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Microporous Cokes Formed in Zeolite Catalysts Enable Efficient Solar Evaporation

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Cokes are inevitably generated during zeolite-catalyzed reactions as deleterious side products that deactivate the catalyst. In this study, we *in-situ* converted cokes into carbons within the confined microporous zeolite structures and evaluated their performances as absorbing materials for solar-driven water evaporation. With a properly chosen zeolite, the coke-derived carbons possessed ordered interconnected pores and tunable compositions. We found that the porous structure and the oxygen content in as-prepared carbons had important influences on their energy conversion efficiencies. Among various investigated carbon materials, the carbon derived from the methanol-to-olefins reaction over zeolite Beta gave the highest conversion efficiency of 72% under simulated sunlight with equivalent solar intensity of 2 suns. This study not only demonstrates the great potential of traditionally useless cokes for solar thermal applications but also provides new insights into the design of carbon-based absorbing materials for efficient solar evaporation.

Introduction

Harvesting solar radiation to produce pure water by evaporation provides an environment-friendly means of seawater desalination and wastewater treatment.¹⁻² To utilize the solar energy efficiently, absorbing materials are usually introduced into water surface to enhance the capture of sunlight. Ideally, the absorbing material should have a broadband absorption property, being able to harvest a large portion of the solar spectrum and convert the absorbed energy into heat with minimum heat loss through radiation and conduction.³⁻⁴ The design of the solar evaporation system is also critical. Significant efforts have been made to optimize the systems: optical concentration or thermal concentration was used to enhance the vapor temperature;⁵⁻⁹ floatable thermal insulating supports were developed to localize the generated heat at the water-air interface;¹⁰⁻¹² a surface thermal insulating layer was also reported to enable further concentration of the heat.¹³

The most often used absorbing materials include metallic plasmonic nanostructures (nanoparticles and their assemblies)^{5-7, 10-12} and carbon-based materials.^{3, 14-18} Despite the strong resonant absorption of plasmonic materials, special synthesis, assembly, and fabrication processes are usually needed to achieve broadband absorption through the hybridization of localized surface plasmon resonance (LSPR).

This fact along with the already high cost of plasmonic metals hinders the large scale production and practical applications of these nanostructures. The long-term stability of plasmonic nanostructures is also a potential issue, because upon repetitive heating, metallic nanocrystals tend to fuse into bulk materials losing their LSPR properties. By comparison, carbon-based absorbing materials have advantages of low cost, easy availability, and high stability. Currently, investigations in this area are mainly focused on crystalline carbons, e.g. graphite,¹⁶ graphene,³ and carbon nanotube,^{14, 17} although there are no evidences of their advantages for solar thermal conversion over amorphous carbons. In fact, the high thermal conductivity of crystalline carbons is unfavorable for heat localization. In comparison with crystalline carbon materials, amorphous carbons are even cheaper and more abundant, and more importantly, they can be easily prepared with tunable textural properties and flexible compositions. There are few studies in the literature using amorphous carbons for solar evaporation, whereas the influences of the pore structure and composition of the carbon on the conversion efficiency were not investigated.¹⁹

Aluminosilicate zeolites are widely used as solid acid catalysts because their well-defined porous structure in molecular dimensions can provide unique size/shape selectivity. The reactions over zeolite catalysts are always accompanied by the formation of coke that mainly consists of various polycyclic aromatics and causes the deactivation of catalyst by blocking the catalytic active sites.²⁰⁻²⁴ The cokes are usually simply burned out to regenerate the zeolite catalysts for the next reaction cycle. In this study, however, we demonstrate that upon a proper pyrolysis process, the cokes can form a continuous carbon framework and be isolated from

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the fully deactivated zeolite catalysts by removing the aluminosilicate. Given that their textural properties (surface area, porous structure, pore size etc.) and the composition vary with the type of feedstock and zeolite, reaction conditions, and post treatment processes, the as-prepared carbon materials provide a platform for investigating how these factors influence the energy conversion efficiency of carbon-based solar thermal agents. The highest solar thermal efficiency that we observed with these coke-derived carbons is 72% under 2 sun illumination, and this performance is comparable with those of many plasmonic solar evaporation systems.⁷

