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## COMMUNICATION

## Immobilization of Cobalt Catalyst on Fullerene in Molecular Devices for Water Reduction†

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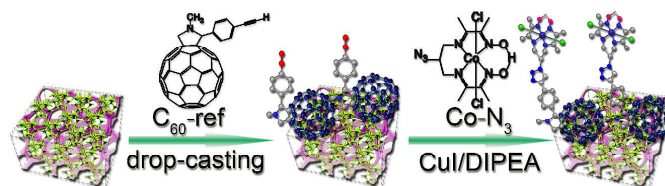
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**A cobalt-based molecular catalyst was successfully grafted to fullerene derivative via ‘click’ chemistry on electrode for both electro-catalytic and light driven water reduction. Using an organic photovoltaic electrode immobilized with cobalt catalyst as photocathode, the photoelectrochemical cell displayed stable photocurrent.**

Hydrogen (H<sub>2</sub>) as an ideal energy carrier has a clean process of energy storage and regeneration cycle without releasing carbon dioxide or other pollutants.<sup>1,2</sup> H<sub>2</sub> production *via* water reduction is a promising strategy to supply this kind of sustainable fuel. Molecular devices<sup>3-11</sup> undertaking electro-catalytic/light-driven proton reduction have attracted intense interests in the community not only due to the ideal model for fundamental study, but also the potential towards highly efficient H<sub>2</sub> production and economic issues. In a molecular device for proton reduction, the molecular catalyst is the heart component. Recently, extensive efforts have been devoted to develop molecular organometallic catalysts, leading to a rapid progress in this field.<sup>2</sup> Developing molecular catalysts for proton reduction based on earth-abundant elements was most feasible.<sup>3,12</sup> In an electro-catalytic device, a key step, in view of application of the molecular catalysts for water splitting in devices<sup>13</sup>, is how to immobilize homogeneous catalysts on the surface of heterogeneous electrodes without losing their reactivity and stability.<sup>14</sup> Therefore, proper methods for combining solid conductors/semiconductors and suitable transition-metal complex catalysts should be developed to efficiently drive the water reduction at a minimum over-potential and under moderate conditions.<sup>5,15</sup> In a light-driven device, besides the immobilization of catalyst on electrode, how to introduce a photosensitizer to harvest photons as well as to undertake charge separation between photosensitizer and catalyst is also a challenge.

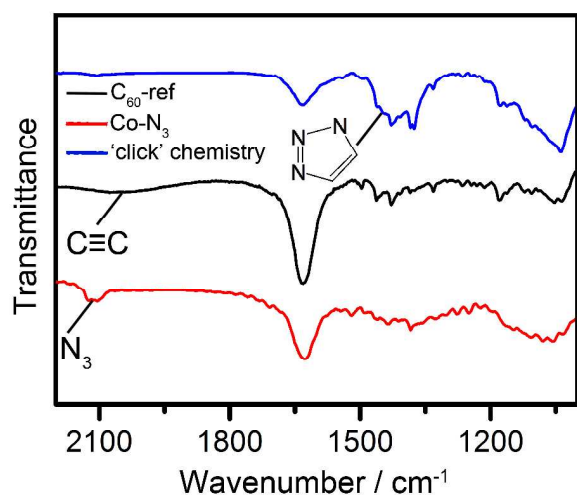
Herein, in this research, we adopted a molecular cobalt-containing hydrogen production catalyst (diimine-dioxime cobalt catalyst, Co-N<sub>3</sub>),<sup>7</sup> which was grafted to C<sub>60</sub> derivative<sup>16</sup> (N-Methyl-2-(4'-ethynyl) phenyl-3,4-fulleropyrrolidine, C<sub>60</sub>-ref) on substrate electrodes *via* click chemistry for both bulk electrolysis and photoelectrochemical cell (PEC). In the bulk electrolysis experiment, carbon cloth (CC)

