Doping Copper Ions in a Metal-Organic Framework (UiO-66-NH$_2$): Location Effect Examined by Ultrafast Spectroscopy

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(Dated: Received on May 3, 2020; Accepted on May 19, 2020)

We constructed two types of copper-doped metal-organic framework (MOF), i.e., Cu@UiO-66-NH$_2$ and Cu-UiO-66-NH$_2$. In the former, Cu$^{2+}$ ions are impregnated in the pore space of the amine-functionalized, Zr-based UiO-66-NH$_2$; while in the latter, Cu$^{2+}$ ions are incorporated to form a bimetal-center MOF, with Zr$^{4+}$ being partially replaced by Cu$^{2+}$ in the Zr−O oxo-clusters. Ultrafast spectroscopy revealed that the photoinduced relaxation kinetics associated with the ligand-to-cluster charge-transfer state is promoted for both Cu-doped MOFs relative to undoped one, but in a sequence of Cu-UiO-66-NH$_2$>Cu@UiO-66-NH$_2$>UiO-66-NH$_2$. Such a sequence turned to be in line with the trend observed in the visible-light photocatalytic hydrogen evolution activity tests on the three MOFs. These findings highlighted the subtle effect of copper-doping location in this Zr-based MOF system, further suggesting that rational engineering of the specific metal-doping location in alike MOF systems to promote the photoinduced charge separation and hence suppress the detrimental charge recombination therein is beneficial for achieving improved performances in MOF-based photocatalysis.

Key words: Metal-organic framework, Copper doping, Location effect, Ultrafast dynamics, Transient absorption spectroscopy, Photocatalysis

I. INTRODUCTION

As a new type of porous crystalline molecular solids, metal-organic frameworks (MOFs) in which metal or metal cluster is coordinated with organic ligands have exhibited intriguing features such as high surface area and porosity, pore-size tunability, functional-group adjustability, and structural tailorability [1, 2]. It has become one of the most promising materials in the fields of gas adsorption, luminescence, magnetic materials, chemical sensing, drug delivery, and heterogeneous catalysis [3]. To tackle the increasingly prominent energy crisis and environmental problems, in recent years researchers have paid particular attention to the photocatalytic aspects of MOF materials, such as organic degradation, hydrogen production, and CO$_2$ reduction [4]. However, the photocatalytic efficiency of a bare MOF system is usually far from being satisfactory. Manipulating the structural and functional complexities of MOFs may lead to improved photocatalytic performances, via, for example modification of organic ligands or metal center [5]. To construct functional MOFs, there are two common strategies: one is to introduce light-absorbing organic ligands (e.g., porphyrin and -NH$_2$) into the framework, while the other is to dope MOFs with light-absorbing metal complex or noble-metal nanoparticles [6].

Metal doping has been proven to be an effective means for improving the photocatalytic performance of MOFs, but the metals used to prepare MOF composites are mainly the precious ones such as Pd, Pt, Au, Ru, Rh, Ir, and Ag [7]. For instance, Shen et al. [8] prepared MIL-125 with metals Au, Pd, and Pt forming an interfacial Schottky barrier, facilitating photoelectron transfer from MIL-125 to noble metals. Guo et al. [9] revealed that Ag-decorated MIL-125 microspheres can greatly improve the photocatalytic efficiency as Ag acts as a co-catalyst. Certainly, the incorporation of noble metals significantly increases the cost of synthesis, and hence it is highly desirable to develop new doping scenarios using earth-abundant metals (or base metals) instead. For instance, Yang et al. [10] constructed copper-doped ZIF-67 and found that such a doped MOF can greatly improve the performance of photodegradation of organic dyes. Note also that partial substitution of metal cations in MOFs could create more structural flexibility and tunability, and such bimetallic assemblies are expected to influence the photocatalytic performances. For instance, Sun et al. [11]...
and Tu et al. [12] constructed bimetal-center UiO-66-NH$_2$(Zr/Ti) and UiO-66(Zr/Ti), respectively, in which Zr is partially replaced by base-metal Ti, and both demonstrated enhanced photocatalytic properties. In addition to such kinds of substitutions with the same group of metals, substitutions with heterozygous metals have also been successfully implemented, forming MOF composites such as MIL-101(Cr/Mg) [13], NH$_2$-MIL-125(Ti/Cu) [14], and MIL-53(Fe/Cu) [15].