Results and discussion

We performed the methanol to aromatics (MTA) reaction over zeolite catalysts using a fixed-bed reactor at 650 °C. Methanol was co-fed with 20 wt% furfuryl alcohol to enhance the selectivity towards aromatics. The details of the reaction conditions are elaborated in the Experimental section. Two types of zeolite, ZSM-5 and Beta in the hydrogen form, were used as catalysts for the reaction. They are both nanocrystalline with crystal sizes less than 300 nm and agglomeration between crystals (Fig. 1a and 1b). After 5 h on stream, the two catalysts were fully deactivated with the conversion of methanol < 10%. The carbon derived from ZSM-5 (denoted as C-ZSM-5-A; ~25 wt% yield relative to the zeolite) was composed of hollow particles that replicated the shape but not the microporous structure of the zeolite crystals (Fig. 1c). X-ray diffraction (XRD) confirms that C-ZSM-5-A does not have structure ordering (Fig. 2a). This result is consistent with previous reports,²⁰⁻²¹ indicating that the coke can only deposit on the external surfaces of ZSM-5 due to the constraint of its small 10-membered rings that prevents the formation of coke intermediates in the microporous channels. In contrast, carbon derived from zeolite Beta (denoted as C-Beta-A; ~60 wt% yield relative to the zeolite) replicated not only the crystal shape but also the microporous structure of the zeolite, as evidenced by the ordered lattice fringes in the transmission electron microscopy (TEM) image (Fig. 1d). The XRD pattern of C-Beta-A shows two peaks at low angles (2 theta: 7 and 15°), confirming the ordered microstructure, while the absence of peaks at higher angles demonstrates its amorphous nature at the atomic level (Fig. 2a).²⁵⁻²⁶ These results indicate that the large 12-membered-ring channels of Beta allow the coke to form

inside, growing into a negative replica of the original zeolite structure. In agreement with TEM and XRD results, C-ZSM-5-A and C-Beta-A exhibit type IV and type I argon (Ar) sorption isotherms, corresponding to non-porous and microporous materials, respectively (Fig. 2b and 2c). Accordingly, C-Beta-A has a larger Brunauer-Emmett-Teller (BET) surface area and a higher pore volume than does C-ZSM-5-A (BET surface area: 919 vs. 112 m²/g; total pore volume: 0.59 vs. 0.25 cm³/g⁻¹) (Table 1). The pore size distribution profiles confirm that C-Beta-A contains uniform micropores centered at ~1.2 nm, while C-ZSM-5-A is essentially a non-porous material. The two carbons have similar compositions containing ~ 4.5 wt% oxygen and ~ 2.4 wt% hydrogen (Table 1).

Fig. 1 TEM images of (a) zeolite ZSM-5, (b) zeolite Beta, (c) C-ZSM-5-A, and (d) C-Beta-A. The right-side images in (c) and (d) are high-magnification images and the corresponding FFTs (inset) to show the structure ordering of these two carbon materials.

To investigate the performance of these coke-derived carbon materials in the application of solar evaporation, we deposited 40 mg of the carbon material from a water suspension onto a cellulose membrane (a piece of Whatman Grade 3 filter paper, area: 4.9 cm²) by simple vacuum filtration. The resulting black membrane floating on the surface of water in a beaker was placed under a solar simulator with the irradiation power density controlled to be 1950 W m⁻² (~ 2 suns). We measured the water mass reduction $m(t)$ due to water evaporation as a function of time t and calculated the solar thermal efficiency η based on the following formula:

Fig. 2 (a) XRD patterns, (b) argon adsorption-desorption isotherms, and (c) pore size distribution profiles of three zeolite-derived carbon materials: C-ZSM-5-A, C-Beta-A and C-Beta-O.

Table 1 Textural properties, compositions, and solar-thermal energy conversion efficiencies of various carbon materials.