substrate electrode was employed and acted as the underlying platform for electron transfer and the template for the self-assembly of C<sub>60</sub>-ref. The cobaloxime catalyst Co-N<sub>3</sub> has been used in bulk electrolysis application with carbon nanotube electrode also prepared *via* a click chemistry strategy by Artero and co-workers.<sup>7</sup> Inspired by the study of electron extraction and transfer by fullerene on electrode and organic photovoltaic (OPV)-based photocathodes for water reduction,<sup>17-20</sup> we further transplanted C<sub>60</sub>-ref clicked by Co-N<sub>3</sub> catalyst electron acceptor onto OPV electrodes, employing Poly(3-hexylthiophene-2,5-diyl) (P3HT) as photosensitizer to construct a PEC cell, which rendered stable photo-catalytic current. The direct linkage between fullerene and catalyst in solar fuel device is proposed for the first time. This work points out a promising step and concept to develop an integrated electro- and photo-material for application in hydrogen evolution.



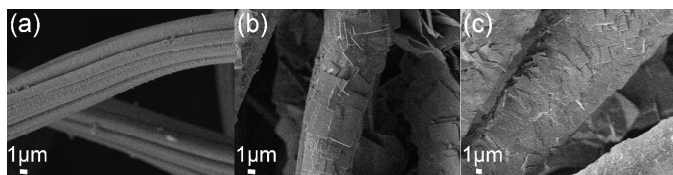
**Scheme 1** Modification of the carbon cloth electrode with C<sub>60</sub>-ref and coupling of Co-N<sub>3</sub> by ‘click’ reaction.

The preparation of electrode for bulk electrolysis consists of grafting C<sub>60</sub>-ref with terminal alkyne on the CC by drop-casting method, and subsequently coupling with Co-N<sub>3</sub> *in situ* via copper (I)-catalyzed azide-alkyne cyclo-addition (CuAAC or ‘click’) reaction, as depicted in Scheme 1. The advantages of this strategy include: (1) C<sub>60</sub>-ref has a robust interaction with CC; (2) the reduction of C<sub>60</sub>-ref cannot dissolve in aqueous condition; (3) the linkage between catalysts and surface is a robust triazole ring that is beneficial for stability of electrode; (4) CuAAC is a convenient fast reaction even regarding heterogeneous coupling conditions.<sup>21</sup>



**Fig. 1** FTIR transmission spectra of  $C_{60}$ -ref in KBr,  $Co-N_3$  in KBr, and the same sample of  $C_{60}$ -ref in KBr modified with  $Co-N_3$ .

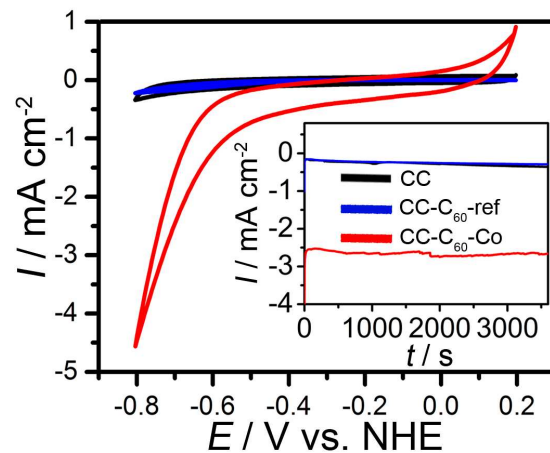
The success of 'click' reaction was identified by FTIR technique. From the FTIR spectra of KBr tablets of  $C_{60}$ -ref,  $Co-N_3$ , and  $Co-N_3$  modified  $C_{60}$ -ref (Fig. 1), one can see  $C_{60}$ -ref shows a characteristic broad peak at  $2076\text{ cm}^{-1}$  assigned to the stretching vibration of terminal alkyne. For  $Co-N_3$  sample, the characteristic asymmetric stretching vibration of  $N_3$  is observed at  $2113\text{ cm}^{-1}$ .<sup>22</sup> After the 'click' reaction, both of the stretching vibration of terminal alkyne in  $C_{60}$ -ref and the characteristic stretching vibration of  $N_3$  are completely disappeared, and the characteristic triazole band at around  $1445\text{ cm}^{-1}$  are appeared,<sup>23, 24</sup> which strongly suggested that the cobalt catalyst was bound to  $C_{60}$  derivative *via* triazole unit. It is mentioned by Artero and co-workers that standard copper-catalyzed conditions for the azide-alkyne cycloaddition reaction could result in substitution of the cobalt ion by copper;<sup>7</sup> However, based on UV-Vis (Fig. S2), EDS (Table S1 and Fig. S8) as well as MS spectra measurements (Fig. S9-S12), we cannot conclude that Co atom in Co catalyst is not replaced by Cu(I) in presence of CuI in our experiment.



