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Partially reversible photochromic behavior of organic-inorganic perovskites with copper(II) chloride*

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Abstract: We report that the ultraviolet (UV) light induced photochromic behavior of layered organic-inorganic perovskite material of $(C_4H_9NH_3)_2CuCl_4$, changed from yellow to brown after irradiation with UV light (10 mW/cm^2) and partially recovered through storage in the dark. $(C_4H_9NH_3)_2CuCl_4$ exhibited two distinct absorption bands centered at 286 nm (band I) and 384 nm (band II), which were attributed to the photo-induced exciton formed in 2D inorganic layers sandwiched by organic layers. The blue shift of band I from 287 to 269 nm as well as the decrease of the intensity of band I and band II could be found when samples were irradiated under UV light for different length of time. The simultaneous weakening of the intensity of the N−H···Cl hydrogen bond as well as the vibration of the long Cu−Cl bond in the distorted $CuCl_6^{4-}$ octahedron could be detected from the Fourier transform infrared (FTIR) spectra, which resulted the change of charge distribution of the dissymmetric Cl−Cu···Cl bond and the resulting photochromic behavior.

Key words: Photochromic behavior, Perovskite, Organic-inorganic hybrid
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INTRODUCTION

Organic-inorganic perovskites have attracted considerable attention due to their opportunity to combine useful properties of both components (Sourisseau *et al.*, 2007; Li, 2008), and thus to design the multifunctional materials (Xu *et al.*, 2006; Jain *et al.*, 2008) for the fundamental researches (Mitzi, 2001; 2004; Geraud *et al.*, 2008). In general, this type of hybrid perovskites forms layered structures consisting of sheets of corner-sharing metal halide octahedra separated by monolayers or bilayers of organic cations. As reported before, the structure of the organic layer and inorganic layer varies when changing the external field, such as thermal field or pressure field. For example, the hybrids based on the alkylamine with long chains exhibit nice heat storage properties due to the solid-solid phase transition caused by the structure variation of the organic layer (Cheng, 2003; Jain *et al.*, 2008). The hydrostatic pressure-induced color change behavior as well as the blue shift of the ultraviolet (UV)-vis absorption correlated to the transition between σ-bonding e_u ligand orbitals to the Cu^{2+} $d(x^2-y^2)$ orbital of the $(C_4H_9NH_3)_2CuCl_4$ hybrids is attributed to the structure change of the inorganic layer, i.e., the reduction of metal-halogen distance (Valiente and Rodriguez, 1996; 1999; Valiente *et al.*, 1999), which induces the rearrangement of the charge distribution of Cl−Cu···Cl unit (Valiente *et al.*, 1999).

For the reason that many of the hybrids own excellent photoelectric properties, the structure variation under external light filed is worthy of attention. However, up to now, there are few reports related to the light-induced structure variation of the

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hybrids with the exception of the photochromism of the azobenzene containing hybrids (Myles *et al.*, 2003).

In this study, we obtained organic-inorganic perovskites with copper(II) chlorides, $(C_4H_9NH_3)_2CuCl_4$, which showed partially reversible photochromism in solid state. The variation of absorption band, Fourier transform infrared (FTIR) spectra, and X-ray diffraction (XRD) as well as surface element with irradiation time for $(C_4H_9NH_3)_2CuCl_4$ will be discussed. The mechanism of the photochromism behavior is correlated to the change of the charge distribution state in the distorted $CuCl_6^{4-}$ octahedron because of the variation of the hydrogen bond intensity in the hybrids.

EXPERIMENTAL

The organic-inorganic hybrid perovskite, $(C_4H_9NH_3)_2CuCl_4$, was prepared by the reaction of butylammonium chloride ($C_4H_9NH_3Cl$) with a stoichiometric amount of copper chloride ($CuCl_2$). Anhydrous $CuCl_2$ powder was added into the solution of $C_4H_9NH_3Cl$ in anhydrous ethanol, and the reaction mixture was stirred under refluxing for 1 h. The solvent was then evaporated completely, giving a golden solid. The solid was recrystallized in anhydrous ethanol and dried at 80 °C in vacuum, and the final hybrid perovskite of $(C_4H_9NH_3)_2CuCl_4$ was obtained as golden sheet-like crystals. Calcd for $(C_4H_9NH_3)_2CuCl_4$: C, 27.2%; N, 7.9%; H, 6.8%; Found: C, 27.21%; N, 7.84%; H, 6.66%. The errors might be caused by the small amount of solvent in the solide that are small and neglected in this discussion.

