Multifunctional Polymers Built on Copper-Thioether Coordination

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Supporting Information

Materials Dichloromethane (DCM) (AR) was purchased from Nanjing black ants Biological Technology Co., Ltd. 2-(methylthio) ethanol (MTEA) (≥98%) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) (≥97%) were supplied by Shanghai Titan Technology Co., Ltd. Acrylic acid (≥99%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 4-dimethylaminopyridine (DMAP) (≥99%) was purchased from Shanghai Haibei Biotechnology Co., Ltd. Dimethylformamide (DMF) (99.5%) was provided by Sinopharm Group Chemical Reagent Co., Ltd. Butyl acrylate (BA) (99%, Sigma-Aldrich) and methyl methacrylate (MMA) (99.0%, Sigma-Aldrich) were purified through alumina oxide columns before using. Acetonitrile (MeCN) (AR) was supplied by Shanghai Ling Feng Chemical Reagent Co., Ltd. Cuprous Bromide (CuBr) and Cupric bromide (CuBr2) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.

Instrumentation

1H NMR The Bruker Av400III HD instrument was used to measure samples at 400 MHz with Acetone-D or Chloroform-D as the solvent.

Gel Permeation Chromatography (GPC) The PL-GPC 220 (Polymer Laboratories) was operated to measure samples on at 40°C in THF with polystyrene (PS) as the calibration standard. The detection was performed with a low rate of 1 mL/min.
**Solid Mechanical Property Experiments** The polymers were hot-pressing at 150 °C following ASTM standard D1708 to prepared the dog-bone-shaped samples (length: ~38 mm, width: ~15 mm, thickness: ~0.5 mm). Tensile tests were operated on a SANS E42.503 tensile tester with a displacement-speed control of 5.0 mm/min. An average over at least three measurements on three identical samples was used the reported results.

**Small Angle X-ray Scattering (SAXS)** SAXS experiments were carried out using the beamline (X-ray Diffraction and Scattering) at the National Synchrotron Radiation Laboratory (Hefei, China) with an X-ray wavelength of 0.154 nm. A Mar345 image plate (2300 × 2300 pixels with a pixel size of 150 mm) was employed to collect 2D SAXS patterns. Samples were prepared as 0.5 mm thin film and all measurements were taken with 10 minutes exposure time. SAXS data was analyzed by Fit2D software from European Synchrotron Radiation Facility, and are reported in units of arbitrary intensity. In all cases the scattering patterns were cylindrical symmetric and were therefore reduced to the 1-D form of intensity versus scattering wave vector magnitude, $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where $\theta$ is the scattering angle.

**Differential Scanning Calorimetry (DSC)** The SDT-Q600 thermal analyzer (TA) was used to determined thermal transitions. The samples (5~10 mg) were loaded into DSC pans, first heated to 130 °C at a rate of 40 °C/min and held to erase any thermal history that was quenched to -70 °C, then reheated to 130 °C at a rate of 20 °C/min. The glass transition temperatures were confirmed during the second heating run.

**Ultraviolet-visible Light Detector (UV)** Films were prepared through the hot-press approach. Then, these films were placed above hydrochloric acid with different time. After that, these films were irradiated under ultraviolet lamp, whose wattage was 500 W and wave length range was 350 ~ 450 nm, at a certain time interval. And UV was conducted by a Shimadzu Autograph UV-2450 with the scan from 200 to 800 nm.
Cyclic Tensile Test The long-striped sample (length: ~38 mm, width: ~5 mm, thickness: ~0.5 mm) were prepared by Hot-press method. The Cycle Test was conducted through a SANS E42.503 tensile tester. The displacement-speed of the Cycle Test was controlled at 5.0 mm/min. Strains becoming greater than 25%, 50%, 100%, 150%, 200% and 250% were the termination condition of stretching process, the force becoming less than 0 N was the termination condition of recovery process.

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES): 100 mg sample was calcined at 600 °C for 1 h, the residual material was dissolved in a 25 mL volumetric flask with 4.8 mol/L of HCl and the concentration of Cu was measured by ICP-3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The results were summarized in Table S2.