**Fig. 2** SEM of bare CC electrode (a),  $CC-C_{60}-Co$  electrode before (b) and after (c) the bulk electrolysis.

The morphologies of the electrodes shown in Fig. 2 are obtained by scanning electron microscope (SEM). Fig. 2a shows the SEM image of bare CC electrode, in which we can see the surface of the CC is quite smooth, while after the modification of  $C_{60}$ -ref reacted by  $Co-N_3$  (coded as  $C_{60}-Co$ ), 2D plate-like structure of fullerene with catalyst was self-assembly on the CC surface (as shown in Fig. 2b). The mechanism for formation of this kind of structure is described as follows; firstly, the subunits in the  $C_{60}$ -ref derivative determines the favored orientation for the formation of the sheetlike structure, and then further associates to form the stacked plate-like structure; secondly, the uniformed structure is ascribed to the strong intermolecular  $\pi-\pi$  interaction<sup>25</sup> between the near fullerene moieties, and  $\pi-\pi$  interaction is also the main reason for binding the nanostructure to the CC electrode stably; the

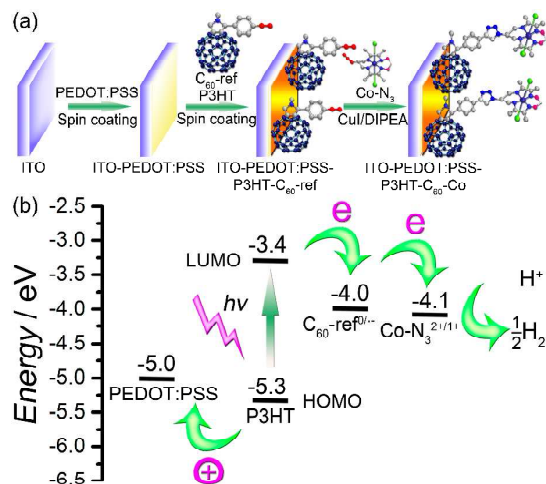
third is the electronic interaction between the donor azo fragment and acceptor fullerene, which attributes to the high self-assembling tendency.<sup>26</sup> Finally, the polarity of the chloroform solvent plays a vital role for the structure as well.<sup>27</sup> The  $C_{60}-Co$  on the surface of CC was extremely stable. After more than 1 h bulk electrolysis, the stacked square-like structure can still be easily recognized (see Fig. 2c), implying the stability of this kind electrode is satisfactory.



**Fig. 3** Cyclic voltammetry of CC electrode,  $CC-C_{60}$ -ref electrode, and  $CC-C_{60}-Co$  electrode in acetate buffer (0.1 M, pH 4.5) saturated with Ar gas at a scan rate of  $50\text{ mV s}^{-1}$ . Inset: evolution of the current density during an electrolysis experiment performed on the corresponding electrodes at  $-1.0\text{ V vs. Ag/AgCl}$  ( $-0.8\text{ V vs. NHE}$ ) in the same testing solution.

