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The Plausible Role of Carbonate in Photo-Catalytic Water Oxidation Processes.

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Abstract: DFT calculations point out that the photo-oxidation of water on GaN is energetically considerably facilitated by adsorbed carbonate. As the redox potential of the couple $CO_3^{\bullet -}/CO_3^{2-}$ is considerably lower than that of the couple $OH^{\bullet}/OH^-$ but still enables the oxidation of water it is suggested that carbonate should be considered as a catalyst/co-catalyst in a variety of catalytic/photo-catalytic/electro-catalytic oxidation processes.

TOC:

$$-\mathrm{Ga{-}OH} \rightarrow -\mathrm{Ga{-}O}\bullet + H^+ + e^-$$

$$\Delta G^{*'} = 6.13\ \mathrm{eV}\ (1.85\ \mathrm{eV}\ \textit{vs}\ \mathrm{NHE})$$

$$\Big\downarrow \quad \Delta(\Delta G^{*'}) = -0.79\ \mathrm{eV}$$

$$-\mathrm{Ga}-\mathrm{CO_3H} \rightarrow -\mathrm{Ga{-}CO_3}\bullet + H^+ + e^-$$

$$\Delta G^{*'} = 5.34\ \mathrm{eV}\ (1.06\ \mathrm{eV}\ \textit{vs}\ \mathrm{NHE})$$

Introduction:

Catalytic/photo-catalytic and electro-catalytic water oxidation (only typical recent articles are cited)[1–12] is a subject of fundamental interest and significance because it is the half reaction required to split water and is the key step in natural and artificial photosynthesis to convert and store solar energy[13–27]. It has recently been suggested that silver and ferric cations might play a catalytic role during photocatalytic water oxidation[28]. Recently, much attention was paid to semiconductor-based photo-catalysis. Successful water splitting has been demonstrated using GaN[29,30] and InGaN[31], wurtzite, GaN/ZnO[29,32,33] that have significant visible light absorption. The commonly accepted mechanism for these oxidations is[14–17,20,22–24,30,34]:

(1) $h^+ + OH^-/H_2O \rightarrow OH^{\cdot}/(OH^{\cdot} + H^+)$

The $OH^{\cdot}$ radicals might remain adsorbed to the surface of the semiconductor[22,24,35]. Reaction (1) is usually followed by:

(2) $OH^{\cdot}$ + substrate → products

Though direct oxidation of substrates adsorbed to the semiconductor surface is plausible[21,25–27,36,37]:

(3) h^+ + substrate → products

In a quite different research the role of carbonate ions was explored in Fenton like oxidation reactions, and it was reported that $CO_3^{\cdot -}$ radical anions are formed instead of $OH^{\cdot}$ radicals[38]. Carbonate is a very low cost reagent with a redox potential of 1.59 V vs. NHE for $CO_3^{\cdot -}/CO_3^{2-}$ [39], in comparison the redox potential of water is $OH^{\cdot}/OH^-$ 1.90 *vs.* NHE or $OH^{\cdot},H^+/H_2O$ 2.730 V *vs.* NHE[40]. So it seemed tempting to investigate the photo-catalytic redox of carbonate instead of water oxidation. The molecular catalysis of the electrochemical and photochemical reduction of CO_2 with earth-abundant metal complexes is another interesting study[41,42], but it differs from our study as we are concentrating on the role of carbonate in photo-catalytic water oxidation processes. The question in this manuscript is whether bicarbonate/carbonate is oxidized via reaction (3). Indeed some experimental results point out that this is the case[43–45] though other explanations for the effect of carbonate were proposed[46,47]. It was decided to analyze the role of carbonate in reaction (3) theoretically. The energetics of the formation of $OH^{\cdot}$ radicals *via* reaction (1) was recently theoretically analysed for TiO_2[14,20,48], α-Al_2O_3, Ga_2O_3[49] and GaN[50]. The latter study investigated the water oxidation mechanism on the prototypical GaN $(10\bar{1}0)$ surface using a combined ab-initio molecular dynamics and molecular cluster model approach taking into account the role of water dissociation and hydrogen bonding within the first solvation shell of the hydroxylated surface. The calculated free energies for the four proton-coupled electron-transfer (PCET) steps of the oxygen evolution reaction indicate that the first PCET step for the conversion of −Ga−OH to $-Ga-O^{\cdot}$ is associated with the highest energy requirement. Investigation of electron-transfer (ET) and proton-transfer (PT) steps separately for the first proton-coupled electron-transfer (PCET) reveals that de-protonation is rate limiting. Comparison with previous results by Shen *et. al.*[51] indicate good agreement for the PCET steps[50]. We decided to follow the method used by Ertem *et. al.*[50] in order of checking the role of carbonate in this photo-catalyzed processes.

