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Bridging Ultrasmall Au Clusters into the Pores of a Covalent Organic Framework for Enhanced Photostability and Photocatalytic Performance

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Dedication ((optional))

Abstract: Gold (Au) clusters loading on various supports were widely used in the fields of energy and biology. However, the poor photostability of Au clusters on support interface under longtime illumination usually results in loss of catalytic performance. Covalent organic frameworks (COFs) with periodic and ultrasmall pore structures are ideal supports for dispersing and stabilizing Au clusters, while it is difficult to encapsulate Au clusters into the ultrasmall pore structures. Herein, a two-dimensional (2D) COF modified with thiol chains (-SH) in its pores was prepared. Taking -SH as nucleation sites, Au NCs can in situ grow within the COF. Ultrasmall pore structure of COF and the strong binding energy of S-Au provide double assurance for improving the dispersibility of Au NCs under longtime light illumination conditions. Interestingly, the artificial Z-scheme photocatalytic system was constructed due to the formation of Au-S-COF bonding bridge, which is deemed to be an ideal means to increase the charge separation efficiency. Such new strategy provides a facile guideline for rationally designing COF support catalysts with controllable activity and high stability.

Introduction

Metal nanoparticles (NPs) and nanoclusters (NCs) have always been a hot topic for their unique optical, electronic and mechanical properties and widely employed in catalysts.^[1] Achieving controllable adjustment to their catalytic performance is significant.^[2] "The quantum size effect" proves the properties of NPs can be greatly influenced by their size.^[3] And previous works have reported that the surface free energy will be enhanced with size minimizing.^[4] When the size of NPs are smaller than 2 nm, high surface free energy will keep the NPs in a "boiling state", which further causes poor stability tending to aggregate and loss of catalytic performance.^[5]

Loading nanomaterials on high-surface-area supports as one of the most important heterogeneous catalysts is a feasible strategy to improve stability and catalytic performance.^[6] In

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recent years, as a promising metal supports, covalent organic frameworks (COFs) have attracted widely attention and been continually developed.^[7] Compared with some traditional supports (q-C₃N₄, metal oxide, etc.), the highly ordered structure and ultrasmall pores of COFs not only can limit the growth of NCs but also realize uniform dispersion of NCs on COF supports.^[8] Via a simple post-treatment, Wang and co-workers prepared a Pd(II)-containing COF showing excellent catalytic performance for the Suzuki-Miyaura coupling reaction.^[9] Zhang et al. embedded Pd NPs and Pt NPs inside the pores of a COF with a size distribution of 1.7±0.2 nm, which exhibited enhanced catalytic performance for Suzuki-Miyaura coupling reaction and nitrophenol reduction.^[10] Ma et al. provided a new strategy of immobilizing a linear ionic polymer with catalytically active into the channels of a Lewis acid-modified COF as a heterogeneous catalyst.^[11] All these excellent works demonstrate the unique advantages of COFs as decorating supports. It is worth noting that the porous and modification performance of COFs as supports have been fully developed, however, the interaction between metal and COF supports has not been deeply explored.



Figure 1. Synthetic scheme of Au@COF.

Au NPs as a prototype with adjustable size among various NPs have drawn extensive attention for their excellent catalytic performance.^[12] However, Au NCs are easier to aggregate for higher surface energy compared with other various NCs and NPs.^[13] Transitional strategy of loading Au NCs on metal oxide,

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Figure 2. a) Structure of COF-V; b) SEM image of COF-V; c) PXRD patterns of COF-V and COF-S-SH; d) Structure of COF-S-SH; e) SEM image of COF-S-SH; f) N₂ adsorption isotherms of COF-V and COF-S-SH; g) Graphic view of COF-V structure; h) Graph of COF-S-SH structure.

SiO₂ is difficult to maintain the stability under longtime in situ photo-irradiation conditions, which is a bottleneck for the development of Au NCs-based catalysts in practical application.^[14] Thus, it is necessary and urgent to develop novel Au NCs catalysts with enhanced stability.