To measure the electro-catalytic activity of the optimal  $CC-C_{60}-Co$  electrode (see Fig. S3) for water reduction, both cyclic voltammetry (CV) measurements and bulk electrolysis were conducted in pH 4.5 acetate buffer (0.1 M) aqueous solution in a three-electrode system. CC-based electrode was used as working electrode (WE), platinum foil (Pt,  $2\text{ cm}^2$ ) was employed as counter electrode (CE) and Ag/AgCl (saturated KCl aqueous solution) was introduced as reference electrode (RE). Fig. 3 shows the CV curves of different electrodes. Both of the CC and  $CC-C_{60}$ -ref electrodes did not show any obvious reduction catalytic current in the scan range. However,  $CC-C_{60}-Co$  electrode rendered a significant catalytic response to the reduction of water, and the catalytic current density was initially as high as  $4\text{ mA cm}^{-2}$  at  $-0.8\text{ V vs. normal hydrogen electrode (NHE)}$ . The onset potential for the  $H_2$  reduction by the  $CC-C_{60}-Co$  electrode is about  $-0.5\text{ V vs. NHE}$ , showing an over potential for the  $H_2$  evolution is ca.  $0.2\text{ V}$ . For the catalytic stability assessment in bulk electrolysis, the electrodes were then equilibrated at a constant potential of  $-0.8\text{ V vs. NHE}$  in same acetate buffer solution for a certain time (see the inset in Fig. 3). The corresponding current density was recorded and the total charge passed through the cell was calculated. The current of  $CC-C_{60}-Co$  electrode is dropped rapidly during first several seconds probably due to desorption of the physically adsorbed catalysts, and then it kept constant at  $2.7\text{ mA cm}^{-2}$  for more than 1 h. The stable fixation of catalyst with fullerene on the electrode surface should be responsible for the constant electrolysis current. After the passage of the charge for one hour, the accumulated charge value was recorded as  $9.57\text{ C}$ . A substantial quantity of  $H_2$ ,  $1.08\text{ mL}$ , in the headspace above the electrolyte was further detected by gas-chromatography and the generated  $H_2$  amount was  $48.1\text{ }\mu\text{mol}$ .<sup>28</sup> Meanwhile, the generated  $O_2$  amount was  $24.3\text{ }\mu\text{mol}$ . The faradaic efficiency of hydrogen evolution was determined to be 97%.

The electrochemistry is a conventional method to determine the amount of catalyst on the bulk electrode. However, in the aqueous solution, it is hard to detect the characteristic reduction peak of catalyst on our CC-C<sub>60</sub>-Co electrode, thus it is impossible to estimate the amount of active catalyst or attached catalyst in aqueous condition. Subsequently, we found it is possible to get all compounds off from CC electrode with a negative potential scan in electrochemistry experiment in acetonitrile (MeCN), ascribing to the good solubility of reduction species in MeCN, and the reduction peak of the cobalt catalyst can be detected as a consequence, which also implies that the catalyst is still survival after electrolysis experiment. The coverage of catalyst on the CC-C<sub>60</sub> electrode can be estimated according to the standard curve of the pure Co-N<sub>3</sub> catalyst in MeCN (Fig. S4 and Fig. S5). According to the calculation, the total amount of catalyst on CC electrode is determined to be 2.6×10<sup>-7</sup> mol cm<sup>-2</sup>, and the turnover number (TON) is 190 in 1 h electrolysis. Taken into account by the morphology of electrode, not all of catalysts are expected to be active for H<sub>2</sub> production in aqueous solution due to the poor wettability of water on electrode. Therefore, it is still difficult for us to get the real amount of active catalyst on electrode and provide a reliable turnover number. As a result, the turnover number reported here is much underestimated. However, the catalytic current of CC-C<sub>60</sub>-Co electrode in this work obtained is ca. a factor of 3 greater than that reported in the cobalt catalyst modified carbon nanotube electrode<sup>7</sup> under the same condition, probably owing to the increment of active catalyst loading on the electrode.