Sample	S_{BET}^a (m^2g^{-1})	V_{total}^b (cm^3g^{-1})	I_D/I_G^c (I_{2D}/I_G)	Elemental content			Efficiency (%) ^d
				C (%)	H (%)	O (%)	
C-ZSM-5-A	112	0.25	1.91 (0.04)	93.1	2.4	4.5	57.4
C-Beta-A	919	0.59	1.99 (0.09)	93.3	2.4	4.3	62.8
C-Beta-O	1704	1.10	1.87 (0.05)	88.1	2.3	9.6	72.5
AC-H	1678	0.77	2.85 (0.01)	91.5	0.8	7.7	59.4
AC-L	1521	1.44	1.62 (0.04)	97.7	0.4	1.9	53.6
CNT	271	0.56	0.98 (0.38)	96.8	0.6	2.6	60.2

^a BET surface area calculated at $P/P_0 = 0.05-0.2$. ^b Total pore volumes estimated at $P/P_0 = 0.95$. ^c Calculated from raw Raman spectra after treatments of baseline correction, peak-splitting and fitting. ^d Heat of evaporation of water $\approx 2380 \text{ kJ}\cdot\text{kg}^{-1}$ at 50°C .

$$\eta = \dot{m}h_{LV}/I \quad (1)$$

where $\dot{m}(t) \equiv dm/dt$ denotes the time derivative of the mass reduction $m(t)$ at thermal equilibrium, h_{LV} is the latent enthalpy of the liquid-vapor phase change, and I is the irradiation power used. Note that the latent enthalpy of water is temperature dependent. This fact has usually been ignored in the literature, in which the h_{LV} value at 100°C ($\sim 2260 \text{ kJ/kg}$) was used for calculation although the water temperature did not reach that high in most systems. Here, we measured the actual equilibrium temperature of water under irradiation and used the h_{LV} value of that temperature (e.g., 2380 kJ/kg at 50°C) to calculate the efficiency.

Fig. 3 (a) Mass loss by water evaporation and (b) temperature evolution at the water surface under the membrane of solar evaporation systems using different carbons as absorbing materials (carbon: 40 mg; evaporation area: 4.9 cm^2 ; illumination power density: $1950 \text{ W}\cdot\text{m}^{-2}$). The results of a pure water system are labelled as blank for comparison purpose.

Our measurements indicate that both C-ZSM-5-A and C-Beta-A enhance the solar thermal efficiency for water evaporation, in comparison with the system of pure water as a control (the blanks in Fig. 3). Specifically, the evaporation rates were $1.69 \text{ kg m}^{-2}\text{h}^{-1}$ with C-ZSM-5-A and $1.85 \text{ kg m}^{-2}\text{h}^{-1}$ with C-Beta-A, which were 3.7 times and 4.1 times that of pure water ($0.45 \text{ kg m}^{-2}\text{h}^{-1}$), and their energy conversion efficiencies were calculated to be 57.4% and 62.8%, respectively (Table 1). Given their similar compositions, we attribute the higher solar thermal efficiency of C-Beta-A relative to C-ZSM-5-A to its porous structure that facilitates the transport of water molecules through the carbon layer.

It has been reported that the wettability of the absorbing material has important effects on the efficiency of solar

evaporation.^{3, 16} The transport of water is expected to be promoted by increasing the affinity of the absorbing material to water. Therefore, we propose that the solar thermal efficiency of the coke-derived carbon can be further enhanced by introducing heteroatoms (e.g. oxygen) to increase the polarity of the carbon framework. To achieve this, we performed a methanol to olefins (MTO) reaction over zeolite Beta under the same reaction conditions for the MTA reaction described earlier except that pure methanol was used as the feed without co-feeding furfuryl alcohol. We expected that a higher content of oxygen in the reaction feed would lead to a higher content of oxygen in the coke and eventually in the final carbon material. Following the processes used for preparing C-ZSM-5-A and C-Beta-A (full deactivation of zeolite, pyrolysis, and removal of aluminosilicate), a new carbon material was obtained and denoted as C-Beta-O. In the XRD pattern of C-Beta-O, there are three visible peaks at low angles, indicating an even higher structural ordering than C-Beta-A (Fig. 2a). As shown in the Ar sorption isotherms (Fig. 2b), C-Beta-O has a similar adsorption behavior and pore size distribution profile as C-Beta-A, but almost doubled total adsorption amount and surface area ($1704 \text{ m}^2/\text{g}$) (Table 1). These results indicate that like C-Beta-A, C-Beta-O is a negative replica of the zeolite Beta, having an ordered microporous structure. One possible reason for the different surface areas between C-Beta-A and C-Beta-O is that in the MTO reaction, cokes were selectively generated in zeolite channels, while in the MTA reaction, cokes were rapidly formed not only in zeolite channels but also in the void spaces among zeolite nanocrystallites, leading to a certain amount of non-porous carbon in the final product. Moreover, as expected, the oxygen content in C-Beta-O is 9.6 wt%, remarkably higher than that in C-Beta-A (Table 1).