Notably, the focus of the above-mentioned reports was mainly on the construction of MOF composites and the resulting improvement of photocatalytic performances. However, it still remains elusive how different doping scenarios affect the photocatalytic properties and the mechanisms behind (e.g., photoinduced charge dynamics usually occurring on an ultrafast timescale). In recent years our group has made efforts in this regard. For instance, in the Pt-doped UiO-66-NH$_2$ system (i.e., Pt nanoparticles being either incorporated in or supported on the MOF), we revealed that the photocatalytic efficiency strongly correlates with the Pt location relative to the MOF [16], and we also addressed such a subtle location effect in another semiconductor/MOF hybrid system [17], both from a mechanistic perspective of ultrafast dynamics.

In this work, we still confined ourselves to the model MOF system of amine-functionalized, Zr-based UiO-66-NH$_2$, in light of the superior chemical and hydrothermal stability of UiO-66 as well as the NH$_2$-modification-induced improvement in visible-light absorption capacity [18]. It is worth mentioning here that MOFs constructed from high-valence metal ions (such as Zr$^{4+}$, Ti$^{4+}$, and Cr$^{3+}$) can form large and rigid multi-nuclear secondary building units with high coordination number to enhance framework ruggedness [1]. The UiO-66 series, first synthesized by Cavka and coworkers in 2008 [19], can be readily constructed from Zr secondary building units and 1,4-benzenedicarboxylic acid (BDC). The doping element we selected is copper (Cu), a common and cost-effective transition metal. We constructed two types of Cu-doped UiO-66-NH$_2$ by deliberately manipulating the doping locations of Cu$^{2+}$ ions. The one is Cu@ UiO-66-NH$_2$, in which Cu$^{2+}$ ions are impregnated in the pore space, synthesized by following the previously reported procedures [16, 20, 21]. The other is Cu-UiO-66-NH$_2$, in which Cu$^{2+}$ ions are truly incorporated into the framework to form a bimetalcenter MOF (i.e., partially replacing Zr$^{4+}$ ions), synthesized for the first time by following the spirit of literatures [14, 16]. By means of ultrafast spectroscopy, we observed promoted relaxation kinetics for the two Cu-doped MOFs relative to the undoped one, but in a sequence of Cu-UiO-66-NH$_2$ > Cu@UiO-66-NH$_2$ > UiO-66-NH$_2$ (in terms of the relaxation rates associated with the ligand-to-cluster charge-transfer state), based on which we proposed plausible mechanisms highlighting the subtle effect of Cu-doping location in such a MOF system. The mechanistic insights enabled a better understanding of the improved photocatalytic hydrogen evolution activity observed on the two Cu-doped MOFs (with significantly different extents) in reference to the undoped one.

II. EXPERIMENTS

A. Materials

Zirconium chloride (ZrCl$_4$), copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O), acetic acid, N,N-dimethylformamide (DMF), methanol, ethanol, ethylene glycol, erythrosin B (ErB), and tri-ethanolamine (TEOA) were purchased from Sinopharm Chemical Reagent Co., Ltd. The 2-amino-1,4-benzenedicarboxylic acid (NH$_2$-BDC) samples were provided by Aladdin. All of the chemicals were utilized without additional purification.

B. Synthesis of samples

1. UiO-66-NH$_2$

The UiO-66-NH$_2$ samples were prepared according to the reported procedures with slight modification. In a typical synthesis, ZrCl$_4$ (0.043 mmol, 10 mg) was dispersed into a DMF solution (5 mL), and 5 mL DMF solution of NH$_2$-BDC (0.044 mmol, 8 mg) was added into the ZrCl$_4$ solution to form a homogeneous mixture. After that, 1.2 mL acetic acid was added into the mixed solution, which was then ultrasonicated for 20 min. The as-obtained mixture was moved to a stainless-steel teflon-lined autoclave of 20 mL and kept at 120℃ for 48 h. The resulting solids were collected by centrifugation and washed with DMF (10 mL) and methanol (10 mL) for three times, and then sequentially immersed in methanol for three days periods and dried overnight at 70℃.