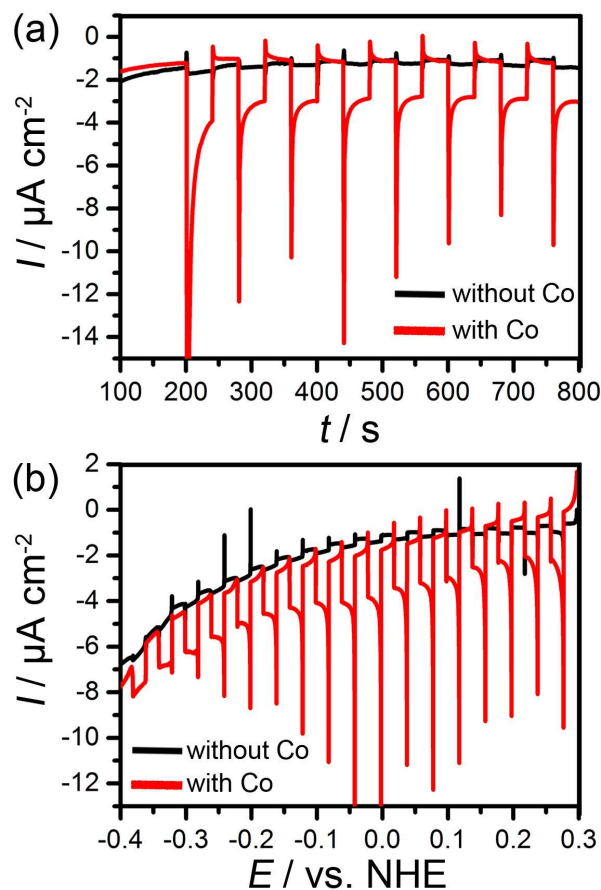


**Fig. 4** (a) Preparation of the organic photovoltaic (OPV)-based PEC electrode with Co catalyst by ‘click’ chemistry. (b) The energy level diagram depicting the relevant energy levels under flat band conditions of all materials used in the photocathode.

In order to fabricate a PEC device, the design of the electrode for electro-catalysis was further transplanted on OPV photocathode (Fig. 4a), adopting P3HT as photosensitizer. Different from Scheme 1, the indium tin oxide conduction glass (ITO) was used as substrate electrode instead of CC. Firstly, the PEDOT:PSS hole transport layer was spin-coated on the surface of ITO, and then, the same operation was performed to form the bulk film of P3HT and C<sub>60</sub>-ref. Finally, the Co-N<sub>3</sub> catalyst was immobilized to C<sub>60</sub>-ref by click chemistry *via* the active sites of acetylene group on electrode surface.

Fig. 4b shows the energy level diagram of different components used in the OPV photocathode. The working principle of photocathode electrode is similar to the classic OPV electrode. The highest occupied molecular orbital (HOMO) level of PEDOT:PSS, -5.0 eV,<sup>29-33</sup> is more positive than that of P3HT, -5.3 eV,<sup>34</sup> implying

that the hole injection from excited P3HT after light harvesting to PEDOT:PSS is thermodynamically feasible.<sup>35</sup> Based on the calculation from electrochemistry,<sup>32</sup> the potentials of C<sub>60</sub>-ref<sup>0/-</sup> and Co-N<sub>3</sub><sup>2+/1+</sup> are estimated to be -4.0 eV and -4.1 eV, respectively (see Fig. S6). Also, the lowest unoccupied molecular orbital (LUMO) level of P3HT is more negative than the reduction potential of C<sub>60</sub>-ref, thus the charge transfer between P3HT and C<sub>60</sub>-ref is also thermodynamically feasible. Then, it is expected to occur an intermolecular charge transfer between reduced fullerene and cobalt catalyst *via* triazole linker to generate cobalt (I) species, which further reduces protons to hydrogen.<sup>7</sup>



**Fig. 5** (a) Transient photocurrent response curves of the OPV photocathodes with and without the immobilization of Co catalyst at -0.3 V vs. Ag/AgCl (-0.1 V vs. NHE) electrode. (b) LSV of the OPV photocathodes with and without Co catalyst. The scan direction was from positive potential (0.2 V vs. NHE) to negative potential (-0.4 V vs. NHE). The scan rate is 1 mV s<sup>-1</sup>.

The OPV photocathode as WE is also evaluated by three electrodes system with Pt as CE and Ag/AgCl as RE. Transient photocurrent response experiments of the electrode with (ITO/PEDOT:PSS/P3HT/C<sub>60</sub>-Co) and without (ITO/PEDOT:PSS/P3HT/C<sub>60</sub>-ref) cobalt catalyst were conducted. Fig. 5a shows the transient photocurrent response of different samples under the same condition and Fig. 5b displays the linear sweep voltammograms (LSV) of the same assembled electrodes. The light with an intensity of 100 mW cm<sup>-2</sup> was periodically illuminated at a bias potential of -0.1 V vs. NHE. The photocurrent reaches a plateau at about 3 μA cm<sup>-2</sup> for the ITO/PEDOT:PSS/P3HT/C<sub>60</sub>-Co electrode, while there is only slight response for ITO/PEDOT:PSS/P3HT/C<sub>60</sub>-ref electrode, confirming that the observed current under light illumination is really photocurrent, and the stable photocurrent plateau demonstrated the high stability of the



cobalt catalyst at the electrode for the reduction of proton. The small electron transfer driving force (0.1 eV) between fullerene and catalyst could be responsible for the low photocurrent.