Computational details and results:

Our model was identical to the cluster model used by Shen *et. al.*[51] $Ga_{15}N_{15}O_2H_{34}(H_2O)_4$. This cluster consists of two surface primitive unit cells of GaN $(10\bar{1}0)$. Broken Ga-N bonds are passivated by the addition of hydrogen atoms; to two surface Ga atoms hydroxide ions, OH^-, are bound, and four water molecules are added to ensure that the local hydrogen-bond structure near the area of interest (*i.e.*, the active site) well represents the aqueous environment.

All our calculations were performed using G09 program[52]. Geometry optimizations in B3LYP level of DFT theory were performed, using the SDD basis set on Ga and the 6-311+G** basis set on all other atoms. In geometry optimizations of some structures we had to use MaxStep = 3, setting the maximum size for an optimization step (the initial trust radius) to 0.03 Bohr or radians, or SCF = QC, which is recommended for difficult-to-converge wave-functions.

Frequencies were calculated for each structure in order to verify that the considered structure is indeed a local minimum. Solvation effects were calculated using the SMD method[53].

For each structure the free energy was calculated. This calculation takes into account the ZPE and thermal correction. The program's default standard state corresponding to an ideal gas at a standard pressure of 1 atm. was changed to use either a standard state of 1 M (most species) or of 55.5 M (for water molecules). The values of free energy for each structure were used to calculate ΔG^0 values for relevant reactions. Following ref. 50 the calculation were performed at pH 4, therefore the reported $\Delta G^{*'}$, includes a correction of -5.46 kcal/mol (−4RT ln(10)) for the free energy of the solvated proton.

Following ref. 50, we report $\Delta G^{*'}$ *vs.* NHE in addition to the real $\Delta G^{*'}$ values. The values vs NHE took into account that $\Delta G(NHE) =$ 4.28 eV, and not zero as the latter value is arbitrarily assigned.

Our calculation concentrates on reaction 4 - the first PCET step for the conversion of −Ga−OH to $-Ga-O^{\cdot}$, as this step was found to be rate limiting.

(4) $- Ga-OH \rightarrow - Ga-O^{\cdot} + H^+ + e^-$

Our calculations differ from those reported in table S2 of ref. 50 using the cluster of Shen *et. al.*[51] as we use different basis sets, they differ from the Ertem *et. al.*[50] calculation as they used a larger cluster. Our results for reaction (4) in comparison to the results using the cluster of Shen *et. al.*[51] as they are given in table. S2 of ref 50, and in comparison of Ertem *et. al.*[50] are given in table 1.

In order to explore the role of carbonate on this reaction we substitute one of the hydroxide ions bound to a surface Ga atom with bicarbonate. The optimized structure is given in fig. 1. In this case the reaction:

(5) $- Ga- CO_3H \rightarrow - Ga-CO_3^{\cdot} + H^+ + e^-$

$\Delta G^{*'} = 5.34$ eV (1.06 eV *vs.* NHE)

is less endoergic by 0.79 eV, moreover, according to Ertem *et. al.*[50], the de-protonation is the rate limiting step, but in

Table 1 - ΔG*' values for reaction 4, comparison of our results with previous results.

ΔG*'					
cluster of Shen *et. al.*[50,51]		cluster of Ertem *et. al.*[50]		Our results	
(eV *vs.* NHE)	eV	(eV *vs.* NHE)	eV	(eV *vs.* NHE)	eV
2.18	6.46	2.32	6.6	1.85	6.13

$-Ga-CO_3H$ the bicarbonate is acidic and the de-protonation is exoergic and is occurring prior to the electron release:

(6) $-Ga-CO_3H \rightarrow -Ga-CO_3^- + H^+$

$\Delta G^{*'} = -0.20$ eV (-4.48 eV *vs* NHE)

The formation of $-Ga-CO_3^{\cdot}$ might be followed either by dimerization of adsorbed carbonate radical anions on the surface according to reaction 7 as earlier proposed[54]:

(7) $2-Ga-CO_3^{\cdot} \rightarrow -Ga-C(O)_2-(O-O)-(O)_2C-Ga-$

The formation of this peroxide on the surface will be followed by its oxidation, a process that requires a considerably lower potential than that of the formation of $-Ga-CO_3^{\cdot}$, yielding O_2. Alternatively the formation of $-Ga-CO_3^{\cdot}$ might be followed by:

(8) $-Ga-CO_3\bullet + H_2O \rightarrow -Ga-OH + CO_3^{\cdot -} + H^+$

$\Delta G^{*'} = -0.33$ eV (-4.61 eV *vs* NHE)

(9) $CO_3\bullet^- + CO_3\bullet^- \rightleftharpoons {}^-O_2COOCO_2^- \rightarrow HCO_4^- + CO_2$

$k_9 = 4.25\text{x}10^6\ M^{-1}s^{-1}$ [55]

(10) $H_2CO_4 \rightleftharpoons HCO_4^- + H^+$

$K_{10} = 2.86\text{x}10^{-4}$ M [56]

(11) $CO_{2(aq)} + HOO^- \rightleftharpoons HCO_4^-$

$K_{11} = 1.13\text{x}10^5\ M^{-1}$; $k_{-11} = 1.8\text{x}10^{-3}\ s^{-1}$ [56]

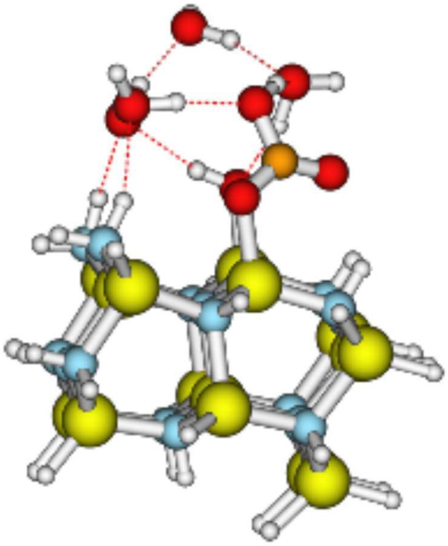


Fig. 1: Carbonated GaN.

Ga- Yellow, C - brown, H - white, O – red, N – blue

The HCO_4^- or the H_2O_2 thus formed will be oxidized photo-catalytically on the GaN:

12) $HOO^- \longrightarrow HOO^{\cdot} + e^-$

13) $2HOO^{\cdot} \longrightarrow H_2O_2 + O_2$

In order of photo-catalytically oxidize carbonate the formation of $-Ga-CO_3H$ is required, therefore the plausibility of substitution of the adsorbed OH^- ions by HCO_3^- ions was enquired. At pH 4, the pH at which all the calculations were performed, there are no HCO_3^- ions in aqueous solutions; CO_2 is the only possible species at this pH.

(14) $-Ga-OH + CO_2 \rightarrow -Ga-CO_3H$

$\Delta G^{*'} = 0.35$ eV (-3.93 eV vs NHE)

Reaction 14 is slightly endoergic, but this result doesn't take into account the point of zero charge (PZC) of GaN. The PZC of GaN is in the range of 8–10 [57]. At pH 4 GaN adsorbs H^+ ions and is positively charged. Therefore we added an H^+ to one adsorbed OH^- ion and CO_2 to the other OH^- ion, in this case reaction (15) is practically thermo-neutral, and suggests that the substitution is plausible.

(15) $-Ga-OH^+ + CO_2 \rightarrow -Ga-CO_3H^+$

$\Delta G^{*'} = 0.08$ eV (-4.20 eV vs NHE)

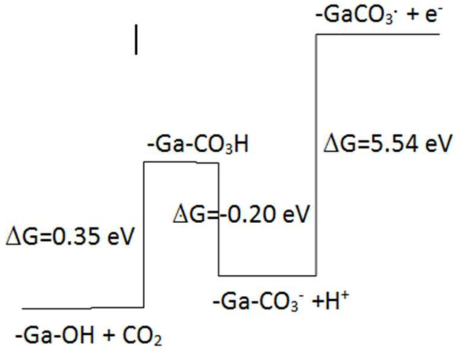
The analogous effect of adsorbed H^+ on TiO_2 on the photo-catalytic oxidation of H_2O was earlier reported[48,58]. Furthermore, reaction (14) will be followed immediately by reaction (6) and the two reactions are clearly exothermic.

A diagram of reactions: 5,6, and 14 in the order of their occurrence is given in scheme 1.

Concluding remarks:

The results reported herein suggest that the photo-catalytic oxidation of water on semiconductors is catalyzed by the adsorption of carbonate to the surface. This adsorption is energetically more favourable below the PZC of the semiconductor. As it is easier to oxidize adsorbed carbonate than to oxidize water one can use semiconductors that absorb light in the visible.

Furthermore one should consider the use of carbonate as a catalyst, or co-catalyst, in catalytic/electro-catalytic water oxidation processes.