Experimental

Preparation of PMMA-b-P(BA-co-MTEA) [M200-b-(B378T248)]. M200-b-(B378T248) was prepared by adding PMMA (1.3 g, 0.065 mmol), BA (5.2 g, 5.8 mL, 40.6 mmol), MTEA (5.9736 g, 40.6 mmol), AIBN (2.1 mg, 0.013 mmol) in the 25 mL flask and 8 mL DMF as the solvent. The flask was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. Then the flask was placed in a water bath at 70 °C and stirred for 9.5 h. After reaction, the polymer was precipitated three times in methanol and dried under vacuum for 2 h at 45 °C to obtain pink solids. Yield: 5.6g, 44.9%. GPC: M_n= 39k, M_w = 58k. 1H NMR (Chloroform-D, δ, ppm) (Figure S3):

- 3.54 (-COOCH_3, 3H), 3.98 (-COOCH_2CH_2CH_2CH_3, 2H), 1.53 (-COOCH_2CH_2CH_3, 2H), 1.31 (-COOCH_2CH_2CH_2CH_3, 2H), 0.87 (-COOCH_2CH_2CH_3, 3H), 4.14 (-COOCH_2CH_2SCH_3, 2H), 2.64 (-COOCH_2CH_2SCH_3, 2H), 2.08 (-COOCH_2CH_2SCH_3, 3H).

Preparation of PMMA-co-PBA-co-PMTEA (M213-B326-T317). M213-B326-T317 was prepared by adding MMA (0.8 g, 0.8 mL, 7.99 mmol), BA (2.56 g, 2.9 mL, 20.0 mL),
MTEA (2.94 g, 20.0 mL), RAFT (7.08 mg, 0.03 mmol) reagent, AIBN(1.05 mg, 0.006 mmol) in the 25 mL reaction the flask and 2 mL DMF as the solvent. The flask was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was placed in an water bath at 70 °C and stirred for 4.5 h. The polymer was precipitated three times in methanol and dried under vacuum for 2 h at 45 °C to obtain pink solids. Yield: 3 g, 47.6%. GPC: $M_n = 42k$, $M_w = 63k$.

$^1$H NMR (Chloroform-D, δ, ppm): 3.52 (−COOCH$_3$,3H), 3.96 (−COOCH$_2$CH$_2$CH$_3$, 2H), 1.52 (−COOCH$_2$CH$_2$CH$_3$, 2H), 1.30 (−COOCH$_2$CH$_2$CH$_3$, 2H), 0.87 (−COOCH$_2$CH$_2$CH$_3$, 3H), 4.14 (−COOCH$_2$CH$_2$SCH$_3$, 2H), 2.64 (−COOCH$_2$CH$_2$SCH$_3$, 2H), 2.08 (−COOCH$_2$CH$_2$SCH$_3$, 3H).

CuBr/CuBr$_2$ coordination with thioether polymer. M$_{200}$-$b$-(B$_{378}$T$_{248}$)-CuBr (3%, 6.6%, 10.5%), M$_{200}$-$b$-(B$_{378}$T$_{248}$)-CuBr$_2$ (7%), M$_{213}$-B$_{326}$-T$_{317}$-CuBr(7.4%) were prepared through a coordination of CuBr/CuBr$_2$ and thioether. These samples were prepared in the same procedure, but with the different mass ratios of CuBr/CuBr$_2$ and thioether polymer. For example, for M$_{200}$-$b$-(B$_{378}$T$_{248}$)-CuBr (6.6%), 1.0 g polymer was dissolved in 6 mL of MeCN and added to 0.1 g CuBr with stirring until colloidal matter was separate out. The matter was then transferred to a Teflon mold and the solvent was allowed to evaporate for 24 h under ambient conditions. The sample was further dried at 45 °C in a vacuum oven.

Self-healing tests. The self-healing tests were performed at room temperature. The dog-bone-shaped samples were prepared by melt-compounding of polymers. The specimen was completely cut into halves and contacted for healing. The self-healing was performed under ambient conditions for 24 hours. The healed sample was used for tensile test.