## Conclusions

In summary, the molecular cobaloxime (Co-N<sub>3</sub>) catalyst was successfully immobilized with fullerene compound (C<sub>60</sub>-ref) by 'click' chemistry *in situ* on carbon cloth (CC) electrode and an organic photovoltaic (OPV) electrode for bulk electrolysis and PEC cell for water reduction. The fabricated CC-C<sub>60</sub>-Co electrode shows efficient hydrogen evolution activity, and a constant catalytic current of 2.7 mA cm<sup>-2</sup> is reached at -0.8 V vs. NHE in bulk electrolysis experiment. The faradaic efficiency of hydrogen evolution was determined to 97% after 1 h electrolysis. The PEC cell based on OPV electrode with cobalt catalyst displayed stable photocurrent, indicating the potential of light driven water splitting to generate hydrogen. Although the photocurrent obtained in this work is not ideal, this is the first time to consider the linkage of fullerene and catalyst together to construct PEC cell based on OPV concept and the methodology provides a simple and reliable approach for the transformation from a homogeneous catalyst to a functional electrode for water reduction. Optimizing the configuration of electrode, tuning the driving force between fullerene and catalyst by structural modification, improving efficiency by preventing the strong electron recombination in the system and developing other metal-based proton reduction catalysts are still on-going, aiming to construct the efficient light-driven water splitting device. The CO<sub>2</sub> reduction is also being considered to be conducted using the same concept, but with different catalysts.

