficiency, low cost and simple procedure since the breakthrough in 1991.<sup>1</sup> So far, the conversion efficiency of DSCs has reached 11% based on conventional iodine electrolytes.<sup>2</sup> However, some problems arise from the use of  $I^-/I_3^-$  redox couple, such as sublimation, the corrosion of metal counter electrodes (CEs) and absorption of visible light.<sup>3,4</sup> Therefore, it is essential to develop alternative redox couples to replace the traditional redox couple. Recently, various organic redox couples including TEMPO/TEMPO<sup>+</sup>,<sup>5</sup> TMTU/TMFDS<sup>2+</sup>,<sup>6</sup> thiolate/disulfide,<sup>7</sup> ferrocene<sup>0/+</sup>,<sup>8</sup> copper(I/II),<sup>9–11</sup> and cobalt(II/III)<sup>12–17</sup> were proposed. One of the redox couples mentioned above, cobalt(II/III), showed an exciting result with D- $\pi$ -A organic dye reported by the Grätzel group. The conversion efficiency has reached 12.3%.<sup>17</sup> This is a promising pathway to improve the performance of the DSC and overcome the drawback of  $I^-/I_3^-$ . However, the volume of cobalt complexes is larger than those of other redox couples. This limited the charge transfer rate and mass transport of the cobalt redox couple in the electrolyte. Therefore, it is necessary to select the thin TiO<sub>2</sub> film and the highly catalytically active CE. In recent years, several types of materials were extensively studied as CEs for DSCs.<sup>18–26</sup> Simple preparation and comparable catalytic activity with Pt for  $I^-/I_3^-$  attract the interest of researchers. However, there are few reports on improving the catalytic activity of CEs for DSCs containing cobalt(II/III).

Based on our previous work on non-Pt catalysts in DSCs,<sup>27–30</sup> intense efforts have been made to seek highly efficient catalysts for cobalt(II/III). One purpose is to improve the catalytic activity of the cobalt redox couple, and the other

is to decrease the cost of catalysts. In this communication, we developed several low-cost materials as CEs to replace Pt in catalyzing cobalt(II/III). It is interesting to see that the highest conversion efficiency of 4.13% has been achieved by employing low-cost commercial titanium carbide (TiC) CEs, higher than the efficiency of Pt by 42%. The synthesized niobium dioxide (NbO<sub>2</sub>), ordered mesoporous carbon (OMC) and common active carbon (Ca) have also shown higher conversion efficiencies than that of Pt.

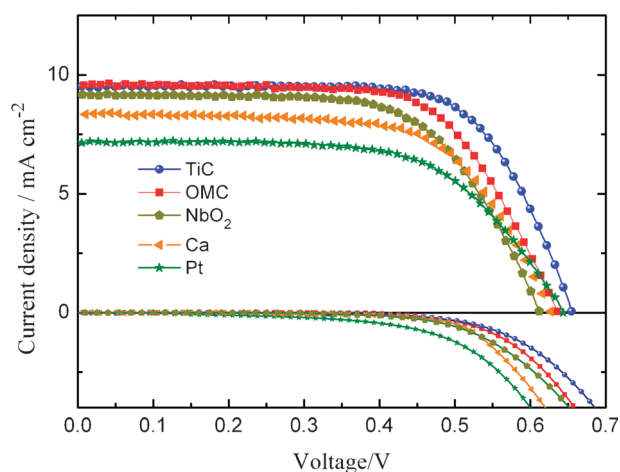
NbO<sub>2</sub> was synthesized according to the literature method developed by our group.<sup>31</sup> In brief, NbCl<sub>5</sub> (1.35 g) was dissolved in 60 mL anhydrous ethanol, followed by the addition of 0.3 g urea. The solution was then vigorously stirred for 2 h, and allowed to stand overnight in an open Petri dish at 50 °C, and then a gel was obtained. The as-prepared gel was annealed at 1100 °C for 3 h under nitrogen. The OMC was prepared using a modified method developed by our group.<sup>29</sup> As for TiC and Ca, they are commercially available. The slurry of CEs was constructed with catalytic materials of CEs (50 mg) and isopropanol (3 mL), all of which needed to be homogenized for 4 h. The CE based on FTO glass was prepared with a simple spray-coating technique.<sup>32</sup> They were then heated at 500 °C for 0.5 h under a nitrogen atmosphere. The thickness of the non-Pt CEs was about 15  $\mu$ m.

