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金属元素替换对锌–铜基金属有机骨架材料的光吸收与能带特性的影响

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摘要:选择常规的锌、铜作为金属离子、对苯二甲酸(BDC)作为有机配体,通过溶剂热法和元素替换法合成出 Zn-Cu 基 MOFs 材料。通过 XRD、UV-Vis DRS、SEM、FT-IR、UPS 和 XPS 等手段表征和研究,发现 Zn(BDC)的光吸收位于紫外光波段(<400 nm),而 Cu(BDC)光吸收拓宽至整个可见光波段(500~1 000 nm)。Zn-Cu 金属离子均匀分散的产物 Zn-Cu-BDC 比其它产物具有更宽的光吸收范围、强度和更窄的带隙;不同的合成途径导致 Zn-Cu 基 MOFs 材料表现出性质差异。

关键词:金属有机骨架;锌–铜;金属元素替换;光吸收;能带

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Effect of Metal Exchange on the Light-Absorbing and Band-Gap Properties of Nanoporous Zn-Cu based MOFs

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Abstract: Cu(Ⅱ) and Zn(Ⅱ) ions were selected as the basic mixed metal nodes connected by organic ligand 1,4-benzenedicarboxylic acid (BDC) and synthesized nanoporous Zn-Cu based mixed-metal MOFs Zn(BDC)-Cu, Cu(BDC)-Zn and Zn-Cu-BDC through different synthetic routes. Through characterization of PXRD, SEM, UV-Vis DRS, FT-IR, XPS and UPS and systematic analysis, it is found that the solar light absorbing range of Zn(BDC) is located in UV band (<400 nm), while Cu(BDC) mainly absorbs the whole visible light (500~1 000 nm). Additionally, the Zn-Cu ions uniformly-dispersed product Zn-Cu-BDC performs better in light-absorption and exhibits lower photo band-gap and HOMO level than the other bi-metallic products Zn(BDC)-Cu and Cu(BDC)-Zn. The investigation might inspire the design of heterogeneous photocatalysts and organic-inorganic hybrids in the aspects of light-absorption and charge transfer and construction methods on metal exchange due to different routes leading to different properties despite of the same components.

Keywords: metal-organic frameworks (MOFs); Zn-Cu; metal exchange; light-absorption; band gap

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0 Introduction

Metal-organic frameworks (MOFs), also namely porous coordination polymers (PCPs), represent for an emerging class of outperforming microporous materials with exponential growth in recent years not only because of their vast array of topologies but also because of their potential application in gas absorption/separation, catalysis, photo-electricity, sensors and so on[1-3]. Incorporation of functionality is straightforward if appropriately derivative organic linkers and metal ions can be synthesized and directly employed in solvothermal material synthesis. But incorporating new metal nodes into the porous frameworks is less predictable and has many limitations[4]. Overly strong metal-ion-linker bonding can lead to formation of amorphous kinetic products to the exclusion of crystalline compounds. Thus it is wise to turn the undesired polymorphs (usually thermodynamically less stable) to crystals in synthetic process through metal exchange, one direction of post-synthetic modification which is extensively reviewed by Farha[5], and by Dincă[4]. Broadly defined, metal exchange (cation exchange) is the partial or complete substitution of a metal ion at the site of another. Although as a research direction, metal exchange at MOFs SBUs (Secondary building units) is still in its infancy.

Since MOF can be viewed as the metal salt of the conjugated base of a weak acid, isomorphous replacement of the node-based metal ions by other metal ions is possible. Although this idea seems simple and feasible, metal exchange reactions in porous MOFs are still rare when compared to linker replacement[6-7] and the metal exchange was only first demonstrated in 2007[8]. This likely due to the commonly-existing notion that properties of a coordination polymer change with varying functional groups on linkers of a framework rather than the metal node, which is usually regarded as an inert structural element. However incorporating different metals in the same framework through metal exchange, *i.e.* trans-metalation may lead to MOFs with novel or multiple or enhanced functions[9-10]. Additionally, the relatively mild conditions during transmetalation process are effective for introducing metal ions that cannot be introduced by direct solvothermal synthesis[5]. This process also offers an alternative route when conventional synthesis at high temperature fails. Moreover, recent research have revealed that heterogenization of homogeneous catalysts through metal substitution or hybridization performs better reactivity, adsorptive ability and/or selectivity in comparison with the parent MOFs[10-16].