2. Cu@UiO-66-NH$_2$

The Cu@UiO-66-NH$_2$ samples were prepared by an impregnation method. UiO-66-NH$_2$ (∼0.50 mmol, 1 g) was dispersed into an ethanol solution (5 mL) of Cu(NO$_3$)$_2$·3H$_2$O (0.05 mmol, 12 mg) at room temperature and then stirred constantly for 2 h. The resulting solids were collected by centrifugation, washed with ethanol for three times and dried at 70℃ to yield a light-green crystalline solid.

3. Cu-UiO-66-NH$_2$

The Cu-UiO-66-NH$_2$ samples were synthesized via an in situ doping method according to the following procedures. A suitable amount of Cu(NO$_3$)$_2$·3H$_2$O, ZrCl$_4$
C. Characterizations

The scanning electron microscopy (SEM) and the energy dispersive X-ray spectrometry (EDS) characterizations were conducted on a FEI Sirion 200 system. The concentrations of Zr\(^{4+}\) and Cu\(^{2+}\) ions were measured using a Thermo Scientific Plasma Quad III inductively coupled plasma mass spectrometry (ICP-MS) with the samples being dissolved in HCl/HNO\(_3\) (3:1, V:V). The crystal structures were examined by powder X-ray diffraction (PXRD) characterizations on a Japan Rigaku Smart Lab rotation anode X-ray diffractometer (using Cu K\(^{α}\) radiation). The Brunauer-Emmet-Teller (BET) specific surface area of the specimens was determined via N\(_2\) adsorption/desorption measurements on a Micromeritics Tristar II 3020 apparatus. The Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 infrared spectrophotometer in the wavenumber range of 400–4000 cm\(^{-1}\). The steady-state ultraviolet-visible (UV-Vis) absorption spectra were recorded on a TU-1901 spectrophotometer (Persee).

The femtosecond time-resolved transient absorption (fs-TA) spectroscopic data were recorded on a Helios pump-probe system (Ultrafast Systems LLC) under ambient conditions. The 400-nm pump pulses (~60 nJ/pulse at the sample cell) were provided by the frequency doubling of the 800-nm output from a Tisapphire regenerative amplifier (Coherent). The white-light continuum probe pulses (500–750 nm) were generated by focusing the 800-nm beam (split from the regenerative amplifier, ~400 nJ/pulse) onto a sapphire plate. The instrument response function was determined to be ~100 fs by a routine cross-correlation procedure. The temporal and spectral profiles (chirp-corrected) of the pump-induced absorbance changes were visualized using an optical fiber-coupled multi-channel spectrometer and further processed by a Surface Xplorer software. All of the MOF samples were dispersed in an ethylene glycol solution in a 0.7-mL quartz cuvette under a continuous magnetic stirring condition ensuring that the photoexcited volume was kept fresh during the measurements.

The photocatalytic hydrogen evolution reactions (HER) were performed in an optical reaction vessel (250 mL) connected to a closed gas circulation swept with high-purity Ar gas. A 300-W Xe lamp was used as the light source with an optical filter (λ>400 nm) to cut off the UV portion. In each run of the HER evaluation, 50 mg catalyst was dispersed in 90 mL H\(_2\)O with the addition of 10 mL triethanolamine (TEOA) as the hole-sacrificial reagent and 10 mg erythrosin B (ErB) dye as the photosensitizer. The reaction solution was stirred continuously and cooled down to room temperature by circulation of cooling water. The amounts of H\(_2\) generation at a 1 h interval were determined using gas chromatography (Fuli, FL9790).