Response towards HCl and H$_2$O$_2$. For HCl, M$_{200}$-$b$-(B$_{378}$T$_{248}$)-CuBr (6.6%) was melt-compounded into thin films (2 cm × 2 cm × 0.1 mm) and covered on a beaker with 5 mL HCl (12 mol/L). UV-vis and photos were taken during the experiment. For
H$_2$O$_2$, M$_{200}$-$b$-(B$_{378}$T$_{248}$)-CuBr (6.6%) was melt-compounded into a stick (3 cm x 0.3 cm x 0.05 cm) and then immersed into H$_2$O$_2$ solution (3% wt and 0.3% wt). Thin films (3 cm x 0.3 cm x 0.05 cm) were also utilized to test H$_2$O$_2$ solution (3% wt and 0.3% wt). Photos were taken during the experiment.

**Estimation of Flory-Huggins Interaction Parameter $\chi$**

Based on the functional group contribution method,$^{1,2}$ the solubility parameters of all components are estimated as:

- $\delta$ (MMA) = 9.18 $\sqrt{\text{cal/cm}^3}$
- $\delta$ (BA) = 9.13 $\sqrt{\text{cal/cm}^3}$
- $\delta$ (MTEA) = 9.68 $\sqrt{\text{cal/cm}^3}$

For the second block P(BA-co-MTEA), it is a random polymer, according to the mixing rule, the equivalent solubility parameters are:

- $\delta$ (B$_{378}$T$_{248}$) = 9.35 $\sqrt{\text{cal/cm}^3}$

Using the following relationship$^2$ for estimating $\chi$:

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^2$$

where $V_1$ is reference volume and we can use the MMA monomer volume, so

$$V_1 = \frac{M}{\rho} = \frac{(100.12 \text{g/mol})}{(0.94 \text{g/cm}^3)} = 106.51 \text{cm}^3/\text{mol}$$

and $R=1.987 \text{cal/K}$

The result at 25°C (298.15K) is:

$\chi$(M$_{200}$/B$_{378}$T$_{248}$) = 0.0052, $\chi N = 4.30$, for this diblock, $T_{ODT} \approx 122 \, ^\circ \text{C}$
Figure S1. $^1$H NMR spectrum for methyl thioethyl acrylate (META) monomers.

Figure S2. $^1$H NMR spectrum for the PMMA block. The inset is the zoom-in spectrum displaying phenyl protons of the RAFT agent. The molecular weight of PMMA block was calculated by comparing the integrated peak areas for phenyl protons and methyl protons (3.6 ppm).
Figure S3. $^1$H NMR spectrum for the diblock polymer, $M_{200}-b-(B_{378}T_{248})$. The number of repeat units of BA and MTEA were determined by the integrated areas under peaks for BA and MTEA in the $^1$H NMR spectrum.

Figure S4. $^1$H NMR spectrum for the random copolymer, $M_{213}-B_{326}-T_{317}$. 
Figure S5. SEC curves for the PMMA macroinitiator, M\textsubscript{200}-'b-(B\textsubscript{378}T\textsubscript{248}) block polymer and M\textsubscript{213}-B\textsubscript{326}-T\textsubscript{317} random copolymer.

Table S1. Molecular characteristics of the synthesized polymers and the associated copper(I) bromide coordinated hybrid materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PMMA</th>
<th>M\textsubscript{200}-'b-(B\textsubscript{378}T\textsubscript{248})-CuBr</th>
<th>M\textsubscript{213}-B\textsubscript{326}-T\textsubscript{317}-CuBr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0%</td>
<td>3%</td>
</tr>
<tr>
<td>(M_n)</td>
<td>11200</td>
<td>38600</td>
<td></td>
</tr>
<tr>
<td>(M_w)</td>
<td>12800</td>
<td>57500</td>
<td></td>
</tr>
<tr>
<td>PDI</td>
<td>1.14</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>(T_{g, BT}) (°C)</td>
<td>-</td>
<td>-21.9</td>
<td>-6.0</td>
</tr>
<tr>
<td>(T_{g, M}) (°C)</td>
<td>98</td>
<td>93</td>
<td>- d</td>
</tr>
</tbody>
</table>