The DSCs were fabricated using the following process. Firstly, the FTO (Nippon Sheet Glass, Co., Ltd.) substrate was treated by TiCl<sub>4</sub> aqueous solution.<sup>33,34</sup> Secondly, commercially available TiO<sub>2</sub> paste (Solaronix T/SP, Solaronix) and 160 nm scattering paste were used to fabricate porous TiO<sub>2</sub> films (*ca.* 3  $\mu$ m active layer and 5  $\mu$ m scattering layer) by the screen printing method on the FTO substrate. The obtained TiO<sub>2</sub> electrodes were dipped into ethanol containing 0.2 mM YD-2 for 1.5 h.<sup>35</sup> The dye-sensitized TiO<sub>2</sub> electrodes and CEs of different catalytic materials or Pt CEs were assembled to form DSCs by sandwiching a redox couple (cobalt(II/III) tris(4,4'-di-*tert*-butyl-2,2'-bipyridine), [Co(dtb)<sub>3</sub>]<sup>2+/3+</sup>) in an electrolyte solution composed of 0.22 M cobalt(II), 0.055 M cobalt(III), 0.2 M 4-*tert*-butylpyridine and 0.1 M LiOCl<sub>4</sub> in acetonitrile. The cobalt redox couple was synthesized by the literature method.<sup>15</sup>

Fig. 1 shows the photovoltaic performance of the DSCs based on CEs of TiC, OMC, NbO<sub>2</sub>, Ca and Pt at 1 sun (AM 1.5 G, 100 mW cm<sup>-2</sup>) and 0 sun illumination. As shown in the figure, the values of open-circuit photovoltage ( $V_{oc}$ ), short-circuit photocurrent density ( $J_{sc}$ ) and fill factor (FF) of the DSCs based

<sup>a</sup> State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, China. E-mail: tinglima@dlut.edu.cn; Fax: +86-411-84986230; Tel: +86-411-84986237

<sup>b</sup> Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 300, Taiwan



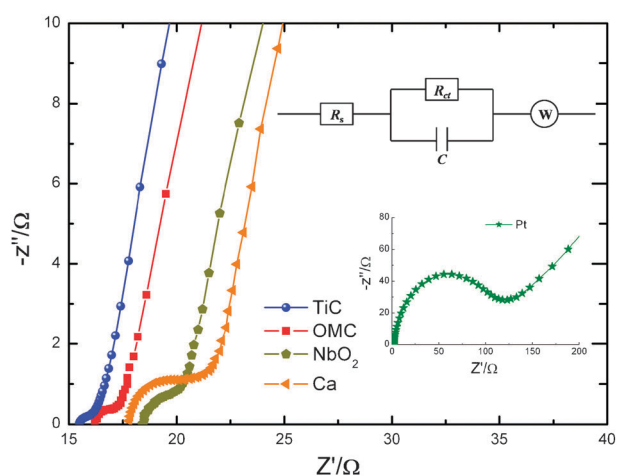
**Fig. 1** Photocurrent–voltage curves of the DSCs based on non-Pt and Pt CEs.

