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Sulfated Carbon Quantum Dots as Efficient Visible-Light Switchable Acid Catalysts for Room-Temperature Ring-Opening Reactions**

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Abstract: *Acid catalytic processes play a classic and important role in modern organic synthesis. How well the acid can be controlled often plays the key role in the controllable synthesis of the products with high conversion yield and selectivity. The preparation of a novel, photo-switchable solid-acid catalyst based on carbon quantum dots is described. The carbon quantum dots are decorated with small amounts of hydrogensulfate groups and thus exhibit a photogenerated acidity that produces a highly efficient acid catalysis of the ring opening of epoxides with methanol and other primary alcohols. This reversible, light-switchable acidity is shown to be due to photoexcitation and charge separation in the carbon quantum dots, which create an electron withdrawing effect from the acidic groups. The catalyst is easily separated by filtration, and we demonstrate multiple cycles of its recovery and reuse.*

In industry, acid catalytic processes play a classic and important role in organic synthesis.[1] Traditional acid catalysts, such as mineral acids, however, suffer from serious disadvantages with respect to cost and difficult separation of the catalyst from the homogeneous reaction mixtures. These issues result in equipment corrosion, energy losses, and demanding manufacturing conditions.[1,2] The use of solid-acid catalysts offers advantages over liquid acids;[2a–h] however, suitable solid-acid catalysts with high activity are often not available, forcing most processes to continue to use homogeneous acids.[2i] Therefore, there is a continuing need to develop solid-acid catalysts from recyclable, nontoxic materials bearing strong acid sites to contribute to the sustainability and efficiency of these processes.[2b,f]

Light-driven catalytic processes have also attracted tremendous interest in the area of organic chemistry, as they potentially offer a sustainable pathway for energy injection and control in green chemical synthesis.[3] Carbon-based nanomaterials have shown great potential in photocatalysis, as well as acid catalysis. As acid catalysts, carbon nanostructures (such as sulfated-graphene/-tube/-active carbon materials) have been used in many catalytic applications.[4] They typically suffer, however, from lack of sufficient surface functionalization and therefore low efficiency, or complex synthesis steps.[3f,5] Consequently, high-efficiency light-driven, or light-enhanced, acid catalysts based on carbon materials are yet to be developed.

We demonstrate herein that carbon quantum dots (CQDs) derived from a graphite rod by an electrochemical method and decorated with hydrogensulfate groups (S-CQDs) have photoinduced proton-generating capacity in solution, under visible light irradiation. As light-enhanced acid-catalysts, we show S-CQDs can catalyze ring-opening reactions, achieving high conversion efficiency at room temperature under visible light irradiation.

The CQDs were produced from a graphite rod by electrochemical methods in pure water.[6a] After a reflux treatment for suitable time in H_2SO_4 solution (Supporting Information, Figure S1), the S-CQDs are obtained. Micrographs obtained from transmission electron microscopy (TEM) of the S-CQDs are displayed in Figure 1a. The images show that the S-CQDs were spherical and fairly monodisperse. The size distribution of the S-CQDs is in the range of 2–9 nm (Figure 1b). The Raman spectrum shows

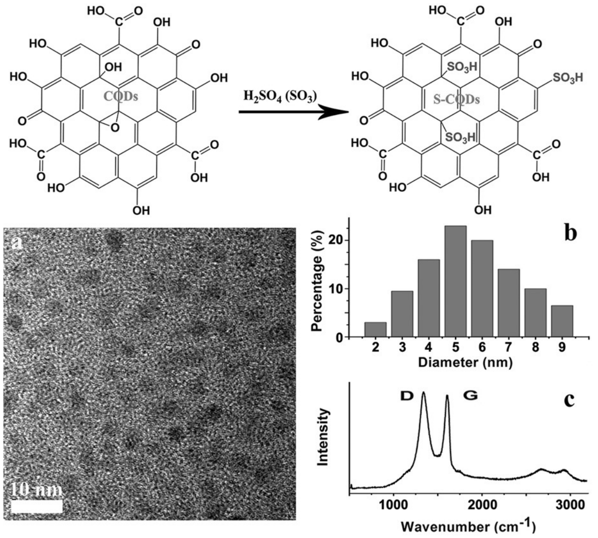

Figure 1. Synthesis process of the S-CQDs. a) Typical TEM image, b) particle size distribution of the obtained S-CQDs and c) Raman spectrum of the S-CQDs.