When used for solar evaporation under the same conditions described above, C-Beta-O gave an evaporation rate of $2.14 \text{ kg m}^{-2}\text{h}^{-1}$ that corresponds to a solar thermal conversion efficiency of 72.5%, surpassing the performances of C-ZSM-5-A and C-Beta-A (Figure 3 and Table 1). The different conversion efficiencies of the three carbon materials are also reflected by the temperature rise of the water measured at the water surface immediately below the floating carbon membrane. As shown in Fig. 3b, the surface temperature of water at equilibrium conditions was 50°C for C-Beta-O, 45°C for C-

Beta-A, 41 °C for C-ZSM-5-A, and 35 °C for pure water. In comparison with C-Beta-A, C-Beta-O has a larger surface area and a higher oxygen content. These two factors may both affect the energy conversion efficiency. However, we infer that the effect of surface area is relatively trivial from the fact that C-Beta-A has an 8-fold larger surface area than C-ZSM-5-A but exhibits only ~ 10% higher conversion efficiency. To demonstrate that these findings generally apply to other types of amorphous carbon, we prepared two activated carbon materials with comparable surface areas ($> 1500 \text{ m}^2/\text{g}$, Fig. 4a) but different oxygen contents (7.7 wt% and 1.9 wt%, respectively), and tested their solar thermal efficiencies under the same conditions as used for the coke-derived carbons (Table 1). The activated carbon containing more oxygen (AC-H) gave a 59.4% conversion efficiency (Fig. 4c), higher than the efficiency (53.6%) of the low-oxygen counterpart (AC-L). On the other hand, we notice that activated carbons show lower efficiencies than coke-derived carbons from zeolites, despite their larger surface areas. These results consolidate the conclusion that the solar thermal efficiency positively correlates with the oxygen content in the carbon materials but has little relation with their surface areas. Note that both

activated carbons and coke-derived carbons are amorphous materials and they follow the same trend that the energy conversion efficiency increases with the oxygen content, but our results indicate that coke-derived carbons are superior to activated carbons with comparable content of oxygen. We attribute the different solar thermal performances between these two types of carbon material to their different porous structures. Coke-derived carbons have inverse structures of zeolite containing three-dimensionally interconnected channels (~1.2 nm in diameter) that allow water to easily evaporate through the absorbing membrane. In contrast, activated carbons prepared by conventional KOH etching method mainly contain isolated ultra-micropores (~5 Å) (Fig. 4b), and consequently the transport of water molecules largely takes place on the external surfaces of the carbon particles, leading to a lower efficiency. Namely, it is not the apparent BET surface area but the area of the surfaces easily accessible for water that determines the energy conversion efficiency. Therefore, both the oxygen content and the proportion of large interconnected pores in the carbon are crucial factors.

Fig. 4 (a) argon adsorption-desorption isotherms, (b) pore size distribution profiles and (c) water evaporation performance of various carbon materials: AC-H, AC-L and a commercial CNT. The experimental conditions of water evaporation are same as described in the caption of Fig. 3.