To date, the systematic research about metal cation exchange in MOFs is lacking. Few research and difficult pace have been made concerning the conductivity and photo-absorption properties, but gas separation and adsorption due to the inert nodes for the transportation of active charges or electrons[17-19] and it is difficult to make MOFs exhibit excellent semi-conductivity, or even conductivity[20-21]. Moreover the details of this fascinating transmetalation are unknown and the bounty of MOFs structures that undergo metal ions substitution present a host of curiosities to be explained. The extent of its use for designing new MOFs in a systematic and predictable manner depends on understanding its mechanism. Hence this work intends to provide the basic structure-property relationship and focuses on the effect of metal exchange on the light-absorbing and band-gap properties of nanoporous Zn-Cu based MOFs. The most commonly used components copper, zinc and 1,4-benzenedicarboxylic acid (BDC) were selected. After precursors MOFs Zn(BDC) and Cu(BDC) were synthesized, Cu(Ⅱ) and Zn(Ⅱ) ions were incorporated into the framework respectively, through metal exchange, to obtain the mixed-metal Zn-Cu based MOFs Zn(BDC)-Cu and Cu(BDC)-Zn. At the meantime, Cu(Ⅱ) and Zn(Ⅱ) ions were constructed simultaneously as the metal nodes by *ab initio* solvothermal synthesis to give product Zn-Cu-BDC for the comparative study (Fig.1). The structures, chemical environments, light-absorption and band-gap properties are investigated thoroughly.

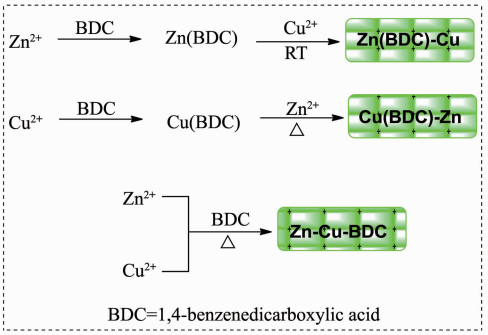


Fig.1　Schematic illustration of the synthetic process of Zn-Cu MOFs

1　Experimental

1.1　Starting materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), 1,4-benzenedicarboxylic acid (BDC), *N*,*N*-dimethylformamide (DMF) and methanol (MeOH) were of analytical grade from commercial sources and used directly without further purification.

1.2　Instruments

Metal ions (Zn and Cu) were analyzed using an iCE3500 atomic absorption spectroscopy (Thermo, America) to obtain the metal contents and ratios. Fourier transformation infra-red spectroscopy (FT-IR) spectra were measured on Frontier FT-IR spectrometer (PerkinElmer, America) using KBr pellets (4000~400 cm^{-1}). UV-Vis diffuse reflectance spectra (UV/Vis DRS) of the samples were recorded on a UV-2600 spectrophotometer (Shimadzu, Japan). Powder X-ray diffraction (XRD) measurements using Cu $K\alpha$ radiation (λ=0.154 06 nm) at room temperature (working voltage /current: 40 kV/40 mA, scanning range: 2°~50°) were carried out in air with a DX-2500 spectrometer (Dandong, China). SEM images were taken on Phenom G2 ProX scanning electron microscope (Netherland). The photoelectron spectra were carried out in an integrated ultrahigh vacuum (UHV) system equipped with multi-technique surface analysis system (Escalab 250Xi, Thermo Scientific, America) photoelectron spectrometer (XPS and UPS). UPS were measured on spectroscopy with a negative bias voltage (–2.0 V) applied to the samples using the He(I) (21.2 eV) line in order to shift the spectra from the spectrometer threshold.

1.3　Synthesis

Zn^{2+}, Cu^{2+} and 1,4-benzenedicarboxylic acid (BDC) are selected as the basic components to construct the coordination polymers and nanoporous frameworks. The synthetic procedures performed according to the former research[22-23] with slight alternation. For Zn(BDC), a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (3.4 mmol, 1.0 g) in DMF (40 mL) was added to a solution of BDC (1.4 mmol, 0.23 g) in DMF (20 mL). The mixture was heated in an autoclave for 36 h at 110 ℃. After slow cooling down to room temperature at 0.1 ℃·min^{-1}, white crystalline product was collected. After repeated centrifugation and washing, the yield was 80 %. According to the same procedures, blue powder Cu(BDC) and Zn-Cu-BDC was synthesized with the molar ratio of $n_{Cu(NO_3)_2 \cdot 3H_2O}$:$n_{BDC}$=2.5:1 and $n_{Zn(NO_3)_2 \cdot 6H_2O}$:$n_{Cu(NO_3)_2 \cdot 3H_2O}$:$n_{BDC}$=1:1:2, respectively. Zn(BDC)-Cu was obtained through metal exchange in the MeOH solution (100 mL) of Zn(BDC) (0.2 g) and $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 g) at room temperature for 48 hours, while Cu(BDC)-Zn were prepared through the solvothermal method with Cu(BDC) (0.2 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.0 g) in DMF (100 mL). All samples were washed with DMF, MeOH and water three times respectively and thermally activated at 100 ℃ for 12 h under vacuum. The metal-organic frameworks were characterized by PXRD, FT-IR and SEM as shown in the following description.