$(C_4H_9NH_3)_2CuCl_4$ thin film was formed on a quartz substrate by spin-coating the anhydrous ethanol solution containing $(C_4H_9NH_3)_2CuCl_4$ crystals with concentration of 20 mg/ml at 800 r/min.

UV-vis absorption spectra were obtained on a Varian Cary 100 Bio UV-vis spectrometer (PerkinElmer Company, UK) with the samples of $(C_4H_9NH_3)_2CuCl_4$ thin films on quartz substrates. FTIR spectra of the $(C_4H_9NH_3)_2CuCl_4$ thin films on NaCl substrates were recorded on a Bruker Vector 22 FTIR (Bruker Company, German). XRD patterns of $(C_4H_9NH_3)_2CuCl_4$ thin films on zero-diffraction quartz plates were collected over the 2θ range of 3°~50° with CuK_α (40 kV, 40 mA) radiation on a Siemens D5000 Bragg-Brentano $\theta\sim2\theta$ diffractometer (Siemens Company, German). The scanning step size was $2\theta=0.04°$ with a counting time of 2 s/step. Energy-dispersive X-ray spectroscopy (EDS) was conducted on X-ray Microanalysis System implemented on the S-3500N scanning electron microscope (Hitachi Company, Japan).

Immediately after the samples were prepared, $(C_4H_9NH_3)_2CuCl_4$ crystals or thin films were introduced into a controlled environmental chamber with a UV lamp. The intensity of the UV light irradiating on the samples was 10 mW/cm^2 and the working distance was 20 cm. The primary wavelengths of the lamp were 297 and 365 nm.

RESULTS AND DISCUSSION

The photochromic behavior of $(C_4H_9NH_3)_2CuCl_4$ films on quartz is shown in Fig.1. The color of $(C_4H_9NH_3)_2CuCl_4$ thin film became dark after irradiation of UV light (10 mW/cm^2) for 1 h, and returned to yellow again after storage in the dark for 24 h.

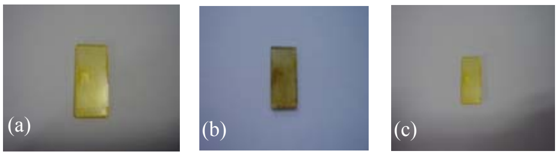
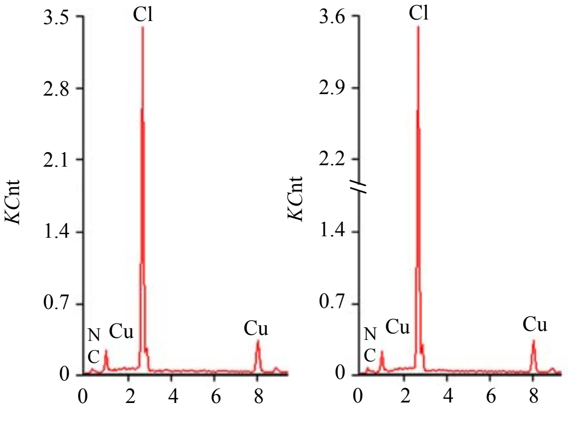


Fig.1 Photochromic behavior of $(C_4H_9NH_3)_2CuCl_4$ film. (a) Before irradiation; (b) After irradiation for 1 h; (c) After 24 h in the dark after irradiation