III. RESULTS AND DISCUSSION

As can be seen from the SEM images (FIG. S1 in supplementary materials), the two Cu-doped UiO-66-NH\(_2\) samples retained the regular octahedron morphology of the undoped one [22], with a size of about 100 nm. The EDS spectra (FIG. S2 in supplementary materials) identified the existence of C, O, Zr, and Cu elements (Al signal comes from the aluminum mesh used) and revealed a Zr:Cu ratio of ~10:1 for both Cu-doped samples. A more accurate determination was from the ICP-MS analysis, i.e., Zr:Cu=10.2:1 and 9.8:1 for Cu@UiO-66-NH\(_2\) and Cu-UiO-66-NH\(_2\), respectively, indicating nearly no difference in terms of the dopant content for the two doped samples. Displayed in FIG. 1 are the PXRD patterns recorded on the three as-synthesized UiO-66-NH\(_2\) samples. A survey in the 2\(_θ\) range of 0°–60° revealed nearly identical patterns for the doped and undoped samples, indicating that the crystallinity and structural integrity of UiO-66-NH\(_2\) were well maintained upon copper doping. Care must be taken to the two small-angle predominant peaks at 7.38° and 8.52°, which are known to correspond to the (111) and (002) surfaces of UiO-66-NH\(_2\), respectively [23, 24]. Zooming into the 5°–10° region (inset of FIG. 1), one can readily detect that the two peaks undergo no discernable shifts for Cu@UiO-66-NH\(_2\) while moving toward higher angles with significant amounts for Cu-UiO-66-NH\(_2\). This is understandable because the doping of Cu\(^{2+}\) ions in the former (where dopants are trapped in the pore space) can only induce tiny distortion of lattice; whilst in the latter the substitution of larger Zr\(^{4+}\) ions in Zr–O oxoclusters by smaller Cu\(^{2+}\) ions forming a bimetal-center MOF (i.e., UiO-66-NH\(_2\) (Zr/Cu)), albeit with almost the same amount of dopant as in the former, can lead to significant lattice shrinkage (refer to Refs. [11, 12, 14] for similar observations). Notably, as for Cu@UiO-66-NH\(_2\), the fact that Cu\(^{2+}\) ions are predominantly impregnated in the pore space of the MOF (rather than coordinated to binding sites) was also bolstered with the relevant BET specific surface area analysis (see FIG. S3 and its accompanying discussion in supplementary materials). All of these characterizations confirmed that the two distinctly different types of Cu-doped UiO-66-NH\(_2\) systems had been successfully constructed as desired.

To glean more information about their chemical structures, we recorded FT-IR spectra (in the
obtain more useful information of temporal evolutions

explicitly similar photoinduced absorption (PA) profiles

probe delays for the three samples, all of which exhibit

shows the fs-TA spectra taken at several representative

an ultrabroad spectral region of 500

2

−

2

probe was from a white-light continuum source covering

photoexcitation in UiO-66-NH

i.e

recorded in 200

−

4

is based on the steady-state UV-Vis absorption spectra

at 400 nm (center wavelength), the selection of which

in reference to the undoped one under photoexcitation.

and temporal evolutions in the two Cu-doped systems

effect the photoexcited charge dynamics involved. To this

af-

ond timescale) including vibrational relaxation within

cluster charge transfer (LCCT) in a rather prompt man-

ions in the

O achiev-

account

global fitting procedure (using 5 kinetic traces with a

relaxation kinetics involved. As shown in FIG. 3(b),

such that the implicit differences among them can be
discriminated, we conducted a careful analysis of the
relaxation kinetics involved. As shown in FIG. 3(b),
in order to eliminate the unwanted influence of differ-
ent probing wavelengths on the kinetics, we executed a

FIG. 1 PXRD patterns recorded on UiO-66-NH

FIG. 2 FT-IR spectra recorded on UiO-66-NH

wavenumber range of 400–4000 cm

3

on the three

MOF samples, as shown in FIG. 2. As for the undoped
UiO-66-NH

3

for the longitudinal and transverse modes of Zr–O

25], the 1570 cm

1

−

1

band reflects the coordination of the -COOH group with Zr

[23], and the 3430 cm

2

band relates to the uncoordinated -NH

[23, 25].

Basically, these bands are almost unaltered upon copper
doping. Nevertheless, when zooming into the narrow re-

of 700–800 cm

3

one can discern a well-resolved

band peaking at ~730 cm

1

for solely Cu-UiO-66-NH

3

as marked by a dashed-dotted line in the inset of FIG.

Such a band unique to Cu-UiO-66-NH

2

−

2. Such a band

2

tributed to the Cu

2+

−

620 nm) to retrieve the characteristic relaxation

time constants. It turned out that the three sets of PA

It has been recognized that in Zr-based MOF sys-
tems the initial photoexcitation of the organic linkers
(acting as photoantennae) normally induces ligand-to-
cluster charge transfer (LCCT) in a rather prompt man-
ner [29], which cannot be resolved in our fs-TA exper-
iments given that the instrument response function is