2　Results and discussion

The metal exchange process in Zn(BDC) with Cu(Ⅱ) ions was performed at room temperature to give Zn(BDC)-Cu, while the transmetalation of Cu(BDC) with Zn(Ⅱ) ions was carried out to give Cu(BDC)-Zn under raised temperature (110 ℃) due to the stability sequence (Cu^{2+} > Zn^{2+}) of cation exchange in Irving-Williams series[24], which describes the general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands. The series, in order of increasing stability, is Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} ≈ Zn^{2+} < Cu^{2+}, and is independent of ligand. To make sure Zn(Ⅱ) and Cu(Ⅱ) highly dispersed uniformly as compared with Zn(BDC)-Cu and Cu(BDC)-Zn, Zn-

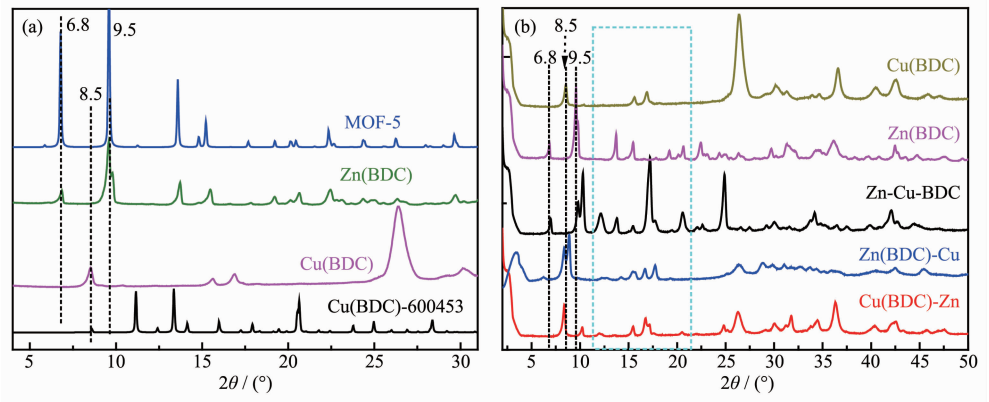
Cu-BDC was synthesized via *ab initio* solvothermal method with the same procedure as Zn(BDC) and Cu(BDC) and obtained as mixed-metal Zn-Cu based MOFs. The ratio of Zn(Ⅱ) and Cu(Ⅱ) ions was determined by atomic absorption spectrometer. The results show that the molar ratios of n_{Cu}:n_{Zn} in the MOFs materials Zn-Cu-BDC, Zn(BDC)-Cu and Cu(BDC)-Zn were 1.1:1.0, 1.5:1.0 and 1.0:2.0, respectively. Similar substitution content could also be found in other Zn-Cu based MOFs[25-26]. Especially for Zn-Cu-BDC, the ratio of n_{Cu}:n_{Zn} (approximately 1:1) indicates the uniformly dispersed Zn-Cu metal ions which act as the co-nodes of the framework.

The photo images of powder MOFs samples were given in Fig.2. As shown in Fig.2, the sample of Zn(BDC) exhibits white, while Cu(BDC) exhibits pure blue. When metals Zn(Ⅱ) and Cu(Ⅱ) are introduced into the framework simultaneously, the color of product Zn-Cu-BDC shows slight change as compared with Cu(BDC) and exhibits bright blue. For the samples of Cu(BDC)-Zn and Zn(BDC)-Cu, when elements Zn or Cu are transmetalled with the elements Cu or Zn in the bulk materials respectively, the colors both exhibit light green. The color changes of mixed-metal Zn-Cu based MOFs indicate the different porous structures or coordination environments which induce the change of light-absorbing properties.