Surface elements of $(C_4H_9NH_3)_2CuCl_4$ films are characterized by EDS analysis (Fig.2). The results represented that no oxygen elements could be detected on the brown film surface. It suggested that the photochromic phenomenon was not an oxidation process. Table 1 gives the amount of the elements on the film surface before and after irradiation. Obviously the content of the elements including Cl, Cu, N and C changed little after irradiation. In the previous studies of the thermal stability for the $(C_4H_9NH_3)_2CuCl_4$ crystals, the decomposition of the hybrids was attributed to the beginning of the evaporation of $C_4H_9NH_2$ and HCl from the perovskite frameworks (Mitzi, 1996). It is indicated that the process of photochromic behavior of the hybrids was



(a) (b)

Fig.2 EDS analysis of $(C_4H_9NH_3)_2CuCl_4$ film before (a) and after (b) UV light irradiation (10 mW/cm^2) for 1 h

Table 1 Elemental analysis on the surface of $(C_4H_9NH_3)_2CuCl_4$ film before and after UV light irradiation (10 mW/cm^2) for 1 h

Element	Amount of elements on the film	
	Before irradiation	After irradiation
CK	19.90 (44.08)	19.67 (43.55)
NK	04.92 (09.34)	05.28 (10.02)
CuL	08.20 (03.43)	08.77 (03.67)
ClK	45.47 (34.13)	45.37 (34.02)
CuK	21.52 (09.01)	20.91 (08.75)
R=ClK/(CuL+CuK)	1.53 (2.74)	1.53 (2.75)

Data represent weight percent (atom percent); K: K shell of the electron structure; L: L shell of the electron structure

neither the thermal-like decomposition nor the oxidation.

The XRD patterns of $(C_4H_9NH_3)_2CuCl_4$ film before and after irradiation are shown in Fig.3. The XRD pattern changed little after exposure to irradiation for 1 h. It is known that the higher order (001) peaks correspond to highly ordered and oriented film structure with the *c*-axis perpendicular to the substrate surface. The interlayer distance (between two separating $CuCl_4^{2-}$ layers) of 1.544 nm (calculated by the Bragg equation, $n\lambda=2d\sin\theta$) is dominated by the organic component. As shown in Fig.4, the $CuCl_6^{4-}$ octahedra are strongly deformed due to the cooperative Jahn-Teller (JT) effects. The lengths of Cu−Cl bond are 0.228 nm ($Cu-Cl_{short}$) and 0.298 nm ($Cu-Cl_{long}$), respectively (Rodriguez *et al.*, 2007), which is much shorter than the interlayer distance. It is indicated that the structure of the organic molecule chain changed little during UV irradiation exposure.

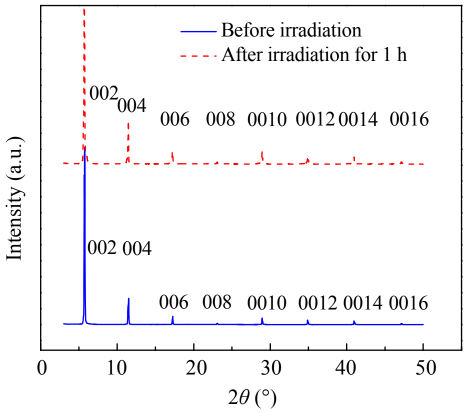
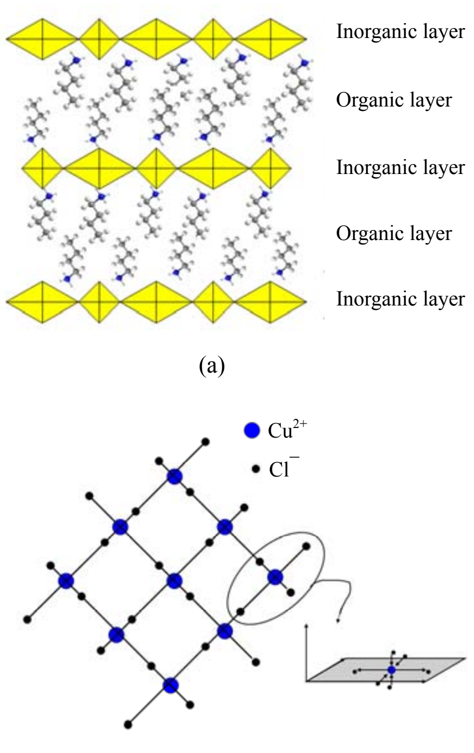