Herein, a thiol chains post-modified COF-S-SH was selected as the support of Au NCs.^[15] The ultrasmall pores (2.8 nm) of this COF not only can limit the growth of Au NCs but also play a role of anchoring Au NCs. Thiol chains were chosen to build a bridge between COF and Au NCs. On one hand, the strong binding energy of S-Au is obviously helpful to stabilize Au NCs. On the other hand, Z-scheme photocatalytic system was constructed due to the formation of Au-S-COF bonding bridge, which possesses the advantages of increasing the charge separation efficiency. Specifically, vinyl-functionalized monomer 1 (2,5-divinylterephthalalde-hyde) and monomer 2 (1,3,5-tris(4aminophenyl)-benzene) were utilized to construct COF-V, where vinyl groups allowed for further chemical modifications with thiol chains (Figure 1). Due to the strong binding interaction of -SH and Au, thiol group inside the pores served as nucleation sites where HAuCl₄•3H₂O can be in situ reduced by L-glutathione (L-GSH) to obtain the final Au@COF. Au NCs loaded on COF support are ultrafine (1.8±0.2 nm), highly dispersed and shows highly photostability under in situ photo-irradiation (λ >420 nm) for 5 h. Furthermore, the Z-scheme photocatalytic system was successfully constructed via Au-S-COF bonding bridge between COF and Au NCs, which was confirmed by the calculation of binding energy and the results of photoelectrochemical (PEC) experiments. As far as we know, this is a rare work to deeply explore the PEC process between metal NCs and COF support. Such strategy provides a guideline for rationally designing COF support catalysts with controllable activity and high stability.

Results and Discussion

First, Fourier-transform infrared (FT-IR) spectra were explored to verify construction of COFs (Figure S1). Compared with

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Figure 3. a) Structure of Au@COF; b) SEM image of Au@COF; c), d), e) TEM images of Au@COF; Inset in c) is distribution statistics of Au NPs size; f) EDSmapping of Au@COF; TEM images of Au@COF radiated using a 300 W Xe arc lamp for g) 0 h and h) 5 h.

monomer 1 and 2, a new peak at 1645 cm⁻¹ in the spectrum appeared, which assigned to the C=N stretching vibration. At the same time, the characteristic peak corresponding to C=O (1690 cm⁻¹) of monomer 1 and N-H (3352 cm⁻¹) of monomer 2 disappeared in the FT-IR spectrum of COF-V. Furthermore, FT-IR spectrum of COF-S-SH shows a peak of thiol group at 2522 cm⁻¹, which confirmed the successful integration of thiol groups (Figure S2). Solid-state ¹³C NMR spectrum of COF-S-SH also indicates the characteristic peak of vinyl groups at 114.2 ppm disappears and the appearance of the alkyl C species of thiol chains at 38.8 ppm (Figure S3).[15] Scanning electron microscopy (SEM) images show the COF-V and COF-S-SH display uniform nanowires with a diameter of approximately 50±5 nm (Figure 2b and 2e). The morphology reveals no obvious change before and after pore-surface modification with thiol chains. Powder X-ray diffraction (PXRD) was utilized to evaluate the periodic structures of as-synthesized COFs. As Figure 2c represents, a high intensity peak of COF-V appeared in the low-angle region at $2\theta = 2.8$ degrees related to the (1 0 0) facet of hexagonal lattice, which is consistent with reported literature.^[15] While COF-S-SH shows a relatively weak peak at 2.8 degrees and a broad peak from 15 to 30 degrees, which result from the appearance of flexible thiol chains distorting the long-range order structure and π - π stacking between layers. Nitrogen-sorption isotherm indicates the porosity and specific surface area of COF-S-SH (290 m² g⁻¹) is much lower than that of COF-V (736 m² g⁻¹), which also proves the appearance of thiol chains in the accessible pores of COF (Figure 2f). Thermogravimetric analysis (TGA) was utilized to evaluate the thermal stability of as-synthesized materials. Figure S4 shows COF-V and COF-S-SH exhibit decomposition temperature (10% weight loss) respectively at 300 °C and 175 °C, which confirm

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Figure 4. a) The UV-vis spectra of RhB in different time under dark condition by adding Au@COF; Inset is optical photos before (left) and after (right) adding Au@COF; b) The removal efficiency of RhB over Au@COF and COF-V under dark condition; c) Recycling removal efficiency of RhB over Au@COF under dark condition; d) The UV-vis spectra of RhB in different time under different irradiation time after Au@COF adsorption saturation; e) The degradation efficiency of RhB over Au@COF v and Au@COF; f) Recycling degradation efficiency of RhB over Au@COF under visible light irradiation.

the excellent thermal stability. And weight loss rate of COF-S-SH is faster than COF-V, which results from the appearance of thiol chains, proving the successful modification of thiol chains. All these above results can demonstrate the successful construction of as-synthesized two COFs. Moreover, the structure of as-synthesized COFs was simulated by Materials Studio software. After geometrical energy minimization, graphic view of COF-V shows periodic pores with a diameter of 28 Å and an interlayer distance of 3.6 Å (Figure 2g).