\(M_n\), \(M_w\) and \(\Phi\) were determined by SEC at 40 °C using polystyrene standards and tetrahydrofuran (THF) as the mobile phase. \(T_{g, BT}\) and \(T_{g, M}\) are the glass transition temperatures for B\textsubscript{378}T\textsubscript{248} and PMMA phases, respectively. M\textsubscript{200}-'b-(B\textsubscript{378}T\textsubscript{248})-CuBr and M\textsubscript{213}-B\textsubscript{326}-T\textsubscript{317}-CuBr are the block polymer and random copolymer in the work. The percentages 0%, 3%, 6.6% and 10.5% are the weight percent of CuBr added to polymers. The glass transition temperature of PMMA was not observed in the hybrid materials.

Table S2. Copper content in polymers determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

<table>
<thead>
<tr>
<th>Samples</th>
<th>M\textsubscript{200}-'b-(B\textsubscript{378}T\textsubscript{248})</th>
<th>M\textsubscript{213}-B\textsubscript{326}-T\textsubscript{317}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuBr (3%)</td>
<td>CuBr (6.6%)</td>
</tr>
<tr>
<td></td>
<td>Cu (mg/L)</td>
<td>Cu (mg)</td>
</tr>
<tr>
<td>Cu (%),</td>
<td>CuBr (%),</td>
<td>CuBr (%),</td>
</tr>
<tr>
<td>CuBr r,</td>
<td>CuBr r,</td>
<td>CuBr r,</td>
</tr>
<tr>
<td>CuBr (mg/L)</td>
<td>52.3</td>
<td>118</td>
</tr>
<tr>
<td>(m_{Cu})</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>CuBr (%)</td>
<td>3.0</td>
<td>6.6</td>
</tr>
<tr>
<td>CuBr r (%)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(F_{Cu:T})</td>
<td>0.16 : 1</td>
<td>0.33 : 1</td>
</tr>
<tr>
<td>(P_{Cu:T})</td>
<td>0.09 : 1</td>
<td>0.21 : 1</td>
</tr>
</tbody>
</table>
CuBr (a%) or CuBr$_2$ (a%) was the polymer sample coordinated with a% (weight percentage) CuBr or CuBr$_2$.

Cu (mg/L): concentration of Cu in polymer (100 mg polymer was calcined at 600 °C, the resulting residue was dissolved in a 25 mL volumetric flask with 4.8 mol/L of HCl and Cu (mg/L) measured by ICP-AES.

$m_{Cu}$: the actual weight of Cu in polymers ($m_{Cu}=\frac{cu(mg/L) \times 25}{10^3}$ mL).

Cu (%): the weight percent of Cu in polymer ($Cu\% = \frac{m_{Cu}}{m_p} \times 100$, $m_p$: the weight of the coordinated polymers).

CuBr (%): the weight percent of CuBr in polymer ($CuBr\% = \frac{Cu\% M_{CuBr}}{M_{Cu}}$, $M_{Cu}$: The molar mass of Cu, $M_{CuBr}$: The molar mass of CuBr).

CuBr$_2$ (%): the weight percent of CuBr$_2$ in polymer ($CuBr_2\% = \frac{Cu\% M_{CuBr_2}}{M_{Cu}}$, $M_{CuBr_2}$: The molar mass of CuBr$_2$).

$F_{Cu:T}$ and $P_{Cu:T}$ were the molar ratios of copper metal to thioether units in the feed and final product, respectively. $F_{Cu:T}$ and $P_{Cu:T}$ were calculated by equation:

$$F_{Cu:T} = \frac{m_{Cu}/M_{Cu}}{m_{polymer}/M_w \times N_T} \quad \text{and} \quad P_{Cu:T} = \frac{m_{CuBr}/M_{CuBr}}{m_{polymer}/M_w \times N_T} \quad \text{molecular weight of the polymers; N$_T$ is the repeat number of thioether units in a polymer chain.}$$

$M_{CuBr_2}$ should be applied in the equation when CuBr$_2$ is used.