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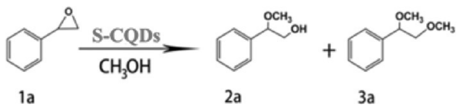
Table 1: Ring opening of styrene oxide with methanol catalyzed by S-CQDs compared to other catalysts.[a]



Entry	Catalyst	t [min]	Conversion [%][b]	Selectivity [%] (**2a**/**3a**)[c]
1	S-CQDs	5	59	99/1
2	S-CQDs ($h\nu$)	5	81	99/1
3	S-CQDs	10	94	97/3
4	S-CQDs ($h\nu$)	10	98	98/2
5	S-CQDs	20	95	95/5
6	S-CQDs	20	4[d]	100
7	GO	5	49	97/3
8	GO ($h\nu$)	5	53	97/3
9	GO	10	90	96/4
10	GO	20	92	95.5/4.5
11	CQDs	10	–	–
12	CQDs ($h\nu$)	10	–	–
13	CQDs	60	–	–
14	H_2SO_4	5	99	99/1
15	p-CH_3-C_6H_4-SO_3H	5	99	–
16	CH_3COOH	60	–	–
17	Norit A	60	7	99

[a] $h\nu$ = light irradiation. All reactions were performed in a quartz three-neck flask. Reactants and catalysts were added into a three-neck flask equipped with a condenser. The reaction mixture was vigorously stirred at room temperatures. In photo experiments, visible-light irradiation (450 W Xe arc lamp with a filter to cut wavelengths < 400 nm and a water-cooling system to maintain a constant temperature were used. Quantities: **1a** (2 mL), methanol (20 mL), catalyst (11 mg). [b] Conversion efficiencies were determined by GC with an FID detector. [c] Selectivity was determined by GC. [d] With 0.1 mL of pyridine.

both the expected G band at 1590 cm^{-1} owing to in-plane vibrations of the sp^2 carbons and the D band at 1320 cm^{-1} owing to the presence of sp^3 defects (Figure 1 c).

We used the epoxide ring-opening reaction to test the activity of S-CQDs as an acid catalyst, as shown in Table 1. Compound **1a** was used as a substrate and methanol as the solvent and nucleophile; the reaction was carried out at room temperature. In the absence of the catalyst, unreacted **1a** was recovered. The reaction of **1a** and methanol was then carried out in the presence of the S-CQD catalyst (entries 1–5); when there was no visible light irradiation, 59 % and 94 % conversion were achieved in 5 and 10 min, respectively (entries 1 and 3). Selectivity was 99 % and 97 % towards 2-methoxy-2-phenylethanol (**2a**), respectively, with small amounts of **3a** also obtained. The yield of **3a** increased with reaction time (entry 5), which indicates that **3a** is a secondary product derived from **2a**. Under visible light irradiation the **2a** yield in 5 min (entry 2) is much higher (22 % higher) than without irradiation (entry 1). Under 10 min light irradiation (entry 4), the reaction yield and selectivity for **2a** both reach 98 %, indicating that irradiation can enhance the catalytic yields. We also investigated the effect of adding 0.1 mL of a base (pyridine); the conversion of **1a** is only 4 % (entry 6), indicating the effect of deprotonating the acid sites present in the catalyst.

Popular carbon materials pure CQDs and graphene oxide (GO), synthesized by Hummer's method without any subsequent treatment, were selected as control samples to compare the catalytic properties of the GO material and the S-CQDs. After 5 min irradiation, the conversion of **1a** on GO reaches only 53 %, and 49 % without irradiation (entries 7 and 8), but their selectivity for **2a** and **3a** are similar. These results show that the catalytic property of the S-CQDs is better than the GO material. The conversion of **1a** can reach 90 % and 92 % on GO in 10 min and 20 min, respectively (entries 9 and 10), but the selectivity for **2a** is decreased by extending the reaction time. The pure CQDs are not active enough for this ring-opening reaction after 10 or 60 min, with no obvious conversion of **1a**, even under light irradiation (entries 11–13); neither **2a** or **3a** were detected.