Previous studies have reported that thiol-functionalized COFs exhibited effective removal ability for mercury ion due to the porous structure and strong binding interaction between thiol group and mercury ion.^[16] Inspired by this strategy, it is expected that thiol-functional COFs can be utilized to induce nucleation and growth of metal NCs inside the accessible pores of COFs. Taking advantage of strong binding energy of S-Au, the thiol groups of COF-S-SH can serve as nucleation sites for Au NCs, and the ultrasmall pores can confine the growth of Au NCs. Such design not only avoids aggregation of Au NCs providing more active sites for the ultrasmall size but also achieves uniform dispersion for order structure of COFs. Specifically, the Au precursor was adsorbed inside the pores of COF-S-SH by dropping a certain concentration of HAuCl₄•3H₂O solution into a suspension of COF-S-SH and stirring for 4 h. Then L-GSH was introduced into above mixture and stirred for 48 h to obtain Au@COF. Transmission electron microscope (TEM) images of Au@COF show that ultrasmall Au NCs are uniformly distributed on COF supports (Figure 3c). The ultrasmall Au NCs possess an average diameter of 1.8±0.2 nm, matching well with the size of pores, which further proves that Au NCs is anchored inside the pores of COF support (Figure 3d). High-resolution transmission electron microscope (HR-TEM) image in Figure 3e indicates crystal faces Au NCs exposing is (1 1 1). And energy dispersive spectrometer (EDS) mapping of Au@COF proves the existence of Au and S (Figure 3f). FT-IR spectrum of Au@COF was given in Figure S5. The disappearance of characteristic peak corresponding to -SH at 2522 cm⁻¹ indicates the formation of S-Au bond. X-ray photoelectron spectroscopy (XPS) was also utilized to further verify the successful grafting of thiol groups and Au NCs. XPS spectra of COF-S-SH shows the sulfur signal at 162.1 eV (Figure S6a), which shift to 163.6 eV in Au@COF S6c), revealing the (Figure successfully post-synthetic modification of S-Au.

In contrast, composite without thiol modified was also synthesized (Figure S9a). As can be seen from Figure S9c and S9d, Au NCs loaded on COF-S-SH are uniform and highly dispersed. Without thiol chains modified on COF support, Au NCs loaded on COF-V aggregate to bigger NPs easily (Figure S9b). In addition, transitional strategy of loading Au NCs on metal oxide and TiO₂ supports fail to achieve the long-term stability under in situ illumination conditions, which limits further development of Au NCs-based catalysts in practical application.^[12] Thus, the longtime photostability was explored by exposing Au@COF under light radiation (λ >420 nm) for 5 h.

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Figure 5. a) Transient photocurrent densities of COF-V and Au@COF under light irradiation ($\lambda > 420$ nm); b) EIS Nyquist plots of COF-V and Au@COF; c) Timeresolved photoluminescence emission decay spectra of COF-V and Au@COF; d) VB-XPS spectra of COF-V; e) Band alignment of Au NCs, COF-V, H₂O/•OH, O₂/•O₂; f) The estimated band gap of COF-V and Au@COF; g) Cyclic voltammogram of Au NCs (electrolyte: acetonitrile containing 0.1 M tetrabutyl ammonium perchlorate); h) ESR spectra of Au@COF in the presence of DMPO as radical scavenger before and after light irradiation; i) Radical trapping experiments of Au@COF under light irradiation.

TEM images show Au NCs supported on COF-S-SH maintain ultrafine and high dispersion before and after continuous light irradiation (Figure 3g and 3h). The result suggests that ultrasmall pore structure of COF and the strong binding energy of S-Au provide double assurance for stabilizing Au NCs under longtime light illumination conditions.