Fig.2 Images of Zn-Cu based MOFs

Before the effect of metal exchange on light-absorption and band gap is elucidated, it is necessary to study and confirm the porous and crystalline structures of the Zn-Cu MOFs with different contents and states of Zn(Ⅱ) and Cu(Ⅱ) ions. To elucidate the porous structure and framework of the synthesized materials Cu(BDC), Zn(BDC), Zn-Cu-BDC, Cu(BDC) and Zn(BDC)-Cu and inspect the crystalline morphologies, XRD patterns, FT-IR spectra and SEM images are presented in Fig.3, 4 and 5, respectively.

As depicted in the powder XRD patterns, Zn(BDC) exhibits instinct peaks at 6.8° and 9.5° while Cu(BDC) at 8.5°, indicating crystalline structure with angstrom-level pores. The powder XRD pattern of Zn(BDC) agrees well with the reference data of single crystal MOF-5 reported by Lillerud[27], strongly suggesting the good phase purity of the precursor Zn(BDC). While the XRD pattern of the precursor Cu(BDC) does not match the single crystal XRD of Cu(BDC) (CCDC: 600453)[28] but exhibits slight change compared with the powder XRD data of Cu(BDC) reported by Koros[23] and Pitchumani[29], as shown in the supporting information (SI) as Fig. S1, respectively, indicating the



Cu(BDC)-600453: pattern simulated from CCDC: 600453

Fig.3 Powder XRD patterns of Zn-Cu based MOFs

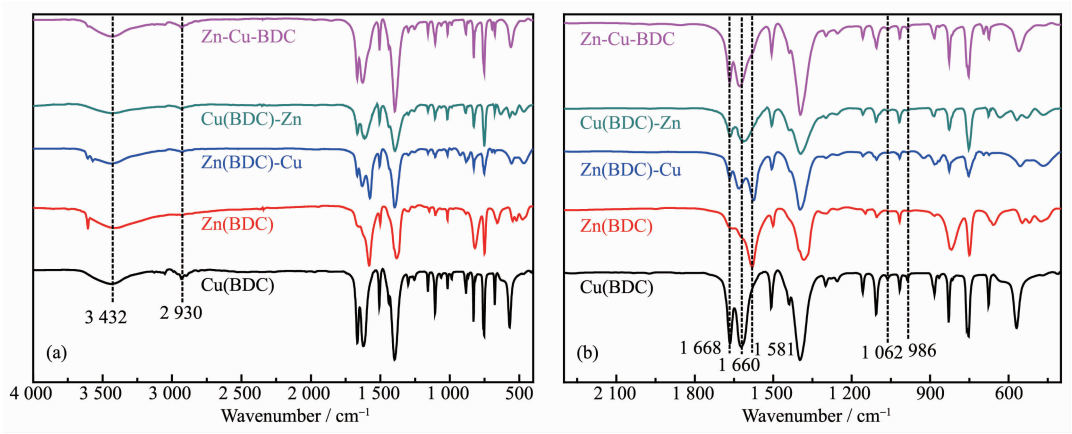
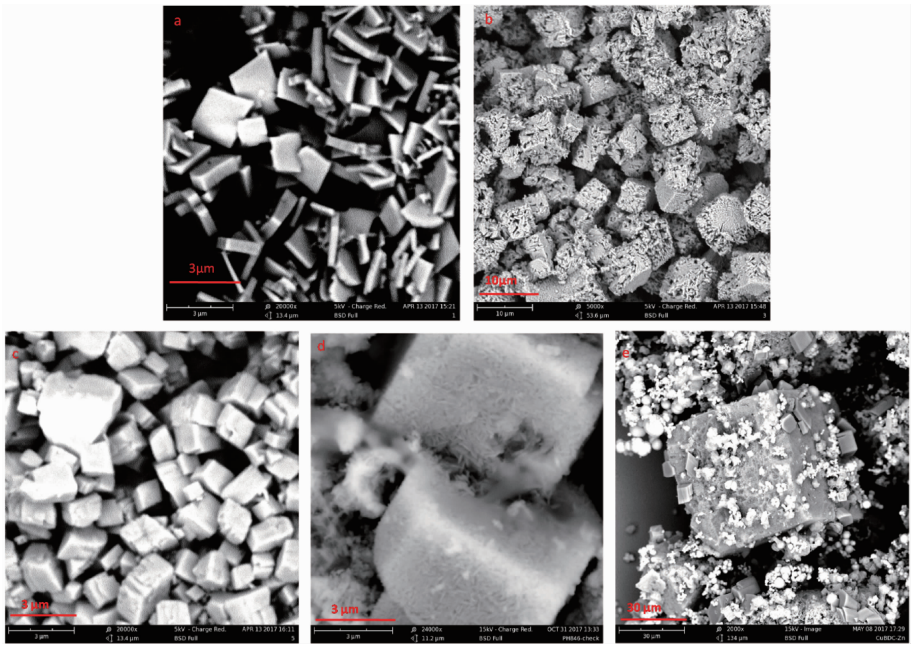