**Table 1** Photocurrent–voltage and EIS parameters of DSCs with different CEs under 1 sun illumination (AM 1.5 G, 100 mW cm<sup>-2</sup>)

Samples	$V_{oc}/V$	$J_{sc}/\text{mA cm}^{-2}$	FF	$\eta/\%$	$R_s/\Omega$	$R_{ct}/\Omega$	$C_{dl}/\mu\text{F}$
TiC	0.64	9.77	0.66	4.13	15.5	0.7	49.1
OMC	0.64	9.59	0.66	4.05	16.2	1.1	30.5
NbO <sub>2</sub>	0.61	9.14	0.65	3.62	18.4	2.8	42.5
Ca	0.63	8.38	0.65	3.43	17.8	7.0	21.6
Pt	0.65	7.23	0.62	2.91	1.6	113.3	2.0

on TiC CEs are 0.64 V, 9.77 mA cm<sup>-2</sup>, and 0.66, respectively, yielding an overall conversion efficiency ( $\eta$ ) of 4.13%. Those values ( $V_{oc}$ ,  $J_{sc}$ , FF and  $\eta$ ) for the Pt CE are 0.65 V, 7.23 mA cm<sup>-2</sup>, 0.62 and 2.91%, respectively. The  $J_{sc}$  and efficiency of DSC with TiC CEs increased by 35% and 42%, respectively, in comparison to that of Pt. The results demonstrate the existence of excellent catalytic activity for cobalt(III) reduction in this system obtained by using TiC CEs. In addition, the photovoltaic results also show the advantage of the other non-Pt catalysts in reducing cobalt(III) to cobalt(II). The corresponding performance parameters of the DSCs are summarized in Table 1.

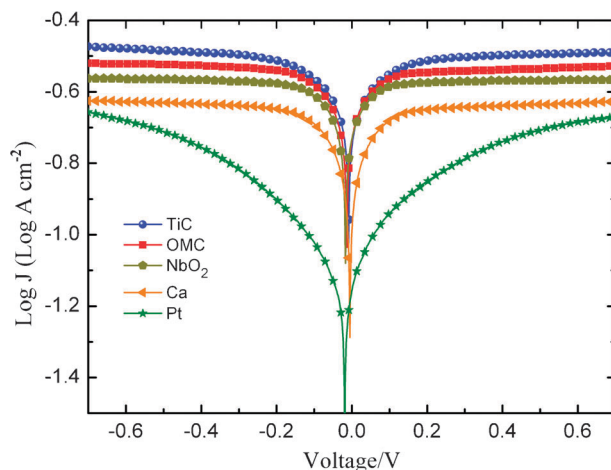
As we know, electrochemical impedance spectroscopy (EIS) is an important method to study the reaction mechanism. Therefore, in order to find out the reason for the improvement of efficiency of DSCs, EIS was employed. Several symmetrical cells were constructed, each cell using two identical electrodes from the following list: TiC, OMC, NbO<sub>2</sub>, Ca and Pt. Fig. 2 shows EIS plots and the equivalent circuit. There are two semicircles in the EIS Nyquist plots of the symmetrical cells. The two semicircles are divided into charge transfer resistance of cobalt(II/III) on the CE (left) and diffusion of cobalt(II/III) in the electrolyte (right). Compared with CEs based on Pt, a larger series resistance ( $R_s$ ) and a smaller charge transfer resistance ( $R_{ct}$ ) on the non-Pt CEs can be observed clearly. A larger arc was observed in the high frequency region in the Pt CE system than that of the non-Pt catalysts system. With respect to photovoltaic performance and EIS fitting data, one can deduce that  $R_{ct}$  of CEs is a major factor in the performance of DSCs. A smaller  $R_{ct}$  suggests higher catalytic activity in the reduction of cobalt(III) to cobalt(II). Due to large volume of the cobalt redox couple, many catalytically active positions on the non-Pt catalyst



**Fig. 2** Typical Nyquist plots from impedance measurements on the symmetrical cells, CE//electrolyte//CE.

surface should be responsible for the high catalytic activity. The chemical capacitance ( $C$ ) indicates that the non-Pt catalysts of TiC, OMC, NbO<sub>2</sub> and Ca have a larger surface area than Pt. In the diffusion region, we can see the high diffusion resistance of the cobalt redox couple in the electrolyte clearly. In conclusion, non-Pt catalysts help to decrease the  $R_{ct}$  and increase catalytic activity significantly. The EIS fitting data are summarized in Table 1.