To investigate the role of the active sites present on the S-CQD particles, further control experiments were performed to compare the activity of S-CQDs with those of various acids, that is, concentrated sulfuric acid, *p*-toluenesulfonic acid, and glacial acetic acid. The results of entries 14 to 16 show that with the first two acids, the ring opening of **1a** with methanol was more facile than with glacial acetic acid, where only the unreacted starting material was isolated. This clearly indicates that carboxylic groups are not the active sites of the S-CQDs; so it seems likely that the hydrogensulfate groups introduced onto the S-CQDs scaffold during synthesis are the active sites. Further evidence is obtained from the elemental analysis, which shows the S-CQDs contain 1.97 wt % sulfur (Supporting Information, Table S1 and Figure S2). We also gave the S-CQDs a thermal treatment at 200 °C to confirm this proposal. It is known that mild heat treatment tends to reconstitute the graphene structure and this affects the removal of some groups. After this treatment, the elemental analysis indicated that the sulfur content of the S-CQDs was negligible; their catalytic activity was also negligible, supporting the hypothesis that the catalytic activity for this reaction is associated with the presence of sulfur atoms. For the mixture of CQDs (5.5 mg) with a small amount of H_2SO_4 (5.5 mg), the result shows that the conversion is 99 %, and the selectivity is 99/1 (**2a**/**3a**, %); and there was no obvious difference in the experiment under light irradiation. The activity of the S-CQDs was also higher than that of the Norit A activated carbon that resulted in only 7 % conversion of **1a** (entry 17).

To further confirm whether or not the catalysis process is truly heterogeneous or is due to leached active species present in the reaction solution, we carried out the reaction under the optimized conditions as described in Table 1, but the S-CQD catalyst was removed from the reaction mixture at 50 % formation of **2a** by filtering and centrifugation. Then in the absence of the catalyst, the reaction solution was stirred at room temperature again. After 60 min, in the absence of the acid catalyst, no further product formation was observed. So it can be concluded that the catalysis process occurs on the S-CQD surface.

IR spectroscopy was used to probe the nature of the acid sites and their interaction with probe molecules. First the sample was activated at 100 °C in 10^{-6} mbar vacuum (Figure 2 a); some functional groups such as carbonyl groups (1649 cm^{-1}) and bisulfate groups (1053 cm^{-1}, SO_3–H stretch-

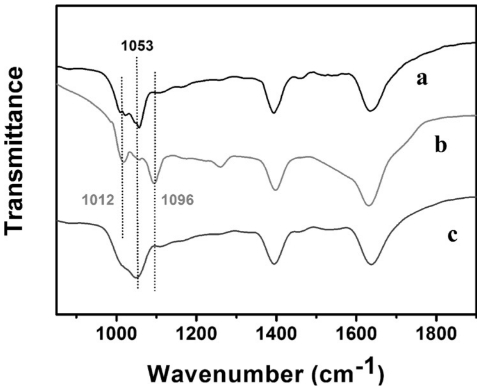


Figure 2. IR spectra of the sample a) after 100 °C vacuum activation; b) after evacuation at 100 °C, and admission of methanol at 36 mbar for 5 min; and c) followed by evacuation under vacuum at 100 °C.

ing) are observed. The band at 1405 cm^{-1} is associated with the $C(sp^2)$ vibration of the graphene lattice. Methanol adsorption on the sample at 100 °C leads to a shift of the 1053 cm^{-1} band towards a higher wavenumber (1096 cm^{-1}). This shift may be related to the interaction of the methanol with the SO_3 group. Indeed, the band at 1053 cm^{-1} is restored after removal of the methanol. On the other hand, bands at 1012 cm^{-1}, associated with a C–O stretching, and at 2940 and 2859 cm^{-1}, associated with C–H stretching of the methoxy group, are also observed upon adsorption of CH_3OH. These changes prove the acidity of the S-CQDs.