In order to assess the effects of as-constructed Au@COF on photocatalytic performance, RhB dye was chosen as a model to evaluate controllable photocatalytic performance of Au@COF. Considering the excellent adsorption capacity of COF materials, the removal efficiency of Au@COF to RhB was investigated. Typically, 10 mg of COF-V or Au@COF added to 50 ml RhB solution (10 mg/L). Then, the absorbance value was monitored with an ultraviolet-visible (UV-vis) spectrophotometry analyzer. As shown in Figure 4a and S12a, upon the addition of COF-V or Au@COF, the characteristic absorbance peak of RhB at 557 nm decreased. Almost all the RhB in system can be adsorbed after 60 min and 10 min for Au@COF and COF-V, respectively. According to the adsorption curves, removal efficiency was calculated. We found that almost 99.5% of RhB were captured after 30 min when COF-V as adsorbent, while Au@COF can only adsorb about 98.3% of RhB within 1 h, which mainly attribute to the blocked porous structure of COF by Au NCs (Figure 4b). And the removal efficiency can maintain more than 93.2% after 5 cycles (Figure 4c). Adsorption saturation of Au@COF was also studied by mixing a solution of RhB dye (20 mL, 10 mg/mL) and Au@COF (1 mg). After 30 min, adsorption reaches a saturated state (Figure S13b). By the standard curve of concentration of RhB versus absorbance (Figure S13a), adsorption capacity is calculated to be 170 mg/g.

Photodegradation efficiency of RhB over COF-V and Au@COF was evaluated after absorbing to saturation. Figure 4d and S12b show the absorbance intensity of RhB (100 mL, 10 mg/L) when Au@COF (10 mg) and COF-V (10 mg) appeared, respectively. As depicted in Figure 4e, the degradation percentage of 97.3% was obtained after visible light irradiation for 30 min when Au@COF was added, which shows 2-fold higher efficiency compared with COF-V. The degradation kinetic

data were fitted according to $-ln(C/C_0)=kt$ where C and k are the concentrations of RhB and rate constant. Compared with COF-V, RhB degradation rates significantly increase from 5.79×10^{-2} min⁻¹ to 9.04×10^{-2} min⁻¹. And the removal efficiency can maintain more than 95.4% after 5 cycles (Figure 4f).

The above results indicate the enhanced photocatalytic performance. To better understand the constructed model between COF support and Au NCs, it is significant to deeply investigate their specific mechanism of enhanced photocatalysis. The transient photocurrent responses of COF-V and Au@COF with several on-off cycles under intermittent visible light irradiation were displayed in Figure 5a. Au@COF possesses higher photocurrent intensity than COF-V, which proves the dispersed Au NCs on COF support successfully promote the generation of more photoexcited charges. As shown in Figure 5b, the electrochemical impedance spectrum (EIS) Nyquist plot of Au@COF is smaller confirming its better electron transport capability. Time-resolved photoluminescence emission decay spectrum were utilized to evaluate the photogenerated carrier separation efficiency. Figure 5c shows the electronic lifetime of Au@COF is longer, which indicates the higher photogenerated carrier separation efficiency. We have further explored the detailed degradation mechanism of RhB. Numerous researches reported that RhB can be efficiency degraded by high oxidative species (•OH, •O₂- and hole h⁺).^[17] Radical trapping experiments and electron spin-resonance spectroscopy (ESR) were carried out to detect the roles of possible active species in photocatalysis process. Figure 5i shows the degradation ratio of RhB decreases to 40.1% and 45.3% after adding EDTA-2Na (hole scavenger) and BQ (superoxide radical scavenger), respectively, while a weak inhibition after adding TBA (hydroxyl radical scavenger). Furthermore, ESR experiments were conducted to confirm the radicals generated in the photocatalytic process (Figure 5h). No signal can be detected for both •O2⁻ and •OH under dark condition. When applying light irradiation (λ >420 nm), there are four characteristic peaks corresponding to $\cdot O_2^{-1}$ can be observed, while no characteristic peak of •OH appears. These results reveal that $\cdot O_2^-$ and h^+ are the main active species. Subsequently, the transport path of carriers was deeply explored by comparing energy band structures. The valence band X-ray photoelectron spectroscopy (VB-XPS) of COF-V is located at 2.07 eV (Figure 5d). The band gap of COF-V and Au@COF can be estimated to be 2.31 eV and 2.18 eV, respectively (Figure 5f), which can be calculated by Kubelka-Munk formula utilizing UVvis diffuse reflectance spectra (DRS) (Figure S15). To further assess the redox properties of Au NCs, the cyclic voltammogram (CV) was employed to obtain highest occupied molecular orbital (HOMO = 1.70 V) and lowest unoccupied molecular orbital (LUMO = -0.45 V) of Au NCs (Figure 5g). The energy band structures of COF-V and Au NCs were given in Figure 5e. As we can see, the VB of COF-V is not positive enough to oxide H₂O to •OH (H₂O/•OH 2.72 V), which is matched with experiment result. The potential level of O₂/•O₂- (-0.33 V) is between CB of COF-V and LUMO of Au NCs, which indicates the COF-V cannot drive the reaction process of O2/•O2under irradiation. And previous works showed Au NCs cannot exhibit degradability to RhB for fast electron-hole recombination, which also proves that Au NCs cannot drive the reaction of $O_2/\bullet O_2^-$. However, ESR experiment shows Au@COF can achieve the reduction of O_2 to $\bullet O_2^-$, which proves COF support can efficiently inhibit the electron-hole recombination of Au clusters. The above results indicate the constructed model between COF support and Au NCs matches well with the Zscheme charge rule where thiol group plays the role of bonding bridge for carriers transportation (Figure 6).^[18]