To further understand the reason for achieving the high efficiency, we measured the Tafel polarization curves for different symmetrical cells. Fig. 3 shows the Tafel curves, which show the logarithmic current density ( $\log J$ ) as a function of voltage. The exchange current density,  $J_0$ , is obtained as the intercept of the extrapolated linear region of the curve when the overpotential is zero. In the curve at high potential (horizontal part), we can obtain the limiting diffusion current density ( $J_{lim}$ ). The  $J_0$  and the  $J_{lim}$  are closely connected with the activity of the catalysts. A higher cathodic slope was found in the symmetrical cells of non-Pt catalysts as compared to that of Pt, as shown in Fig. 3. This indicates a high  $J_0$  on the electrode surface of the non-Pt catalysts. This means non-Pt catalysts can catalyze the reduction



**Fig. 3** Tafel curves of the symmetrical cells fabricated with two identical CEs.

of cobalt(III) to cobalt(II) better than Pt. Furthermore, the  $J_0$  can be obtained according to the following eqn (1):

$$J_0 = \frac{RT}{nFR_{ct}} \quad (1)$$

where  $R_{ct}$  can be obtained from the EIS.  $R$ ,  $T$ ,  $n$  and  $F$  are constants.  $J_0$  varies inversely with  $R_{ct}$ . The introduction of non-Pt catalysts caused an increase in the exchange current density. This demonstrates that the catalytic activity of non-Pt for cobalt(II/III) is higher than that of Pt. The Tafel results are in good agreement with EIS data.

In conclusion, we developed several highly catalytic non-Pt catalysts for the reduction of cobalt(II/III). The DSCs based on commercial TiC CEs showed the highest efficiency of 4.13%, 42% higher than that based on Pt CE. The other non-Pt catalysts also displayed excellent photovoltaic performance. Based on the EIS and Tafel-polarization studies, the non-Pt catalysts showed higher catalytic activity than that of the Pt. Our results demonstrated that non-Pt catalysts were potential alternatives to the expensive and scarce Pt for low-cost DSCs. It is also expected that low-cost carbides are promising catalysts for the organic redox couples in DSCs.

This work is supported by the National High Technology Research and Development Program for Advanced Materials of China (Grant 2009AA03Z220) and the National Natural Science Foundation of China (Grant No. 50773008). This research is also supported by the State Key Laboratory of Fine Chemicals of China.