We also tested a commercial carbon nanotube (CNT) material that has a BET surface area of $271 \text{ m}^2/\text{g}$ (Fig. 4a and Table 1). The characterization by using Raman spectroscopy reveals that this CNT sample has a markedly lower value of the intensity ratio between the D band at 1350 cm^{-1} and G band at 1590 cm^{-1} (I_D/I_G), as compared with those amorphous carbons materials tested in this study, indicating a higher degree of structural ordering at the atomic level.²⁷⁻²⁹ Under the same experimental conditions, 40 mg of CNT gave a water evaporation rate of $1.77 \text{ kg m}^{-2}\text{h}^{-1}$, corresponding to an energy conversion efficiency of 60.2%. This undistinguished performance implies that the crystallinity of carbon (or the degree of graphitization) is not an important influential factor to the solar thermal conversion efficiency either.

Finally, it is worth noting that the solar evaporation system we described above has been optimized. For instance, depositing 40 mg of C-Beta-O on the cellulose membrane gives rise to a carbon surface layer of ~ 110 μm , as estimated from the area of the membrane and the density of carbon. This thickness proved to be the optimal tradeoff between the sunlight capture and heat conduction to the underneath

water, and deviation from the optimal thickness led to decreases in energy conversion efficiency (Fig. 5a). Moreover, although the tested carbon materials can self-float on the surface of water, the use of a cellulose membrane as a heat-insulating layer is necessary for achieving a high energy efficiency. Without a cellulose membrane, 40 mg of C-Beta-O floating on the water surface gave a solar thermal efficiency of only 62% under the same illumination conditions. The role of the cellulose membrane is clearly illustrated by the infrared (IR) thermal images in Fig. 5b, where a sharp temperature gradient was formed at the water/air interface by the membrane meaning an efficient heat confinement, while the system with self-floating carbon showed obvious heat dissipation into non-evaporative bulk water.

Conclusions

In summary, cokes produced from zeolite-catalyzed reactions can be easily converted to porous carbons and then used as photo-thermal agents for solar-driven water evaporation. The textural properties and compositions of the carbon can be

tuned by varying the type of zeolite and reaction conditions. One of the coke-derived carbons, C-Beta-O, outperformed other carbon materials including a carbon from zeolite ZSM-5, activated carbons and commercial carbon nanotubes, in terms of solar thermal efficiency, due to its ordered interconnected porous structure replicated from zeolite Beta and high content of oxygen in the framework. The integration of three-dimensional pore structure, large pore size and high affinity to water in C-Beta-O promoted the transport of water, leading to an energy conversion efficiency as high as 72% under 2 suns. In addition, the BET surface areas and crystallinity of carbon materials proved not to be influential factors for the solar thermal conversion efficiency.

Fig. 5 (a) the variation of solar thermal energy conversion efficiency of C-Beta-O with the thickness of the carbon layer under $1950 \text{ W}\cdot\text{m}^{-2}$ solar illumination. (b) IR thermal images of the water evaporation systems using C-Beta-O with and without a cellulose membrane. The exact temperatures at water surface were measured by a thermometer to be 50 and 33 °C, respectively. The insets are photo pictures of the two systems, showing that C-Beta-O can self-float on the water surface without a supporting membrane.

Experimental

Chemicals

Zeolite ZSM-5 ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 50:1$) and zeolite Beta ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 25:1$) were purchased from Alfa Aesar company. A carbon nanotube (CNT) sample and an activated carbon material (AC-L) were purchased from SunYoung Chemical Co., Ltd. Other chemicals of GC/LC grade were purchased from Sigma-Aldrich without further purification.

Preparation of coke-derived carbon materials

C-ZSM-5-A and C-Beta-A were prepared from zeolite ZSM-5 and Beta, respectively, by using the mixture of methanol and 2-methylfuran (4:1, w/w) as the reaction feedstock. Typically, 0.5 g of ZSM-5 (or Beta) catalyst was placed in a vertical quartz reactor and the reactor temperature was then raised to 550 °C under dry nitrogen flow (50 mL/min). After 60 min, the temperature of the reactor was raised to 650 °C and the liquid feedstock (mixture of methanol and 2-methylfuran) was pumped into reactor using a high-performance liquid chromatography pump at a flow rate of 0.04 mL/min (keeping N_2 flow unchanged). After 5 h of reaction, the liquid feed was turned off and the reaction bed was heated up at 750 °C for another 1 h under a N_2 flow. The reactor was then cooled

down to the room temperature. The zeolite catalyst was taken out of the bed and washed with a HF solution (47%) twice to completely remove the aluminosilicates. The obtained carbon (C-Beta-O) was washed with water and ethanol, and dried in the oven.