It appears from the data in Table 1 that the yield of **2a** on the S-CQD catalyst can be enhanced under visible light irradiation; we next investigate the possible mechanisms for the enhancement. As shown by the data in Figure 3a, S-CQDs are excellent photostimulated electron acceptors under visible light, since their visible light-excited photolumincence (PL)[6b] at 400–800 nm is quenched efficiently by electron-donating molecules in solution. The result shows that the intensity of the PL peak at about 560 nm upon 485 nm excitation is quenched by electron-donating *N*,*N*-diethylaniline (DEA, 0.88 V vs. NHE). The luminescence decay (Figure 3b) of the S-CQDs reveals that they have a Stern–Volmer quenching constant of 18.2 $L\,mol^{-1}$ ($K_{SV} = \tau_F{}^{\circ}k_q$), further indicating that they can serve as good photoinduced electron acceptors.[3h–j] This photo-induced electron-accepting property would tend to withdraw electron density from the sulfonate (SO_3^-) group, thereby increasing its acidity. Based on this, we hypothesize that the S-CQDs are exhibiting a light-induced enhancement of their proton acidity. To further investigate this hypothesis and investigate the mechanism, we present the following experiments.

To further clarify the action of light on the S-CQDs (to explain the mechanism, we call it CQD-SO_3H here), we examined the pH value before and after light exposure. A small decrease in pH value was observed when the solution was illuminated, indicating that photons can promote the following ionization: $\text{CQD-SO}_3\text{H} + \text{H}_2\text{O} \rightarrow (\text{CQD-SO}_3)^- + \text{H}_3\text{O}^+$. This pH change (ΔpH) of the S-CQDs in aqueous solution was further investigated as shown in Figure 3c. The ΔpH (after about 10 min to reach equilibrium) was stable and reversible, and reached the same level in repeated light ON/OFF cycles. The temperature of the solution was controlled by a cooling system and no significant temperature change was measured. The pH probe was also shielded from direct exposure to the light. The ΔpH under different light intensities and for different concentrations of S-CQDs was also investigated (Figure 3d). When the concentration of S-CQDs in the solution was 0.1 $mg\,mL^{-1}$ and 0.05 $mg\,mL^{-1}$, only a small difference was observed; however, a substantial increase in ΔpH was observed at 0.5 $mg\,mL^{-1}$. ΔpH increases,