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## Notes and references

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- Zhang, M. Wang, Y. Yang, T. Yao and L. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 13803.
- Jiang, F. Li, B. Zhang, X. Li, X. Wang, F. Huang and L. Sun, *Angew. Chem. Int. Ed.*, 2013, **52**, 3398.
- J.-J. Wang, Z.-J. Li, X.-B. Li, X.-B. Fan, Q.-Y. Meng, S. Yu, C.-B. Li, J.-X. Li, C.-H. Tung and L.-Z. Wu, *ChemSusChem*, 2014, DOI: 10.1002/cssc.201400096.
- A. Krawicz, J. Yang, E. Anzenberg, J. Yano, I. D. Sharp and G. F. Moore, *J. Am. Chem. Soc.*, 2013, **135**, 11861.
- A. J. Clough, J. W. Yoo, M. H. Mecklenburg and S. C. Marinescu, *J. Am. Chem. Soc.*, 2015, **137**, 118.
- T. Nann, S. K. Ibrahim, P.-M. Woi, S. Xu, J. Ziegler and C. J. Pickett, *Angew. Chem. Int. Ed.*, 2010, **49**, 1574.
- E. S. Andreiadis, P.-A. Jacques, P. D. Tran, A. Leyris, M. Chavarot-Kerlidou, B. Jousselme, M. Matheron, J. Pecaut, S. Palacin, M. Fontecave and V. Artero, *Nat. Chem.*, 2013, **5**, 48.
- A. Call, Z. Codola, F. Acuna-Pares and J. Lloret-Fillol, *Chem. Eur. J.*, 2014, **20**, 6171.
- C.-B. Li, Z.-J. Li, S. Yu, G.-X. Wang, F. Wang, Q.-Y. Meng, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, *Energy Environ. Sci.*, 2013, **6**, 2597.
- P.-A. Jacques, V. Artero, J. Pecaut and M. Fontecave, *PNAS*, 2009, **106**, 20627.
- L. Tong, A. Iwase, A. Nattestad, U. Bach, M. Weidener, G. Goetz, A. Mishra, P. Baeuerle, R. Amal, G. G. Wallace and A. J. Mozer, *Energy Environ. Sci.*, 2012, **5**, 9472.
- L. Li, L. Duan, F. Wen, C. Li, M. Wang, A. Hagfeld and L. Sun, *Chem. Commun.*, 2012, **48**, 988.
- P. D. Tran, V. Artero and M. Fontecave, *Energy Environ. Sci.*, 2010, **3**, 727.
- F. Li, L. Li, L. Tong, Q. Daniel, M. Gothelid and L. Sun, *Chem. Commun.*, 2014, **50**, 13948.
- F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li and L. Sun, *Angew. Chem. Int. Ed.*, 2011, **50**, 12276.
- A. Lembo, P. Tagliatesta and D. M. Guldi, *J. Phys. Chem. A*, 2006, **110**, 11424.
- T. Bourgeteau, D. Tondelier, B. Geffroy, R. Brisse, C. Laberty-Robert, S. Campidelli, R. de Bettignies, V. Artero, S. Palacin and B. Jousselme, *Energy Environ. Sci.*, 2013, **6**, 2706.
- A. Guerrero, M. Haro, S. Bellani, M. R. Antognazza, L. Meda, S. Gimenez and J. Bisquert, *Energy Environ. Sci.*, 2014, **7**, 3666.
- M. Haro, C. Solis, G. Molina, L. Otero, J. Bisquert, S. Gimenez and A. Guerrero, *J. Phys. Chem. C*, 2015, **119**, 6488.
- L. Zhang, S. S. Roy, C. R. English, R. J. Hamers, M. S. Arnold and T. L. Andrew, *ACS Nano*, 2015, **9**, 2510.
- L. Tong, M. Gothelid and L. Sun, *Chem. Commun.*, 2012, **48**, 10025.
- L. Luo and C. D. Frisbie, *J. Am. Chem. Soc.*, 2010, **132**, 8854.
- H. B. Li, Q. L. Zheng and C. P. Han, *Analyst*, 2010, **135**, 1360.
- J. D. Kim, Y. Oba, M. Ohnuma, M. S. Jun, Y. Tanaka, T. Mori, Y. W. Choi and Y. G. Yoon, *J. Electrochem. Soc.*, 2010, **157**, B1872.
- T. Wakahara, M. Sathish, K. i. Miyazawa, C. Hu, Y. Tateyama, Y. Nemoto, T. Sasaki and O. Ito, *J. Am. Chem. Soc.*, 2009, **131**, 9940.
- K. S. Kumar and A. Patnaik, *Langmuir*, 2011, **27**, 11017.
- M. Sathish and K. i. Miyazawa, *J. Am. Chem. Soc.*, 2007, **129**, 13816.
- H. B. Yang, J. Miao, S.-F. Hung, F. Huo, H. M. Chen and B. Liu, *ACS Nano*, 2014, **8**, 10403.
- R. L. Chamousis, L. Chang, W. J. Watterson, R. D. Montgomery, R. P. Taylor, A. J. Moule, S. E. Shaheen, B. Ilan, J. van de Lagemaat and F. E. Osterloh, *J. Mater. Chem. A*, 2014, **2**, 16608.
- D. A. Rider, B. J. Worfolk, K. D. Harris, A. Lalany, K. Shahbazi, M. D. Fleischauer, M. J. Brett and J. M. Buriak, *Adv. Funct. Mater.*, 2010, **20**, 2404.
- I. S. Oh, G. M. Kim, S. H. Han and S. Y. Oh, *Electronic Mater. Lett.*, 2013, **9**, 375.
- S. Kumar, C. Borriello, G. Nenna, R. Rosentsveig and T. Di Luccio, *Eur. Phys. J. B*, 2012, **85**, 160.
- J. Weickert, H. Sun, C. Palumbiny, H. C. Hesse and L. Schmidt-Mende, *Solar Energy Mater. Solar Cells*, 2010, **94**, 2371.
- M. Vasilopoulou, A. Soutlati, D. G. Georgiadou, T. Stergiopoulos, L. C. Palilis, S. Kennou, N. A. Stathopoulos, D. Davazoglou and P. Argitis, *J. Mater. Chem. A*, 2014, **2**, 1738.
- H. Tian, J. Oscarsson, E. Gabriellsson, S. K. Eriksson, R. Lindblad, B. Xu, Y. Hao, G. Boschloo, E. M. J. Johansson, J. M. Gardner, A. Hagfeldt, H. Rensmo and L. Sun, *Sci. Rep.*, 2014, **4**, 4282.