C-Beta-O was prepared by following the same procedure described above for C-Beta-A, except that methanol alone was used as the feedstock and its flow rate was 0.01 mL/min. The activated carbon AC-H was prepared following the below method: 23.5 g of furfuryl alcohol was added into 60 mL of acetone solvent, and stirred for 5 minutes vigorously. The polymerization of furfuryl alcohol using 2 g of *p*-toluenesulfonic acid as a catalyst was conducted at 120 °C for 5 h with condensed reflux. After removing acetone by vacuum evaporation, the resultant solid product was carbonized at 600 °C for 5 h and activated by KOH ($m_{\text{carbon}}/m_{\text{KOH}} = 1:2.5$, w/w) at 800 °C for 1 h in nitrogen atmosphere. Finally the resultant activated carbon was collected, washed with dilute HCl solution (1 M) and water thoroughly, and dried at 80 °C overnight.

Characterization

Powder X-ray diffraction patterns were recorded on using Bruker D8 Advance instrument with $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Ar adsorption-desorption isotherms were measured at liquid argon temperature (87K) on a Micromeritics 3Flex apparatus after vacuum sample degassing for 10 h at 300 °C. BET surface areas were determined using data points in a relative pressure range of 0.05–0.2. Pore size distribution and pore volume were determined using density functional theory (DFT) method, assuming a slit-shaped geometry, and total pore volumes were estimated at $P/P_0 = 0.95$. The contents of carbon, hydrogen and oxygen in various carbon materials were determined by using a CHNS elemental analyzer (Thermo scientific Flash 2000). TEM was performed on a FEI Titan-ST microscope operated at 300 kV. Raman spectra were recorded on a Horiba Aramis apparatus with an incident wavelength of 473 nm.

Solar-driven water evaporation experiments

The solar-driven water evaporation experiments were performed at room temperature. A glass beaker (40 mL and 2.5 cm in inner diameter) was wrapped up with fiberglass for thermal insulation and filled with 30 mL of water. A cellulose membrane with carbon material deposited was placed on the surface of water. The beaker was then placed on an electronic balance to monitor the real-time water mass change. A sun simulator was used to provide illumination at intensity of $1950 \text{ kW}\cdot\text{m}^{-2}$ (~ 2 suns). The weight loss of the water was recorded regularly for calculating the water evaporation rate. A temperature monitor device (K type, CEM DT-8891E) was used to monitor the temperature at the water surface under the membrane.