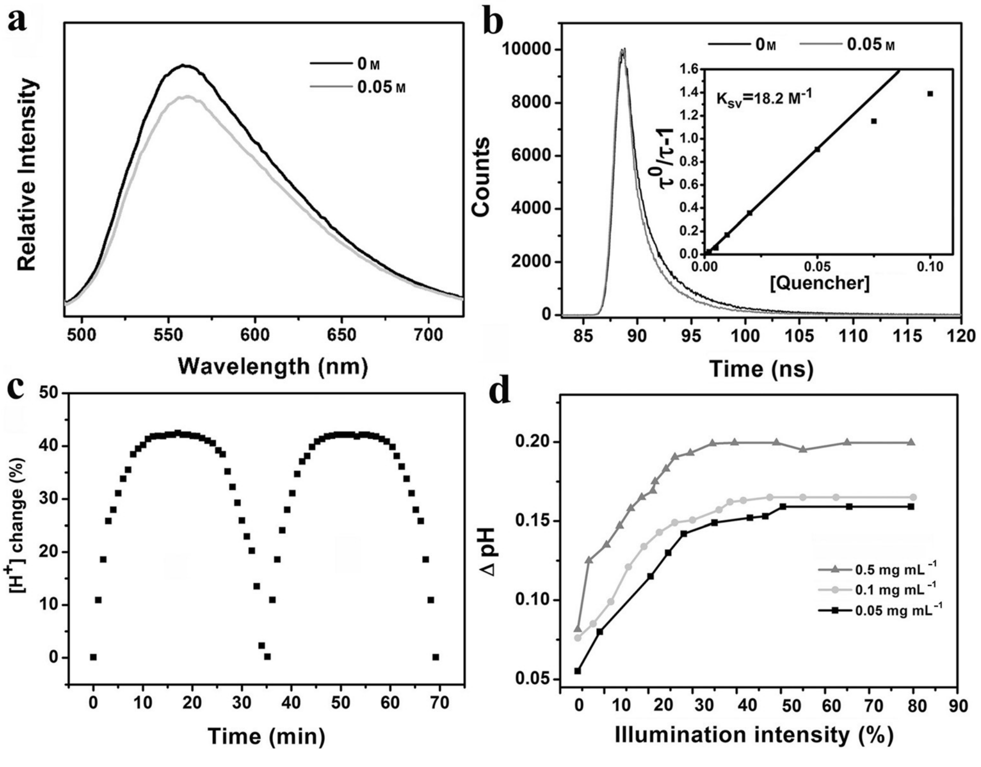


Figure 3. a) Luminescence emission spectra (485 nm excitation) of the S-CQDs in toluene without and with a quencher, DEA (0.05 M). b) Luminescence decays of the S-CQDs with DEA. Inset: Stern–Volmer plots for the quenching of luminescence (485 nm excitation) of the CQDs by DEA. c) pH value responses of S-CQDs under visible light irradiation. d) pH change versus illumination intensity (% of 150 $mW\,cm^{-2}$) for different S-CQD concentrations.

in all cases, with light intensity up to about 25% (of 150 mW cm^{-2}). Beyond this, the effect plateaus at all concentrations of catalyst, suggesting that there is an effective equilibrium limit in the mechanism of light-induced enhancement of their proton acidity.

Based on earlier studies, it is known that CQDs can adsorb visible light and thus generate electron–hole pairs.[7a,b] To further understand the phenomena observed here, theoretical calculations have been employed to investigate the orbital energy levels involved. We start with the calculation of the highest occupied and lowest unoccupied molecular orbitals of the CQD with one un-ionized $-SO_3H$. As shown in Figure 4a and b, both HOMO and LUMO are dominated by the CQD framework, indicating that the electrons in the HOMO can be excited to the LUMO if sufficient energy is provided. At the equilibrium state, however, the SO_3H groups are partially ionized, and as a result both $-SO_3^-$ and $-SO_3H$ are likely to be present on the same CQD. Thus an additional model with both $-SO_3^-$ and $-SO_3H$ present was employed and calculated. Clearly, the release of one proton (H^+) leaves one net charge localized at the $-SO_3^-$, which now dominates the HOMO (Figure 4c), indicating its energy level is higher that the occupied states of the CQD. The LUMO remains dominated by the CQD (see Figure 4d). Based on the above, we can speculate the following possible mode of excitation when such a partially ionized system is exposed to light. In the first step, electrons in the CQD are excited to the LUMO and holes are generated in the CQD. Their energy levels are lower than HOMO and therefore in the second step the HOMO electron (which is $-SO_3^-$ localized) transfers to the CQD to combine with the holes. Once this occurs, the net charge is no longer localized on the $-SO_3$, being shared across the carbon atom lattice. This situation is analogous to the well-known electron withdrawing effects in fluorinated carboxylic and sulfonic acids and the result is an increase in acidity. Such a deviation from equilibrium will be maintained by the continuing light irradiation, since the photoexcited electrons will tend to continuously recombine with the holes. On removal of the irradiation, the dark equilibrium will re-establish and the pH will increase back to the origin value. In other words, the acid change is switchable through controlling the light intensity.