Fig.3 XRD patterns of $(C_4H_9NH_3)_2CuCl_4$ film before and after UV light irradiation (10mW/cm^2) for 1 h

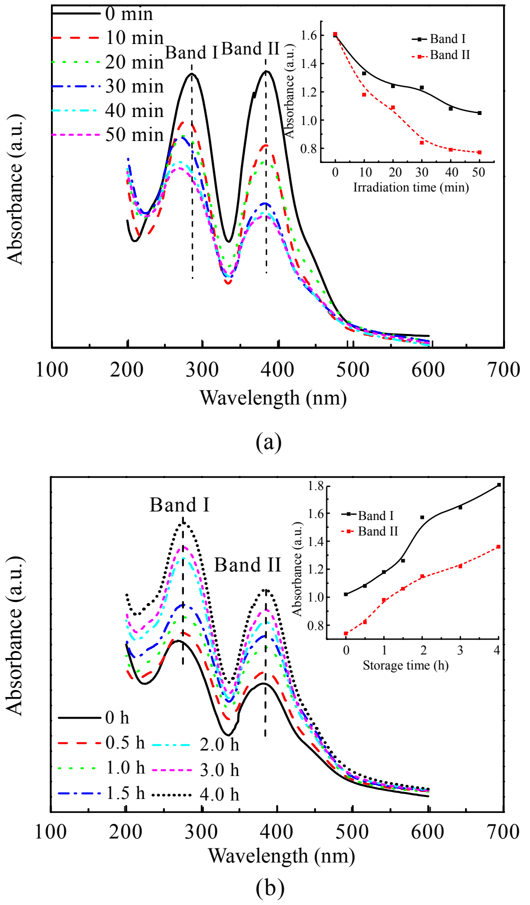


(a)

(b)

Fig.4 Organic-inorganic hybrid structure of $(C_4H_9NH_3)_2CuCl_4$ (a) and inorganic structure of JT distorted $CuCl_6^{4-}$: Cu···Cl of long bond and Cu−Cl of short bond due to JT distortion (b)

Fig.5 gives normalized UV-vis absorption spectra of the $(C_4H_9NH_3)_2CuCl_4$ film with background correction measured at room temperature. As reported (Valiente and Rodriguez, 1999), $(C_4H_9NH_3)_2CuCl_4$ exhibits two distinct absorption bands centered at 286 nm (band I) and 384 nm (band II), due to the photo-induced exciton formed in the 2D inorganic layers sandwiched by organic layers. It is reported that in the inorganic layer of the composites, $CuCl_6^{4-}$ usually displays an elongated octahedron (D_{4h}) for JT distortion (Valiente and Rodriguez, 1999), which causes the separation of these peaks (Valiente and Rodriguez, 1996). The peak of band II at 384 nm is assigned to the transition from π-bonding e_u ligand orbitals, mostly constructed from the equatorial Cl^- π-orbitals, to the Cu^{2+} $d(x^2-y^2)$ orbital, while the peak of band I at 286 nm comes from the transition between σ-bonding e_u ligand orbitals to the Cu^{2+} $d(x^2-y^2)$ orbital (Valiente and Rodriguez, 1996; Valiente *et al.*, 1999).