Acknowledgements

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Notes and references

1. T. Oki and S. Kanae, *Science*, 2006, **313**, 1068-1072.
2. N. S. Lewis, *Science*, 2007, **315**, 798-801.
3. Y. Ito; Y. Tanabe; J. Han; T. Fujita; K. Tanigaki and M. Chen, *Adv. Mater.*, 2015, **27**, 4302-4307.
4. L. Zhang; B. Tang; J. Wu; R. Li and P. Wang, *Adv. Mater.*, 2015, **27**, 4889-4894.
5. O. Neumann; C. Feronti; A. D. Neumann; A. Dong; K. Schell; B. Lu; E. Kim; M. Quinn; S. Thompson; N. Grady; P. Nordlander; M. Oden and N. J. Halas, *PNAS*, 2013, **110**, 11677-11681.
6. O. Neumann; A. S. Urban; J. Day; S. Lal; P. Nordlander and N. J. Halas, *ACS Nano*, 2013, **7**, 42-49.
7. Z. H. Wang; Y. M. Liu; P. Tao; Q. C. Shen; N. Yi; F. Y. Zhang; Q. L. Liu; C. Y. Song; D. Zhang; W. Shang and T. Deng, *Small*, 2014, **10**, 3234-3239.
8. J. Huang; C. Liu; Y. Zhu; S. Masala; E. Alarousu; Y. Han and A. Fratalocchi, *Nature Nanotech.*, 2016, **11**, 60-66.
9. C. X. Liu; J. F. Huang; C. E. Hsiung; Y. Tian; J. J. Wang; Y. Han and A. Fratalocchi, *Adv. Sustainable Syst.*, 2017, DOI: 10.1002/adsu.201600013.
10. Y. Liu; S. Yu; R. Feng; A. Bernard; Y. Liu; Y. Zhang; H. Duan; W. Shang; P. Tao; C. Song and T. Deng, *Adv. Mater.*, 2015, **27**, 2768-2774.
11. L. Zhou; Y. Tan; D. Ji; B. Zhu; P. Zhang; J. Xu; Q. Gan; Z. Yu and J. Zhu, *Sci. Adv.*, 2016, **2**, DOI: 10.1126/sciadv.1501227.
12. L. Zhou; Y. Tan; J. Wang; W. Xu; Y. Yuan; W. Cai; S. Zhu and J. Zhu, *Nature Photon.*, 2016, **10**, 393-398.
13. G. Ni; G. Li; S. V. Boriskina; H. Li; W. Yang; T. Zhang and G. Chen, *Nature Energy*, 2016, **1**, DOI: 10.1038/nenergy.2016.1126.
14. E. Miyako; H. Nagata; K. Hirano and T. Hirotsu, *Adv. Mater.*, 2009, **21**, 2819-2823.
15. Y. Zeng; J. Yao; B. A. Horri; K. Wang; Y. Wu; D. Li and H. Wang, *Energy Environ. Sci.*, 2011, **4**, 4074-4078.
16. H. Ghasemi; G. Ni; A. M. Marconnet; J. Loomis; S. Yerci; N. Miljkovic and G. Chen, *Nature Commun.*, 2014, **5**, DOI: 10.1038/ncomms5449.
17. Y. C. Wang; L. B. Zhang and P. Wang, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1223-1230.
18. J. Zhou; Z. Sun; M. Chen; J. Wang; W. Qiao; D. Long and L. Ling, *Adv. Funct. Mater.*, 2016, **26**, 5368-5375.
19. Y. M. Liu; J. W. Chen; D. W. Guo; M. Y. Cao and L. Jiang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 13645-13652.
20. F. Schmidt; C. Hoffmann; F. Giordanino; S. Bordiga; P. Simon; W. Carrillo-Cabrera and S. Kaskel, *J. Catal.*, 2013, **307**, 238-245.
21. K. Urata; S. Furukawa and T. Komatsu, *Appl. Catal. A: Gen.*, 2014, **475**, 335-340.
22. M. Milina; S. Mitchell; D. Cooke; P. Crivelli and J. Perez-Ramirez, *Angew. Chem. Int. Ed.*, 2015, **54**, 1591-1594.
23. S. Muller; Y. Liu; M. Vishnuvarthan; X. Y. Sun; A. C. van Veen; G. L. Haller; M. Sanchez-Sanchez and J. A. Lercher, *J. Catal.*, 2015, **325**, 48-59.
24. A. Astafan; M. A. Bengelem; Y. Pouilloux; J. Patarin; N. Bats; C. Bouchy; T. J. Daou and L. Pinard, *J. Catal.*, 2016, **336**, 1-10.
25. K. Kim; M. Choi and R. Ryoo, *Carbon*, 2013, **60**, 175-185.
26. K. Kim; T. Lee; Y. Kwon; Y. Seo; J. Song; J. K. Park; H. Lee; J. Y. Park; H. Ihee; S. J. Cho and R. Ryoo, *Nature*, 2016, **535**, 131-135.
27. G. H. Qin; Z. W. Fang and C. Y. Wang, *Dalton Trans.*, 2015, **44**, 5735-5745.
28. Y. Z. Jiao; H. T. Zhang; T. Dong; P. Shen; Y. J. Cai; H. L. Zhang and S. J. Zhang, *J. Mater. Sci.*, 2017, **52**, 3233-3243.
29. L. Rivoira; J. Juarez; H. Falcon; M. G. Costa; O. Anunziata and A. Beltramone, *Catal. Today*, 2017, **282**, 123-132.