## Notes and references

- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
- Y. Chiba, *J. Appl. Phys.*, 2006, **45**, L638.
- H. Nusbaumer, S. M. Zakeeruddin, J. E. Moser and M. Grätzel, *Chemistry*, 2003, **9**, 3756.
- Q. Wang, S. Ito, M. Grätzel, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, T. Bessho and H. Imai, *J. Phys. Chem. B*, 2006, **110**, 25210.
- Z. Zhang, *Adv. Funct. Mater.*, 2008, **18**, 341.
- Y. Liu, J. R. Jennings, M. Parameswaran and Q. Wang, *Energy Environ. Sci.*, 2010, **4**, 564.
- M. Wang, N. Chamberland, L. Breau, J. E. Moser, R. Humphry-Baker, B. Marsan, S. M. Zakeeruddin and M. Grätzel, *Nat. Chem.*, 2010, **2**, 385.
- T. Daeneke, T. H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach and L. Spiccia, *Nat. Chem.*, 2011, **3**, 213.
- Y. Bai, Q. Yu, N. Cai, Y. Wang, M. Zhang and P. Wang, *Chem. Commun.*, 2011, **47**, 4376.
- M. Inamo, K. Aoki, N. Ono and H. D. Takagi, *Inorg. Chem. Commun.*, 2005, **8**, 979.
- S. Hattori, Y. Wada, S. Yanagida and S. Fukuzumi, *J. Am. Chem. Soc.*, 2005, **127**, 9648.
- H. Nusbaumer, J.-E. Moser, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Grätzel, *J. Phys. Chem. B*, 2001, **105**, 10461.
- S. A. Sapp, *J. Am. Chem. Soc.*, 2002, **124**, 11215.
- P. Cameron, L. Peter, S. Zakeeruddin and M. Grätzel, *Coord. Chem. Rev.*, 2004, **248**, 1447.
- S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo and A. Hagfeldt, *J. Am. Chem. Soc.*, 2010, **132**, 16714.
- E. A. Gibson, A. L. Smeigh, L. c. Le Pleux, L. Hammarström, F. Odobel, G. Boschloo and A. Hagfeldt, *J. Phys. Chem. C*, 2011, **115**, 9772.
- A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. d. Khaja Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.
- T. N. Murakami, S. Ito, Q. Wang, M. K. Nazeeruddin, T. Bessho, I. Cesar, P. Liska, R. Humphry-Baker, P. Comte and P. Pechy, *J. Electrochem. Soc.*, 2006, **153**, A2255.
- A. Kay and M. Grätzel, *Sol. Energy Mater. Sol. Cells*, 1996, **44**, 99.
- E. Ramasamy and J. Lee, *Chem. Commun.*, 2010, **46**, 2136.
- S. Q. Fan, B. Fang, J. H. Kim, J. J. Kim, J. S. Yu and J. Ko, *Appl. Phys. Lett.*, 2010, **96**, 063501.
- Q. W. Jiang, G. R. Li, F. Wang and X. P. Gao, *Electrochem. Commun.*, 2010, **12**, 924.
- B.-X. Lei, W. J. Fang, Y.-F. Hou, J. Y. Liao, D. B. Kuang and C. Y. Su, *J. Photochem. Photobiol., A*, 2010, **216**, 8.
- K. P. Acharya, H. Khatir, S. Marsillac, B. Ullrich, P. Anzenbacher and M. Zamkov, *Appl. Phys. Lett.*, 2010, **97**, 201108.
- B. Fan, X. Mei, K. Sun and J. Ouyang, *Appl. Phys. Lett.*, 2008, **93**, 143103.
- X. Xin, M. He, W. Han, J. Jung and Z. Lin, *Angew. Chem., Int. Ed.*, 2011, **50**, 11739.
- M. Wu, X. Lin, A. Hagfeldt and T. Ma, *Chem. Commun.*, 2011, **47**, 4535.
- M. Wu, X. Lin, A. Hagfeldt and T. Ma, *Angew. Chem., Int. Ed.*, 2011, **50**, 3520.
- M. Wu, X. Lin, T. Wang, J. Qiu and T. Ma, *Energy Environ. Sci.*, 2011, **4**, 2308.
- M. Wu, Q. Zhang, J. Xiao, C. Ma, X. Lin, C. Miao, Y. He, Y. Gao, A. Hagfeldt and T. Ma, *J. Mater. Chem.*, 2011, **21**, 10761.
- X. Lin, M. Wu, Y. Wang, A. Hagfeldt and T. Ma, *Chem. Commun.*, 2011, **47**, 11489.
- L. Yang, L. Wu, M. Wu, G. Xin, H. Lin and T. Ma, *Electrochem. Commun.*, 2010, **12**, 1000.
- X. Xin, M. Scheiner, M. Ye and Z. Lin, *Langmuir*, 2011, **27**, 14594.
- X. Xin, J. Wang, W. Han, M. Ye and Z. Lin, *Nanoscale*, 2012, **4**, 964.
- T. Bessho, S. M. Zakeeruddin, C. Y. Yeh, E. W. G. Diau and M. Grätzel, *Angew. Chem., Int. Ed.*, 2010, **49**, 6646.