Fig.4　(a) FT-IR spectra of Zn-Cu based MOFs; (b) Magnification of Fig.(a) within 2 200~500 cm^{-1} wavenumber



(a) Cu(BDC), (b) Zn(BDC), (c) Zn-Cu-BDC, (d) Zn(BDC)-Cu, (e) Cu(BDC)-Zn

Fig.5　SEM images of Zn-Cu based MOFs

existing crystal structure and phase purity of Cu (BDC). For Cu(BDC), after Cu frameworks are reacted with Zn(Ⅱ) at 110 ℃, Cu(BDC)-Zn is obtained and the diffraction angles of 8.5° and 15° ~17.5° retain, confirming the basic framework similar with Cu(BDC). The new peaks at 10.2° and around 25° give the evidence that Zn(Ⅱ) are employed into the framework and get new framework of Cu(BDC)-Zn, but the lack of the typical diffraction peak 6.8° of Zn(BDC) in Cu(BDC)-Zn indicates Zn(Ⅱ) does not replace Cu(Ⅱ) to build and form the basic structure as the same as Zn (BDC). That is to say, Zn^{2+} are inserted into the pores and do not substitute Cu^{2+} to serve as the framework nodes of Cu(BDC)-Zn. While the process is reversed, in other words metals Cu are introduced into the frameworks of Zn(BDC) to replace Zn(Ⅱ) mildly at room temperature and obtain Zn(BDC)-Cu, similar XRD patterns are observed but the typical diffraction peak of 6.8° in Zn(BDC) retains, indicating that Zn(Ⅱ) can be replaced with Cu(Ⅱ) due to metal exchange effect as illuminated well by Lah[30]. Interestingly, when Zn(Ⅱ) and Cu(Ⅱ) are introduced into the frameworks simultaneously to form Zn-Cu-BDC, the diffraction angles of Zn(BDC) and Cu(BDC) are detected in the same pattern and only one shape of crystals are observed in SEM image (Fig.4c), which means that within Zn-Cu-

BDC crystals Zn(Ⅱ) and Cu(Ⅱ) are constructed in the frameworks uniformly together with BDC ligands as metal nodes but not insertion elements.

The different chemical environments in Zn-Cu-BDC, Cu(BDC)-Zn and Zn(BDC)-Cu can be also testified through FT-IR spectra (Fig.4) due to the evident peak intensity changes of -C=O group stretching mode in 1 668 and 1 660 cm^{-1} (Cu(BDC)) and 1 581 cm^{-1} (Zn(BDC)) after the metal-exchange processes are carried out. While Cu(Ⅱ) ions coordinate with BDC, the peaks of 1 668 and 1 660 cm^{-1} in both Cu(BDC)-Zn, Zn(BDC)-Cu and Zn-Cu-BDC stay clear compared with Cu(BDC). The typical stretching peak (1 581 cm^{-1}) in Zn(BDC), which is ascribed to vibration of -C=O groups coordinated with Zn(Ⅱ) ions, could only be evidently observed in Zn(BDC)-Cu and Zn-Cu-BDC, not found in Cu(BDC)-Zn, indicating that Zn(Ⅱ) ions do not replace Cu to build the basic structure of Cu (BDC)-Zn. The result is in coincidence with the XRD analysis and conclusions and confirms the less stability of Zn^{2+} high spin octahedral metal complexes than that of Cu^{2+}.

Further, to elucidate the crystal morphologies and periodic porous structures, SEM images of the Cu and Zn based MOFs are presented in Fig.5. As shown in Fig.5, Cu (BDC) exhibit planar crystals of about 1 μm in length and width with smooth surface. As well researched, Cu(BDC) contains paddle-wheel-like bi-copper clusters with the pseudo-octahedral centre of Cu(Ⅱ) ion and every 1,4-BDC fragment links two such clusters to yield a two-dimensional open structure[28,31]. In contrast, Zn(BDC) consists of a 3D network constructed from Zn^{2+} ions bridged by deprotonated formic acid moieties and consequently a porous and crystalline coordination polymer with pores of about 1 μm is obtained. The μm-scale pores will play significant role at the diffusion of small molecules in photocatalysis. After Cu(Ⅱ) ions are introduced into Zn(BDC) during the mild process of metal exchange to form Zn(BDC)-Cu, the μm-scale pores disappear and little crystals of needle shape and one-dimension line are observed within the pores (Fig.5d). However, for Cu(BDC)-Zn complicated crystalline structures are seen as cubic crystals with larger size and disorderly shapes with both crystalline and amorphous morphogies compared with the Cu(BDC) crystals[32]. This might be caused by the dissociation and re-construction of Cu(BDC) induced with Zn^{2+}. While Zn(Ⅱ) and Cu(Ⅱ) are constructed in the frameworks of Zn-Cu-BDC simultaneously, little crystals of cubic shape and about 1 μm in size are found, evidencing the collective structure effect of Zn(Ⅱ) and Cu(Ⅱ) ions as the framework nodes in Zn-Cu-BDC as analysed by PXRD characterization. The SEM images further demonstrate the excellent effect Cu substitution of Zn, and the reverse process does not work well.