Figure 6. Photogenerated electron transport rules between Au NCs and COF support (e⁻ in LUMO and h⁺ in HOMO represent photogenerated electron and hole of Au NCs, respectively; e⁻ in CB and h⁺ in VB represent the photogenerated electron and hole of COF-V, respectively).

The novel composite Au@COF shows efficient adsorption and degradation abilities increasing the feasibility of the material in practical applications, which possesses industrially valuable to purify flowing wastewater. Thus, we explored the purification ability of Au@COF for a continuous flowing pollution system. A round filter paper with Au@COF coating onto its surface was prepared. Figure 7a illustrates the detailed SEM images of filter paper. The simplified schematic of purification device as illustrated in Figure 7b, a sieve plate is put at the bottom of extraction column, which prevents Au@COF from flowing out. After optimizing the parameters for the continuous flow process, the device worked well at room temperature. Utilizing RhB solution as a model, a clarified solution flowed out from tail tube of the column. Then the filter paper was taken out from column and irradiated with light radiation (λ >420 nm). Figure 7b shows the color of filter paper changed from red to yellow after irradiating for 30 min, which proved the complete degradation of adsorbed RhB. The same process was carried out 5 cycles, UVvis spectrum and corresponding images were showed in Figure S16 and Figure 7b, which proves Au@COF still retains high photocatalytic activity and adsorption capacity. It is obvious that Au@COF have great potential in practical applications.

Bisphenol A (BPA) as one of typical endocrine disruptive compounds (EDC) is extremely harmful to the normal operation of the liver and kidney in the human body, and even induces heart disease.^[19] Motivated by the efficient adsorption capacity and enhanced photocatalytic activity of Au@COF towards dyes, thus, the ability of Au@COF to degrade BPA in water was investigated. A process similar to RhB experimental tests was implemented. After 30 min, almost 98.44% of BPA were captured in the dark (Figure S18a). After adsorbing to saturation

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state for BPA, the photocatalytic degradation efficiency was subsequently evaluated. More than 90% of BPA can be degraded by Au@COF after 30 min under light irradiation (Figure S18b). And the kinetic constant k is calculated to be 1.14×10^{-1} by fitting the kinetic curves (Figure S18c). Moreover, high degradation efficiency of BPA over Au@COF can retain after 5 cycles (Figure S18d).



Figure 7. Schematic diagrams of a) filter paper model and b) filter device.

Conclusion

In summary, a facile strategy to bridge ultrasmall Au NCs into pores of a covalent organic framework for enhanced photostability and photocatalytic performance has been developed. Specifically, a novel composite material of loading Au NCs on a thiol-modified COF was prepared. The ultrasmall pores of COF support and strong binding energy of S-Au provided double assurance for the photostability of Au NCs. Furthermore, PEC experiments show Z-scheme photocatalytic system is constructed by the formation of COF-S-Au bonding bridge, which can effectively promote charge separation, enhancing photocatalytic performance. Such design provides a new way to develop COF support catalysts with controllable activity and high stability.