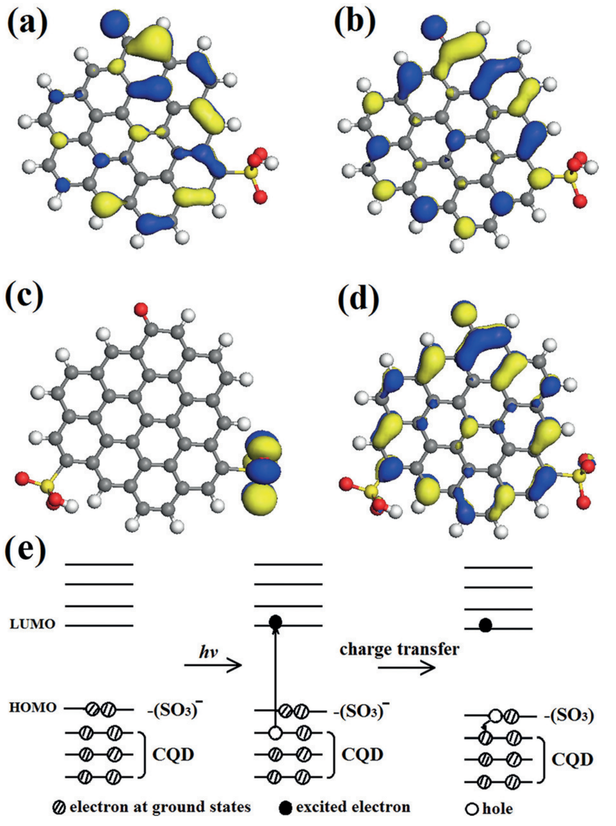


Figure 4. Calculated frontier orbitals for CQD, with C, H, O, and S indicated as gray, white, red, and yellow spheres. a) HOMO and b) LUMO are for CQD with un-ionized $-SO_3H$, c) and d) are for CQD with partially ionized $-SO_3H$. Herein only two $-SO_3H$ groups are employed in the model; models having more groups were tested and do not show essential difference. e) The mechanism of photoexcitation and charge transfer of S-CQDs under light irradiation.

Based on the above results and discussion, the proton generation mechanism and the catalytic role for the ring opening reaction of S-CQDs under visible light irradiation is proposed in Figure 4e. With light irradiation, additional protons are released from the ionization of $-SO_3H$, and as a result, a stronger acid environment is offered for the open-ring reaction, and higher yield and selectivity of the product **2a** are obtained than that without light irradiation.

The reusability of the S-CQDs was also investigated for the ring opening reaction of **1a** with methanol under identical conditions as described in Table 1. After the reaction time, the catalyst was separated from the mixture by filtering and high speed centrifugation, then the recovered catalyst was reused with no further treatment. After three consecutive cycles, the catalyst gave almost identical catalytic properties. Meanwhile, compared to fresh catalyst, no obvious changes were observed in the Raman spectrum and elemental analysis of the catalyst after the reaction (Supporting Information, Figures S3 and S4), which indicates this kind of catalyst is very stable. We also studied the effect of other alcohols such as ethanol, 1-propanol, and *tert*-butanol as nucleophiles; the results show that S-CQDs also have catalytic activities for these alcohols (Supporting Information, Tables S2 and S3). The S-CQDs also have catalytic activity for other reactions, such as the esterification reaction (Supporting Information, Table S4), which show its potential in other applications.

In summary, we demonstrate that S-CQDs can act as high-performance visible-light-induced acid photocatalysts. Their photogenerated proton property makes this material a highly efficient, recyclable acid catalyst for the ring-opening of epoxides with methanol and other primary alcohols as nucleophile and solvent. The use of S-CQDs as visible-light-responsive and controllable photocatalysts is a novel application of carbon-based nanomaterials for green chemistry. We hope that our findings will stimulate the development of similar light-sensitive, switchable, and recyclable green photocatalysts for important industrial processes.

Keywords: hydrogensulfate · photocatalysis · quantum dots · ring-opening reactions · visible-light switchable

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[1] a) M. Kitano, K. Nakajima, J. N. Kondo, S. Hayashi, M. Hara, *J. Am. Chem. Soc.* **2010**, *132*, 6622–6623; b) A. Corma, *Chem. Rev.* **1995**, *95*, 559–614; c) I. Čorić, B. List, *Nature* **2012**, *483*, 315–319.