≈100 fs. Subsequently, such a LCCT state (localized on
the linker) undergoes fast decays (typically on a picosec-
ond timescale) including vibrational relaxation within
the photoexcited linker (i.e., the observed \( \tau_1 \) process)
and the following nonradiative trapping of the LCCT
state (i.e., the observed \( \tau_2 \) process), eventually leading
to the formation of a charge-separation state whose life-
time is typically on a nano- to micro-second timescale
[29]. Apparently, copper doping turned out to result
in acceleration for both the \( \tau_1 \) and \( \tau_2 \) processes in our
Zr-based MOF systems of UiO-66-NH

value of \( \tau_1 \) is reduced by ~17% while that of \( \tau_2 \) by
~38%. This can be understood as follows. In this
case the copper doping is by impregnation of Cu

ion in the pore space of MOF rather than by (par-
tial) substitution of Zr

+ with Cu

+ ions in the Zr–O

oxo-clusters, and hence will not bring on a signifi-
cant change for the LCCT state given that the metal
clusters are not modified upon doping. Thus the vibra-
tional relaxation within the LCCT state (described by \( \tau_1 \))
would not be affected significantly. Nevertheless, such an impregnation-type copper doping inevitably introduces structural defects into the MOF [30, 31] and hence increases the density of the trap states (locating in between the ground state and the excited LCCT state), thereby promoting the trapping process (described by $\tau_2$) with a relatively larger extent. However, the above situation has changed for Cu-UiO-66-NH$_2$ that features a different doping type (i.e., forming a bimetal center in the clusters). Its values of $\tau_1$ and $\tau_2$ are substantially reduced by $\sim$73% and $\sim$64%, respectively, relative to those of the undoped MOF. In this particular type of bimetal-center MOF, the partial replacement of Zr$^{4+}$ (with a smaller electronegativity of 1.33) by Cu$^{2+}$ (with a larger electronegativity of 1.90) in the Zr–O oxo-clusters will strengthen the electron-accepting ability of the newly formed bimetal Zr/Cu center. Such a metal substitution (though partial) in the Zr–O oxo-clusters could promote the event of LCCT [11, 12], and interestingly it also turned out to dramatically modify the vibronic density of the excited LCCT state, as manifested as a pronounced acceleration of the vibrational relaxation within this state (refer to the $\sim$73% decrease in terms of $\tau_1$). Moreover, it is worth noting that the metal-substitution-induced crystal shrinkage in this MOF could also introduce a certain amount of structural defects [32], most likely increasing the density of the trap states as well. Given the increased densities for both the upper LCCT vibronic states and the lower trap states, the trapping process therein can also be significantly accelerated as observed (refer to the $\sim$64% in terms of $\tau_2$).

Considering that the mean value $\langle \tau \rangle$ is usually regarded as a good (yet crude) indicator for overall evaluating the charge-separation efficiency in a photocatalytic nanosystem [33], we calculated the $\langle \tau \rangle$ values for all the three investigated MOFs, as also given in Table I. The $\langle \tau \rangle$ values for Cu@UiO-66-NH$_2$ and Cu-UiO-66-NH$_2$ are reduced by $\sim$39% and $\sim$65%, respectively, relative to that for UiO-66-NH$_2$. Also, the extents of mean relaxation acceleration are in the sequence of Cu-UiO-66-NH$_2$ > Cu@UiO-66-NH$_2$ > UiO-66-NH$_2$, disclosing the trend in terms of the efficiency in forming charge-separation states in the three MOF systems, which was further verified by the visible-light photocatalytic HER activity tests on the three samples (under exactly the same conditions) as exhibited in FIG. 4.

The H$_2$ generation rates for UiO-66-NH$_2$, Cu@UiO-66-NH$_2$, and Cu-UiO-66-NH$_2$ were found to be about 90, 250, and 3061 μmol·g$^{-1}$·h$^{-1}$. The two doped MOF systems of Cu@UiO-66-NH$_2$ and Cu-UiO-66-NH$_2$ turned out to achieve $\sim$2.8- and 34-fold improvement in terms of the photocatalytic HER activity. Markedly, albeit with a similar amount of copper doping (i.e., $\sim$10:1 for Zr:Cu), the Cu-UiO-66-NH$_2$ system gave rise to an enhancement factor of more than one order of magnitude (cf. 34 vs. 2.8) relative to the Cu@UiO-66-NH$_2$ system, highlighting the important role of copper-doping location in such a MOF system. By virtue of the dramatically improved HER performance of Cu-UiO-66-NH$_2$, in conjunction with the ultrafast spectroscopic analysis,}

![FIG. 3](image-url) (a) fs-TA spectra (excitation at 400 nm) and (b) kinetic traces recorded on UiO-66-NH$_2$, Cu@UiO-66-NH$_2$, and Cu-UiO-66-NH$_2$.