UV-Vis absorption spectroscopy is a direct and facile tool to study the photo-responsive characteristics and photo band gaps of materials as effective charge transfer will decrease the electronic transition energy and finally cause red-shift phenomenon in the light-response spectrum[33]. As shown in Fig.6, Zn(BDC) absorbs UV light below 400 nm and thus emerges as white, while Cu(BDC) owes light-absorption mainly located between 500~1 000 nm with maximal peak at 718 nm and finally exhibits pure blue, as seen clearly in Fig.2. After Zn(Ⅱ) ions are introduced into the frameworks of Cu(BDC), the light-absorption of product Cu(BDC)-Zn does not show significant change. But when Cu(Ⅱ) ions are build into the framework of Zn(BDC) and obtain the product Zn(BDC)-Cu, the UV-Vis spectrum changes greatly and exhibits visible-light photo response compared to the precursor Zn(BDC). Moreover, when Zn(Ⅱ) and Cu(Ⅱ) are constructed as the building units together with BDC,

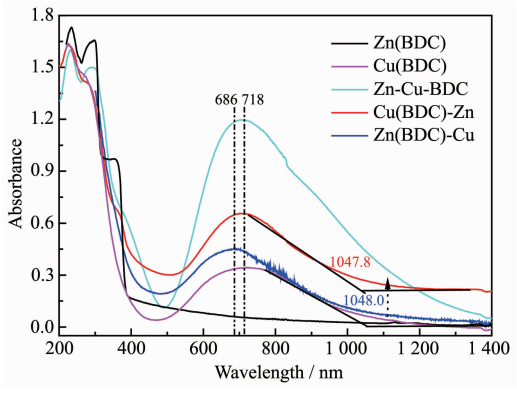


Fig.6 UV-Vis DRS spectra of Zn-Cu based MOFs

Table 1　Light-absorbing and band gap properties of Zn-Cu based MOFs

MOFs	n_{Cu}:n_{Zn}	UPS_{HOMO} /eV	λ_{max} / nm	E_{opt}[a] / eV	λ_{onset} / nm	E_{opt}[b] / eV
Zn(BDC)	—	5.2	360.5	2.84	379.7	2.70
Cu(BDC)	—	4.5	728.8	1.41	1 048.0	1.18
Zn-Cu-BDC	1.1:1.0	2.6	718	1.73	>1 200	<1.03
Zn(BDC)-Cu	1.5:1.0	4.5	686	1.81	1 047.8	1.18
Cu(BDC)-Zn	1.0:2.0	5.5	718	1.73	1 047.8	1.18

[a] Calculated from λ_{max}; [b] Calculated from λ_{onset}.

for Zn-Cu-BDC not only the visible-light photo-responsive intensity increases greatly but also the onset of light-absorbing peak exhibits much more red-shift (>1 200 nm). The light-absorbing properties and band-gaps are calculated and summarized in Table 1. As presented in the table, the band-gaps of both light-absorbing maximum and onset decrease after Cu(Ⅱ) is introduced into the structure of Zn-Cu based MOFs as basic building units in comparison with Zn(BDC). Following the above results and analysis, it can be concluded that Cu(Ⅱ) ions act more effectively in charge transfer and electron transition induced by light and uniformly dispersed active sites work better in light absorption and charge transfer. Moreover, it might give some inspiration for the design and construction of single-atom catalysts or heterogenization of homogeneous catalysts.