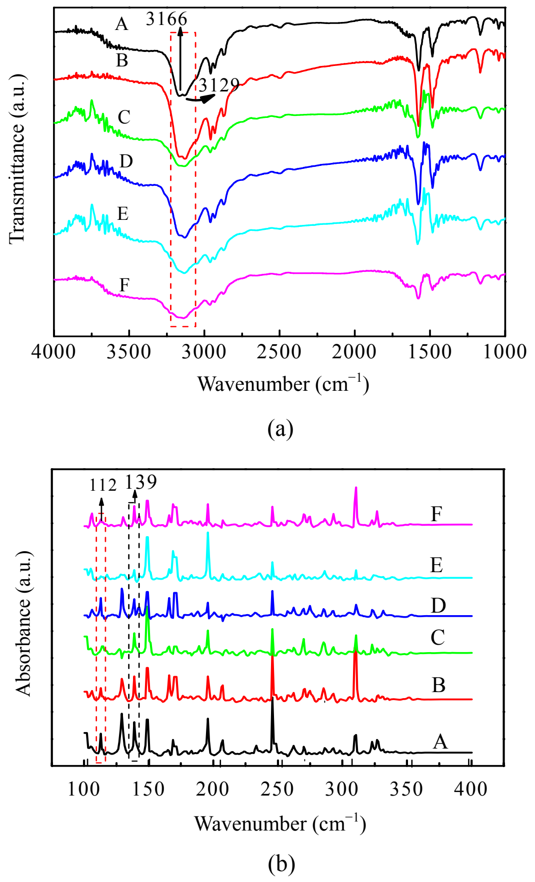
(a)

(b)

Fig.5 Time-resolved spectra of yellow $(C_4H_9NH_3)_2CuCl_4$ film irradiated by UV lamp with interval time of 30 min (a) and brown $(C_4H_9NH_3)_2CuCl_4$ stored in the dark room with different lengths of time (b) in the solid state. Band I: $e_u(\sigma)\rightarrow b_{1g}(x^2-y^2)$, band II: $e_u(\pi)\rightarrow b_{1g}(x^2-y^2)$

Upon irradiation with UV light for different lengths of time, the peak of band I blue shifted from 287 to 269 nm (Fig.5a). The intensities of band I and band II decreased respectively with different lengths of irradiation time (the inset in Fig.5a). When the samples were stored in the dark, the UV-vis spectrum of the $(C_4H_9NH_3)_2CuCl_4$ film recovered to some extent. The peak of band I shifted from 269 nm back to 276 nm (Fig.5b). Correspondingly, the intensities of band I and band II increased respectively (the inset of Fig.5b). The phenomenon mentioned above indicated that the charge transfer from the Cl^- π-orbitals to Cu^{2+} $d(x^2-y^2)$ orbital changed upon UV irradiation as well as the following storage in the dark. That is to say, the charge distribution of the σ- and π-bonding e_u ligand orbitals as well as the probability of the electron transition from Cl^- π-orbitals to Cu^{2+} $d(x^2-y^2)$ orbital would influence the UV-vis absorption behavior of the hybrids.

The FTIR spectra of the hybrid $(C_4H_9NH_3)_2CuCl_4$ film under UV-vis irradiation for different lengths of time are shown in Fig.6. The intensity ratio of $-NH_3^+$ asymmetric stretching vibration (ν_{as}) band (at 3166 cm^{-1}) over symmetric stretching vibration (ν_s) band (at 3129 cm^{-1}) became smaller after irradiation, and ν_{as} became a shoulder. Simultaneously, $-NH_3^+$ stretching vibration band shifted to a longer wavenumber (i.e., ν_{as}=3167 cm^{-1}, ν_s=3137 cm^{-1}), as shown in Fig.7. All of these observations indicate the decrease of the intensity of the N−H···Cl hydrogen bond (Wselucha-Birczynska *et al.*, 2003). After restoring in the dark for 24 h, the value of $(I\nu_{as}/(I\nu_s))$ was recoveried a little (Fig.6a), due to the partial recovery of the hydrogen bond. As we know, the structure of the hybrid $(C_4H_9NH_3)_2CuCl_4$ is stabilized by the hydrogen bond between amine cation and the Cl in the $CuCl_6^{4-}$ octahedron. Hence, the variation of the hydrogen bond will inevitably change the vibration behavior of the $CuCl_6^{4-}$ octahedron. Far-infrared spectra (Fig.6b) showed structure changes in $CuCl_6^{4-}$ octahedron during the UV light illumination. As shown in Fig.8, intensity reduction of the bands at 112 and 139 cm^{-1} upon irradiation could be observed and both of the bands intensity came back a little after the samples stored in the dark for 2 h. The band at 112 cm^{-1} might be attributed to the stretch of the long Cu−Cl bond while the band at 139 cm^{-1} to the motion of the long-bonded Cl atoms (Smith, 1976). That is, the applied UV irradiation decreased the vibration behavior of the long Cu-Cl bond in the distorted $CuCl_6^{4-}$ octahedron. Other peaks at about 195 cm^{-1}, 245 cm^{-1} and 310 cm^{-1} might be attributed to the vibrations of $CuCl_4^{2-}$ ions (Smith, 1976). These peaks showed irregular changes during this progress, which might be caused by the partially reversible changes of N−H···Cl-hydrogen bond. In addition, the Cl−Cu−Cl bond is a dominant structural factor influencing the electronic structure of such organic-inorganic hybrid compounds (Valiente and Rodriguez, 1999; Sourisseau *et al.*, 2007). In fact, the main interaction responsible for rotation and/or the tilt of the $CuCl_6^{4-}$ octahedra is the hydrogen bonding between ammonium parts and halide atoms. It is assumed that the change of hydrogen bonding during structural transitions, which involve a change of geometrical characteristics of inorganic sheets in photochromism, will lead to the blue shift of band I as well as the intensity changes of band I and band II.