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_1$/ps</th>
<th>$\tau_2$/ps</th>
<th>$\langle \tau \rangle$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66-NH$_2$</td>
<td>23.3±0.7 (45%)</td>
<td>418±8 (55%)</td>
<td>401±8</td>
</tr>
<tr>
<td>Cu@UiO-66-NH$_2$</td>
<td>19.4±0.8 (43%)</td>
<td>258±6 (57%)</td>
<td>245±6</td>
</tr>
<tr>
<td>Cu-UiO-66-NH$_2$</td>
<td>6.3±0.2 (67%)</td>
<td>153±4 (33%)</td>
<td>142±3</td>
</tr>
</tbody>
</table>

TABLE I The relaxation time constants $\tau_i$ (i=1 and 2) retrieved from the global fitting (with a biexponential function) on the observed kinetic traces for the three investigated MOFs. Given in parentheses is the statistical weight $A_i$ for each $\tau_i$ (i=1 and 2) component. The mean value $\langle \tau \rangle$ is calculated according to the equation $\langle \tau \rangle = \frac{\sum (A_i \times \tau_i^2)}{\sum (A_i \times \tau_i)}$.

DOI:10.1063/1674-0068/cjcp2005070 ©2020 Chinese Physical Society
FIG. 4 The visible-light photocatalytic HER activity tests performed on UiO-66-NH$_2$, Cu@UiO-66-NH$_2$, and Cu-UiO-66-NH$_2$. The TEOA-ErB-MOF system was used in the tests, where TEOA acts as a hole-sacrificial agent and ErB serves as a photosensitizer.

sis, it can be suggested that properly engineering the specific metal-doping location in alike MOF systems so as to promote charge separation (and hence suppress charge recombination) therein would be of instructive value to MOF-based photocatalysis.

IV. CONCLUSION

In conclusion, in order to interrogate the subtle metal-doping location effect on photoinduced charge dynamics and the related photocatalytic performances of the amine-functionalized and Zr-based MOF system of UiO-66-NH$_2$, we have designed and synthesized two types of copper-doped UiO-66-NH$_2$. One is of an impregnation type, i.e., Cu@UiO-66-NH$_2$ where the Cu$^{2+}$ ions are trapped in the pore space of MOF, while the other is of a metal-substitution type, i.e., Cu-UiO-66-NH$_2$ where the Cu$^{2+}$ ions partially replace Zr$^{4+}$ ions in the Zr−O oxo-clusters forming a bimetal-center MOF. Notably, to the best of our knowledge, the construction of the latter system has not yet been reported so far. With the aid of various characterizations including SEM, EDS, ICP-MS, PXRD, BET, and FT-IR, we identified the different doping fashions of the two copper-doped MOFs. More importantly, by means of femtosecond time-resolved TA spectroscopy we revealed their different photoinduced relaxation kinetics associated with the ligand-to-cluster charge-transfer state, pointing to different charge-separation efficiencies in a sequence of Cu-UiO-66-NH$_2$>Cu@UiO-66-NH$_2$>UiO-66-NH$_2$. These observations echoed well to those from the visible-light photocatalytic HER evaluation on the three MOFs. Strikingly, the metal-substitution type of doping brought on a H$_2$ generation rate much higher (more than one order of magnitude) than the impregnation type of doping. By unraveling the elusive effect of copper-doping location in this Zr-based MOF system, we envision that the information from this work would be of enlightening value for MOF-based photocatalysis in terms of rational engineering of specific metal-doping locations in MOFs with an aim to promote the photoinduced charge separation and hence suppress the detrimental charge recombination therein.

Supplementary materials: SEM images, EDS mapping spectra, BET analysis, and steady-state UV-Vis absorption spectra are given.

V. ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program on Nano Science and Technology of the Ministry of Science and Technology of China (No.2016YFA0200602 and No.2018YFA020702), the National Natural Science Foundation of China (No.21573211 and No.21633007), and the Anhui Initiative in Quantum Information Technologies (No.AHY090200).


DOI:10.1063/1674-0068/cjcp2005070 ©2020 Chinese Physical Society