Scheme 1: A diagram of reactions: 5,6, and 14 in the order of their occurrence

This result suggests that in employing GaN in photo-electro-chemical cells for solar water splitting[50], it is preferred to saturate the surface of GaN with bicarbonate ions, and employing GaN in photo-electro-chemical cells for solar O_2 production. This process demands less energy and is more efficient as the visible light used in this process is shifted to the red in comparison to the process described by Ertem et al.[50].

References:

1 I. Katsounaros, S. Cherevko, A. R. Zeradjanin and K. J. J. Mayrhofer, *Angew. Chemie - Int. Ed.*, 2014, **53**, 102–121.

2 A. R. Parent, R. H. Crabtree and G. W. Brudvig, *Chem. Soc. Rev.*, 2013, 2247–2252.

3 Y. Qiu, L. Xin and W. Li, *Langmuir*, 2014, **30**, 7893–7901.

4 A. M. Smith, L. Trotochaud, M. S. Burke and S. W. Boettcher, *Chem. Commun.*, 2014, **51**, 5261–5263.

5 Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060–2086.

6 K. Toyoda, R. Hinogami, N. Miyata and M. Aizawa, *J. Phys. Chem. C*, 2015, 150312100247004.

7 S. Malkhandi, P. Trinh, A. K. Manohar, a. Manivannan, M. Balasubramanian, G. K. S. Prakash and S. R. Narayanan, *J. Phys. Chem. C*, 2015, 150402160211001.

8 D. Friebel, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A. Nilsson and A. T. Bell, *J. Am. Chem. Soc.*, 2015, **137**, 1305–1313.

9 S. Chen, J. Duan, M. Jaroniec and S. Z. Qiao, *Angew. Chemie - Int. Ed.*, 2013, **52**, 13567–13570.

10 J. C. Hidalgo-Acosta, M. a. Méndez, M. D. Scanlon, H. Vrubel, V. Amstutz, W. Adamiak, M. Opallo and H. H. Girault, *Chem. Sci.*, 2015, **6**, 1761–1769.

11 W. Fan, Q. Zhang, Y. Wang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2632–49.

12 S. Xie, Q. Zhang, G. Liu, Y. Wang, *Chem. Commun.*, 2016, **52**, 35–59.

13 J. Cheng, X. Liu, J. a Kattirtzi, J. VandeVondele and M. Sprik, *Angew. Chem. Int. Ed. Engl.*, 2014, 1–5.

14 L. Gomathi Devi and R. Kavitha, *RSC Adv.*, 2014, **4**, 28265.

15 W. Kim, T. Tachikawa, G. Moon, T. Majima and W. Choi, *Angew. Chemie Int. Ed.*, 2014, **53**, 14036–14041.

16 F. Le Formal, E. Pastor, S. D. Tilley, C. a Mesa, S. R. Pendlebury, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2015, 150502122150001.

17 M. Valenti, D. Dolat, G. Biskos, a. Schmidt-Ott and W. A. Smith, *J. Phys. Chem. C*, 2015, **119**, 2096–2104.

18 X. Yu, B. Kim and Y. K. Kim, *ACS Catal.*, 2013, **3**, 2479–2486.

19 W.-N. Zhao and Z.-P. Liu, *Chem. Sci.*, 2014, **5**, 2256.

20 M. L. ArunaKumari and L. Gomathi Devi, *Environ. Sci. Water Res. Technol.*, 2015, **1**, 177–187.

21 J. Zhang and Y. Nosaka, *J. Phys. Chem. C*, 2014, 118, 10824–10832.

22 L. Yang, H. Zhou, T. Fan and D. Zhang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6810–26.

23 Y. Nakabayashi and Y. Nosaka, *J. Phys. Chem. C*, 2013, **117**, 23832–23839.

24 J. F. Montoya, M. F. Atitar, D. W. Bahnemann, J. Peral and P. Salvador, *J. Phys. Chem. C*, 2014, 140618152648005.

25 H. Chen, C. E. Nanayakkara and V. H. Grassian, *Chem. Rev.*, 2012, **112**, 5919–5948.

26 J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, *Chem. Rev.*, 2014, 114, 9919-9986.

27 D. Yang, J. Zhao, H. Liu, Z. Zheng, M. O. Adebajo, H. Wang, X. Liu, H. Zhang, J. C. Zhao, J. Bell and H. Zhu, *Chem. - A Eur. J.*, 2013, **19**, 5113–5119.

28 J. Schneider, D. W. Bahnemann, *J. Phys. Chem. Letters,* 2013, **4**, 3479-3483.

29 K. Maeda, K.; Teramura, K.; Saito, N.; Inoue, Y.; Domen, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1004–1010.