[2] a) K. Tanabe, W. F. Hölderich, *Appl. Catal. A* **1999**, *181*, 399–434; b) J. H. Clark, *Acc. Chem. Res.* **2002**, *35*, 791–797; c) A. Corma, *Chem. Rev.* **1997**, *97*, 2373–2420; d) P. Chen, *Nat. Chem.* **2011**, *3*, 839–840; e) R. A. Sheldon, R. S. Downing, *Appl. Catal. A* **1999**, *189*, 163–183; f) J. H. Clark, *Green Chem.* **1999**, *1*, 1–8; g) T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641–3666; h) M. A. Harmer, Q. Sun, *Appl. Catal. A* **2001**, *221*, 45–62; i) A. Takagaki, C. Tagusagawa, S. Hayashi, M. Hara, K. Domen, *Energy Environ. Sci.* **2010**, *3*, 82–93.

[3] a) X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891–2959; b) H. Li, X. He, Z. Kang, H. Huang, Y. Liu, J. Liu, S. Lian, C. H. A. Tsang, X. Yang, S. T. Lee, *Angew. Chem. Int. Ed.* **2010**, *49*, 4430–4434; *Angew. Chem.* **2010**, *122*, 4532–4536; c) D. R. MacFarlane, N. Tachikawa, M. Forsyth, J. M. Pringle, P. C. Howlett, G. D. Elliott, J. H. Davis, M. Watanabe, P. Simon, C. A. Angell, *Energy Environ. Sci.* **2014**, *7*, 232–250; d) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, *8*, 621–629; e) D. A. Nicewicz, D. W. MacMillan, *Science* **2008**, *322*, 77–80; f) F. Su, S. C. Mathew, G. Lipner, X. Fu, M. Antonietti, S. Blechert, X. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 16299–16301; g) J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl, D. S. Su, *Science* **2008**, *322*, 73–77; h) X. Wang, L. Cao, F. Lu, M. J. Meziani, H. Li, G. Qi, B. Zhou, B. A. Harruff, F. Kermarrec, Y.-P. Sun, *Chem. Commun.* **2009**, 3774–3776; i) H. Li, R. Liu, S. Lian, Y. Liu, H. Huang, Z. Kang, *Nanoscale* **2013**, *5*, 3289–3297; j) H. Zhang, H. Huang, H. Ming, H. Li, L. Zhang, Y. Liu, Z. Kang, *J. Mater. Chem.* **2012**, *22*, 10501–10506.

[4] a) S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Chem. Rev.* **2014**, *114*, 6179–6212; b) Q. Yue, M. H. Wang, J. Wei, Y. H. Deng, T. Y. Liu, R. C. Che, B. Tu, D. Y. Zhao, *Angew. Chem. Int. Ed.* **2012**, *51*, 10368–10372; *Angew. Chem.* **2012**, *124*, 10514–10518.

[5] a) L. Song, S. Zhang, X. Wu, H. Tian, Q. Wei, *Ind. Eng. Chem. Res.* **2012**, *51*, 9510–9514; b) K. Nakajima, M. Hara, *ACS Catal.* **2012**, *2*, 1296–1304; c) B. Chang, J. Fu, Y. Tian, X. Dong, *J. Phys. Chem. C* **2013**, *117*, 6252–6258; d) F. Liu, J. Sun, L. Zhu, X. Meng, C. Qi, F.-S. Xiao, *J. Mater. Chem.* **2012**, *22*, 5495–5502.

[6] a) H. Ming, Z. Ma, Y. Liu, K. Pan, H. Yu, F. Wang, Z. Kang, *Dalton Trans.* **2012**, *41*, 9526–9531; b) W. Li, Z. Zhang, B. Kong, S. Feng, J. Wang, L. Wang, J. Yang, F. Zhang, P. Wu, D. Zhao, *Angew. Chem. Int. Ed.* **2013**, *52*, 8151–8155; *Angew. Chem.* **2013**, *125*, 8309–8313.

[7] a) T. F. Yeh, C. Y. Teng, S. J. Chen, H. Teng, *Adv. Mater.* **2014**, *26*, 3297–3303; b) H. Li, Z. Kang, Y. Liu, S.-T. Lee, *J. Mater. Chem.* **2012**, *22*, 24230–24253.

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