To demonstrate the band-gaps of Zn-Cu based MOFs thoroughly, photoelectron spectra (UPS and XPS) were measured and treated (Fig.7, 8 and S2) to determine the highest occupied molecular orbital (HOMO) and the chemical environment of surface elements. To calculate the band gap (HOMO-LUMO), it is suggested that the LUMO value should be obtained through inverse photoelectron spectroscopy (IPES)[34], but effective signal has not be detective in our measurement to determine the LUMO value. However, in the previous reports, the LUMO lies around the Fermi energy level and does not show significant fluctuation for the photocatalysts[35-37]. Hence the HOMO values measured by UPS were used to evaluate the band gaps. The calculated HOMO values and band-gaps are summarized in Table 1. As shown in Table 1 and Fig.S2, the HOMO value of Cu(BDC) (4.5 eV) is lower than that of Zn(BDC) (5.2 eV), indicating the easier electron transition and better conductivity of Cu(Ⅱ). After Zn(Ⅱ) or Cu(Ⅱ) ions are introduced into the frameworks, the HOMO change. For Cu(BDC)-Zn (5.5 eV) and Zn(BDC)-Cu (4.5 eV), the HOMO values change slightly. Noticeably, when Zn(Ⅱ) and Cu(Ⅱ) are constructed into the frame-work homogeneously and simultaneously, the HOMO value (2.6 eV) of product Zn-Cu-BDC decreases greatly while the data of other products range from 4.5 to 5.5 eV. The result is in coincidence with the optical band-gaps determined by UV-Vis spectra and further demonstrates the availability and efficiency of atom-level uniform dispersion for the active sites in photocatalytic materials.

Specially, XPS is performed to evaluate the

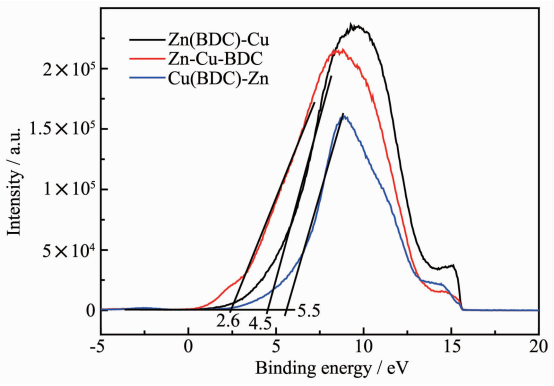


Fig.7　UPS spectra of Zn-Cu based MOFs

change in surface chemical bonding and element binding energy of the coordination polymers. As shown in Fig.8 and S3, showing the characteristic XPS core levels of C1*s*, O1*s*, Cu2*p* and Zn2*p* lines of the Zn and Cu based MOFs surface, significant changes of element binding energy can be found for Zn-Cu-BDC and Zn(BDC)-Cu as compared with the sole-metal MOFs Cu(BDC) and Zn(BDC). In C1*s* spectra,