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Keywords: Z-scheme photocatalytic system • covalent organic framework • Au cluster • photostability • pores

- a) T. Yasukawa, H. Miyamura, S. Kobayashi, *Chem. Soc. Rev.* 2014, 43, 1450-1461; b) M. E. Hafez, H. Ma, W. Ma, Y. Long, *Angew. Chem. Int. Ed.* 2019, 58, 6327-6332; c) S. Lee, Y. Wy, Y. W. Lee, K. Ham, S. W. Han, *Small* 2017, *13*, 1701633.
- [2] a) N. L. Rosi, C. S. Thaxton, C. A. Mirkin, *Angew. Chem. Int. Ed.* 2004, 43, 5500-5503; b) E. Auyeung, W. Morris, J. E. Mondloch, J. T. Hupp, O. K. Farha, C. A. Mirkin, *J. Am. Chem. Soc.* 2015, 137, 1658–1662; c) L. A. Gugliotti, D. L. Feldheim, B. E. Eaton, *J. Am. Chem. Soc.* 2005, 127, 17814-17818; d) R. Gill, F. Patolsky, E. Katz, I. Willner, *Angew. Chem. Int. Ed.* 2005, 44, 4554-4557.
- [3] a) G. C. Bleier, J. Watt, C. K. Simocko, J. M. Lavin, D. L. Huber, Angew. Chem. Int. Ed. 2018, 57, 7678-7681; b) H. Lee, I. I. Nedrygailov, C. Lee, G. A. Somorjai, J. Y. Park, Angew. Chem. Int. Ed. 2015, 54, 2340-2344.
- [4] W. Heni, L. Vonna, H. Haidara, *Nano Lett.* **2015**, *15*, 442–449.
- [5] a) Z. Yan, M. G. Taylor, A. Mascareno, G. Mpourmpakis, *Nano Lett.* 2018, *18*, 2696–2704; b) E. K. Fox, F. E. Haddassi, J. Hierrezuelo, T. Ninjbadgar, J. K. Stolarczyk, J. Merlin, D. F. Brougham, *Small* 2018, *14*, 1802278.
- [6] a) A. T. Bell, *Science* 2003, *299*, 1688-1691; b) N. Ostojic, Z. Duan, A. Galyamova, G. Henkelman, R. M. Crooks, *J. Am. Chem. Soc.* 2018, *140*, 13775–13785; c) M. Zhao, K. Deng, L. He, Y. Liu, G. Li, H. Zhao, Z. Tang, *J. Am. Chem. Soc.* 2014, *136*, 1738–1741; d) X. Qiao, X. Chen, C. Huang, A. Li, X. Li, Z. Lu, T. Wang, *Angew. Chem. Int. Ed.* 2019, *58*, 16523-16527.
- a) D. Sun, S. Jang, S. J. Yim, L. Ye, D. P. Kim, *Adv. Funct. Mater.* 2018, 28, 1707110; b) K. Cui, W. Zhong, L. Li, Z. Zhuang, L. Li, J. Bi, Y. Yu, *Small* 2019, *15*, 1804419; c) S. Lin, C. S. Diercks, Y. B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science* 2015, *349*, 1208-1213.
- [8] a) A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* 2005, *310*, 1166-1170; b) S. Y. Ding, W. Wang, *Chem. Soc. Rev.* 2013, *42*, 548-568; c) P. Pachfule, S. Kandambeth, D. D. Di'azbc, R. Banerjee, *Chem. Commun.* 2014, *50*, 3169-3172; d) Y. Xu, X. Shi, R. Hua, R. Zhang, Y. Yao, B. Zhao, T. Liu, J. Zheng, G. Lu, *Appl. Catal. B Environ.* 2019, *260*, 118142.
- [9] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, J. Am. Chem. Soc. 2011, 133, 19816-19822.
- [10] S. Lu, Y. Hu, S. Wan, R. McCaffrey, Y. Jin, H. Gu, W. Zhang, J. Am. Chem. Soc. 2017, 139, 17082–17088.
- [11] Q. Sun, B. Aguila, J. Perman, N. Nguyen, S. Ma, J. Am. Chem. Soc. 2016, 138, 15790–15796.
- [12] a) B. Weng, K. Q. Lu, Z. Tang, H. M. Chen, Y. J. Xu, *Nat. Commun.* 2018, 9, 1543; b) J. Zhai, Y. Jia, L. Zhao, Q. Yuan, F. Gao, X. Zhang, P. Cai, L. Gao, J. Guo, S. Yi, Z. Chai, Y. Zhao, X. Gao, *ACS Nano.* 2018, 12, 4378; c) R. Cai, P. R. Ellis, J. Yin, J. Liu, C. M. Brown, R. Griffin, G. Chang, D. Yang, J. Ren, K. Cooke, P. T. Bishop, W. Theis, R. E. Palmer, *Small* 2018, 14, 1703734.
- a) S. Liu, Y. J. Xu, Sci. Rep. 2016, 6, 22742; b) Y. S. Chen, P. V. Kamat, J. Am. Chem. Soc. 2014, 136, 6075–6082; c) F. X. Xiao, Z. Zeng, S. H. Hsu, S. F. Hung, H. M. Chen, B. Liu, ACS Appl. Mater. Interfaces 2015, 7, 28105–28109.
- [14] a) B. Weng, K. Q. Lu, Z. Tang, H. M. Chen, Y. J. Xu, Nat. Commun. 2018, 9, 1543; b) A. Kogo, N. Sakai, T. Tatsuma, *Electrochem. Commun.* 2010, *12*, 996–999.
- [15] a) Q. Sun, B. Aguila, J. Perman, L. D. Earl, C. W. Abney, Y. Cheng, H.
 Wei, N. Nguyen, L. Wojtas, S. Ma, *J. Am. Chem. Soc.* 2017, *139*, 2786–2793; b) Q. Jiang, Y. Li, X. Zhao, P. Xiong, X. Yu, Y. Xu, L. Chen, *J. Mater. Chem. A* 2018, *6*, 17977–17981.