(a)

(b)

Fig.6 ($(C_4H_9NH_3)_2CuCl_4$ film was irradiated with UV light (297 and 365 nm) with different lengths of time. Infrared (a) and Far-Infared (b) Spectra were obtained after (A) 0, (B) 10, (C) 20, (D) 40, (E) 60 min of exposure and then stored in the dark for 2 h (F)

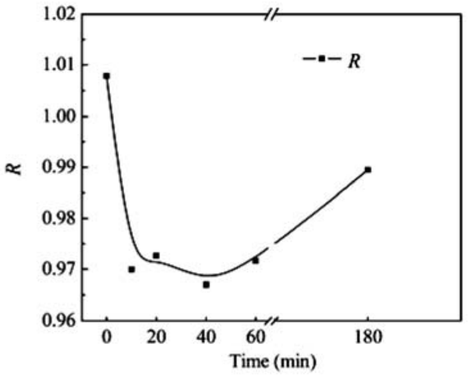


Fig.7 Intensity ration of -NH_3^+ asymmetric stretching vibration band over symmetric stretching vibration band, $R=Iv_{as}/(Iv_s)$ in Fig.6a

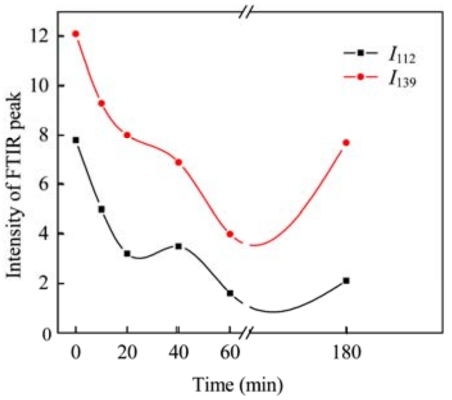


Fig.8 Intensity of peaks at 112 and 139 cm^{-1} in Fig.6b

CONCLUSION

In this study, we obtained organic-inorganic perovskites with copper(II) chlorides, $(C_4H_9NH_3)_2CuCl_4$, which showed partly reversible photochromism in solid state. EDS analysis indicated that the process of photochromic behavior of the hybrids was neither the thermal-like decomposition nor the oxidation. The XRD pattern represented that the structure of the organic molecule chain changed little during UV irradiation process. Two characteristic absorption bands centered at 286 (band I) and 384 nm (band II), which were derived from JT distortion of the elongated $CuCl_6^{4-}$ octahedron, can be detected. The blue shift of band I from 287 to 269 nm as well as the intensity decrease of band I and band II can be found when samples were irradiated under UV light for different lengths of time. The simultaneous decrease of the intensity of the N−H···Cl-hydrogen bond as well as the vibration of the long Cu−Cl bond in the distorted $CuCl_6^{4-}$ octahedron can be detected from the FTIR spectra, which induced the change of the charge distribution of the dissymmetric Cl−Cu···Cl bond and the resulting photochromic behavior.

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