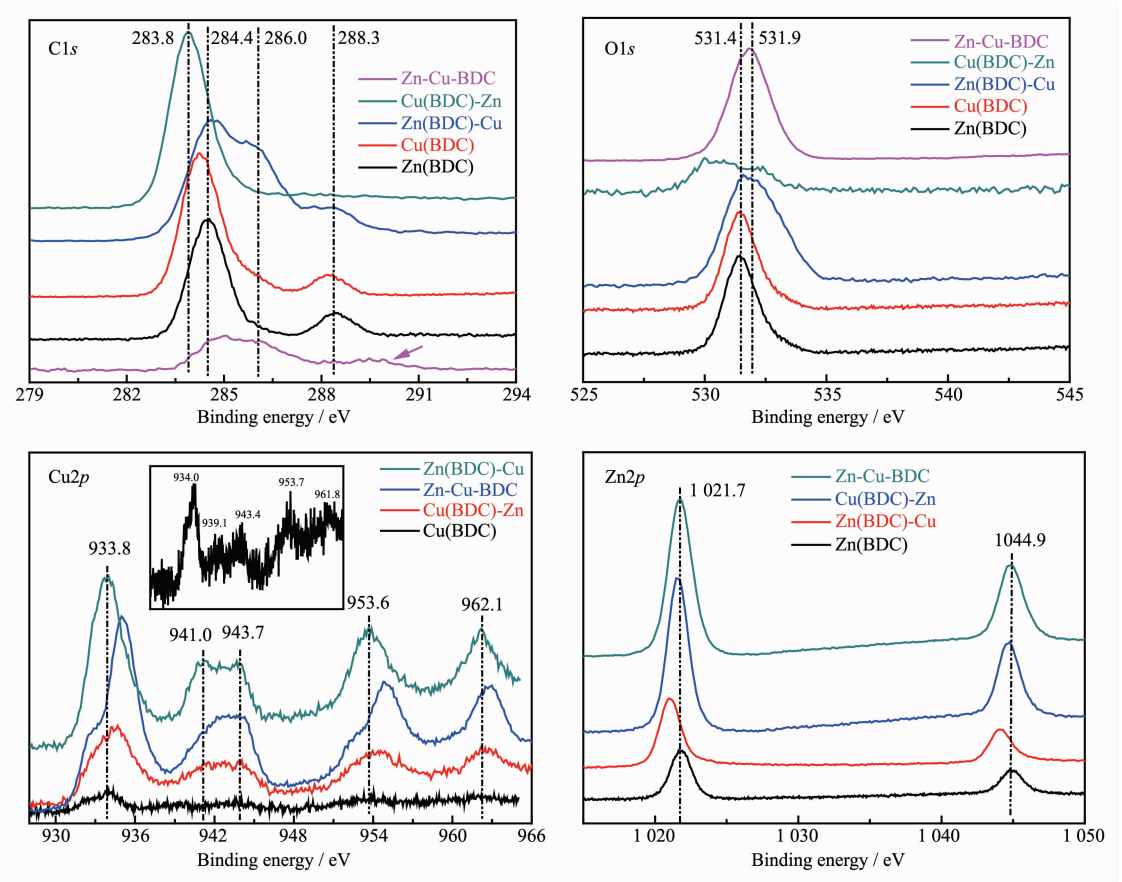


Fig.8 XPS profiles of Zn-Cu based MOFs

peak 1 (284.4 eV for Zn(BDC) and 284.0 eV for Cu(BDC)) of C1*s* results from aromatic carbons in the organic compound BDC; peak 2 (286.0 eV) originates from carbons bonded to O, which is not found in Zn(BDC), Cu(BDC) and Cu(BDC)-Zn, indicating the joint impact on -COOH by Zn and Cu in Zn-Cu-BDC and Zn(BDC)-Cu; and peak 3 (288.3 eV) with highest binding energy derived from carboxylic carbons of the organic molecule, which are consistent with the values as reported in the literature[37-38]. At the meantime, for O1*s* spectra the blue shift of low-energy peak (531.4 eV) and appearance of high-energy peak (531.9 eV) also verifies the co-effect of Zn(Ⅱ) and Cu(Ⅱ) on the carboxylic groups in BDC ligands. In Cu2*p* profiles, which exhibits broad peak in the range of 930 ~966 eV, the peaks of 933.8 eV (which is associated to the $2p_{3/2}$ orbital of copper) and 953.6 eV present slightly blue shift for Zn-Cu-BDC and Cu(BDC)-Zn, while in Zn2*p* profiles the peaks of 1 021.7 and 1 044.9 eV show slightly red shift for Zn(BDC)-Cu with the other peaks almost are unchanged. This suggests that introduction of Zn(Ⅱ) or Cu(Ⅱ) does not affect the valence of the frameworks metal nodes, but changes the chemical environments. Overall, different routes cause different element bonding states for the coordination polymers of Zn and Cu.

Except for band gap, what is the intrinsic reason of causing broader light-absorbing range and increased photo-responsive intensity of bi-metal based MOFs (Zn-Cu-BDC) than sole-metal based MOFs(Cu(BDC))? In this stage according to the above-mentioned data, we cannot demonstrate the fundamental factor, but the enhancement effect of electric transition induced by the neighboring nodes should be taken into account and it is advisable to perform first-principle density functional theory (DFT) and time-dependent density functional theory (TDDFT) predictions that are verified and validated with experimental results, which is underway in our research group.

3 Conclusions

The widely-researched Zn and Cu as the metal sources and 1,4-benzenedicarboxylic acid (BDC) as the ligands were selected to construct mixed-metal nanoporous Zn-Cu based MOFs and the bi-metallic products were synthesized. The target product Zn-Cu-BDC was obtained by solvothermal synthetic method while Zn(BDC)-Cu and Cu(BDC)-Zn were constructed with metal substitution method. Through comparative study, it was found that although the bi-metallic products all contain Zn an Cu atoms in the frameworks, the Zn-Cu metal ions uniformly-dispersed product Zn-Cu-BDC performs better in light-absorbing wavelength range and intensity with lower photo onset band-gap and HOMO level. The results should give some inspiration on the design of heterogeneous photocatalysts and organic-inorganic hybrids in the aspects of light-absorption and charge transfer and construction methods on metal exchange due to different routes leading to different properties although they owe the same components.

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Supporting information is available at http://www.wjhxxb.cn

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