10.1002/anie.201916154

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- [16] S. Y. Ding, M. Dong, Y. W. Wang, Y. T. Chen, H. Z. Wang, C. Y. Su, W. Wang, J. Am. Chem. Soc. 2016, 138, 3031-3037.
- [17] a) C. Worathitanon, K. Jangyubol, P. Ruengrung, W. Donphai, W. Klysubunc, N. Chanlekc, P. Prasitchoked, M. Chareonpanich, *Appl. Catal. B Environ.* **2019**, *241*, 359–366; b) Q. Liu, C. Zeng, L. Ai, Z. Hao, J. Jiang, *Appl. Catal. B Environ.* **2018**, *224*, 38–45; c) M. Shakeel, M. Arif, G. Yasin, B. Li, H. D. Khan, *Appl. Catal. B Environ.* **2019**, *242*, 485–498.
- [18] a) X. Wu, J. Zhao, L. Wang, M. Han, M. Zhang, H. Wang, H. Huang, Y. Liu, Z. Kang, *Appl. Catal. B Environ.* **2017**, *206*, 501–509; b) J. Bian, J. Feng, Z. Zhang, Z. Li, Y. Zhang, Y. Liu, S. Ali, Y. Qu, L. Bai, J. Xie, D. Tang, X. Li, F. Bai, J. Tang, L. Jing, *Angew. Chem. Int. Ed.* **2019**, *58*, 10873-10878; c) J. Cui, Y. Qi, B. Dong, L. Mu, Q. Ding, G. Liu, M. Jia, F. Zhang, C. Li, *Appl. Catal. B Environ.* **2019**, *241*, 1-7; d) S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Asai, Z. Li, S. S. K. Ma, F. Zhang, K. Domen, C. Li, *Angew. Chem. Int. Ed.* **2015**, *127*, 8618-8621.
- [19] a) L. K. Lin, A. Uzunoglu, L. A. Stanciu, *Small* **2018**, *14*, 1702828; b) T. D. P. Allsop, R. Neal, C. Wang, D. A. Nagel, A. V. Hine, P. Culverhouse, J. D. A. Castañón, D. J. Webb, S. Scarano, M. Minunni, *Biosens. Bioelectron.* **2019**, *135*, 102–110; c) D. N. Pei, A. Y. Zhang, X. Q. Pan, Y. Si, H. Q. Yu, *Anal. Chem.* **2018**, *90*, 3165–3173.

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