30 D. Wang, A. Pierre, M. G. Kibria, K. Cui, X. Han, K. H. Bevan, H. Guo, S. Paradis, A. R. Hakima and Z. Mi, *Nano Lett.*, 2011, **11**, 2353–2357.

31 M. G. Kibria, H. P. T. Nguyen, K. Cui, S. Zhao, D. Liu, H. Guo, M. L. Trudeau, S. Paradis, A. R. Hakima and Z. Mi, *ACS Nano*, 2013, **7**, 7886–7893.

32 K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi and K. Domen, *J. Am. Chem. Soc.*, 2005, **127**, 8286–8287.

33 A. Xiong, T. Yoshinaga, T. Ikeda, M. Takashima, T. Hisatomi, K. Maeda, T. Setoyama, T. Teranishi and K. Domen, *Eur. J. Inorg. Chem.*, 2014, 767–772.

34 V. Diesen and M. Jonsson, *J. Phys. Chem. C*, 2014, **118**, 10083–10087.

35 M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362–7.

36 R. Daghrir, P. Drogui and D. Robert, *Ind. Eng. Chem. Res.*, 2013, **52**, 3581–3599.

37 K. Nakata, T. Ochiai, T. Murakami and A. Fujishima, *Electrochim. Acta*, 2012, **84**, 103–111.

38 A. Burg, D. Shamir, I. Shusterman, H. Kornweitz and D. Meyerstein, *Chem. Commun.*, 2014, **50**, 13096–13099.

39 R. E. Huie, C. L. Clifton and P. Neta, *Int. J. Radiat. Appl. Instrumentation. Part C. Radiat. Phys. Chem.*, 1991, **38**, 477–481.

40 D. M. Stanbury, *Adv. Inorg. Chem.*, 1989, **33**, 69–138.

41 S. F. Bandar AlOtaibi Defa Wang, Jinhua Ye, and Zetian Mi, *ACS Catal.*, 2015, 5342-5348.

42 L. Chen, Z. Guo, X.-G. Wei, C. Gallenkamp, J. Bonin, E. Anxolabéhère-Mallart, K.-C. Lau, T.-C. Lau and M. Robert, *J. Am. Chem. Soc.*, 2015, **137**, 10918–10921.

43 Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han and C. Li, *Chem. Rev.*, 2014, 57.

44 M. *Ni*, M.K.H. *Leung*, *Leung*, D.Y.C. *Sumathy*, Renewable and Sustainable Energy Rev., 2007, 11, 401-425.

45 H. Arakawa, C. Shiraishi, M. Tatemoto, H. Kishida, D. Usui, a. Suma, a. Takamisawa and T. Yamaguchi, *Proc. SPIE*, 2007, 6650, 665003–665003–10.

46 K. Sayama, R. Abe, H. Arakawa and H. Sugihara, *Catal. Commun.*, 2006, **7**, 96–99.

47 M. A. Nadeem, A. Ajmal, R. N. Malik, I. Majeed and H. Idriss, *RSC Adv.*, 2014, 37003–37026.

48 C. Chen, T. Shi, W. Chang, J. Zhao, *Chem. Cat. Chem., 2015*, 7, 724-731

49 C. C. Nguyen, N. N. Vu and T.-O. Do, *J. Mater. Chem. A*, 2015, **00**, 1–15.

50 M. Z. Ertem, N. Kharche, V. S. Batista, M. S. Hybertsen, J. C. Tully and J. T. Muckerman, *ACS Catal.*, 2015, 2317–2323.

51 X. Shen, Y. Small and J. Wang, P. B. Allen, M. V. Fernandez-Serra, M. S. Hybertsen, and J. T. Muckerman, *J. Phys. Chem. A*, 2010, **114**, 13695–13704.

52. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

53 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

54 K. SAYAMA, *cat. Surv. Japan*, 2000, **4**, 75–80.

55 K. S. Haygarth, T. W. Marin, I. Janik, K. Kanjana, C. M. Stanisky and D. M. Bartels, *J. Phys. Chem. A*, 2010, **114**, 2142–2150.

56 E. V. Bakhmutova-Albert, H. Yao, D. E. Denevan and D. E. Richardson, *Inorg. Chem.*, 2010, **49**, 11287–11296.

57 V. Stevanović, S. Lany, D. S. Ginley, W. Tumas and A. Zunger, *Phys. Chem. Chem. Phys.*, 2014, **16**, 3706–14.

58 K. Sayama and H. Arakawa, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 1647–1654.

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