Figure S6. Differential scanning calorimetry (DSC) curves of the M$_{213}$-B$_{326}$-T$_{317}$ random copolymer and the CuBr coordinated material. Arrows indicate the glass transition temperatures.

Table S3. Tensile properties of pure polymers and their CuBr-coordinated materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\sigma_b$ (MPa)</th>
<th>$E$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>Toughness (MJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$<em>{200}$-b-(B$</em>{378}$T$_{248}$)</td>
<td>0.3 ± 0.1</td>
<td>0.1 ± 0.1</td>
<td>293 ± 43</td>
<td>0.5</td>
</tr>
<tr>
<td>M$<em>{200}$-b-(B$</em>{378}$T$_{248}$)-CuBr (3%)</td>
<td>0.7 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>427 ± 58</td>
<td>1.9</td>
</tr>
</tbody>
</table>
**Table:**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile strain (%)</th>
<th>Tensile toughness (MPa)</th>
<th>Tensile strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M200-b-(B378T248)-CuBr (6.6%)</td>
<td>2.0 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>665 ± 7</td>
<td>7.5</td>
</tr>
<tr>
<td>M200-b-(B378T248)-CuBr (10.5%)</td>
<td>7.0 ± 1.9</td>
<td>4.4 ± 0.9</td>
<td>468 ± 51</td>
<td>19</td>
</tr>
<tr>
<td>M213-B326-T317-CuBr (7.4%)</td>
<td>0.05 ± 0.1</td>
<td>0.1 ± 0.1</td>
<td>599 ± 70</td>
<td>0.3</td>
</tr>
<tr>
<td>M200-b-(B378T248)-CuBr (7%)</td>
<td>0.7 ± 0.4</td>
<td>2.0 ± 0.6</td>
<td>34 ± 65</td>
<td>0.2</td>
</tr>
<tr>
<td>M410-b-(B365T257)-CuBr (6.1%)</td>
<td>5.2 ± 1.1</td>
<td>11 ± 3</td>
<td>157 ± 31</td>
<td>5.2</td>
</tr>
</tbody>
</table>

* Room temperature Young’s modulus (E) determined from the slope of the fitting line to the linear elastic regime of stress-strain curves.  

**Calculation of recovery ratios in the cyclic tests:**

\[
\text{Elastic Recovery} = \frac{\varepsilon_{\text{max}} - \varepsilon_{0,\text{max}}}{\varepsilon_{\text{max}}}
\]

Here, \( \varepsilon_{\text{max}} \) is the maximum strain being applied to the specimen; \( \varepsilon_{0,\text{max}} \) is the strain in the relaxed state (stress is zero) after reaching the maximum strain.

**Figure S7.** Representative engineering stress *versus* strain curves for pure M200-b-(B378T248) block polymers. M200-b-(B378T248) (Healing) is the damaged specimen after 24 hours of self-healing. The damaged sample was very weak in mechanical strength.
**Figure S8.** Representative engineering stress versus strain curves for $M_{213-B_{326-T_{317}}-CuBr(7.4\%)}$. $M_{213-B_{326-T_{317}}-CuBr(7.4\%)}(\text{Healing})$ was the damaged specimen after 24 hours self-healing.

**Figure S9.** XPS spectrum of Cl 2p for $M_{200-b-(B_{376-T_{248}})}-CuBr(6.6\%)$ after the treatment with HCl vapor. The peaks at 198 and 201 eV indicated the existence of chloride.
**Figure S10.** XPS spectrum of Br 3d for (A) M$_{200}$-b-(B$_{378}$T$_{248}$)-CuBr(6.6%) (Black curve) polymers without any treatment; (B) Polymers treated by H$_2$O$_2$ (3% wt) solution (Red curve); (C) Polymers after the treatment with HCl vapor (Blue). No obvious shift of peaks for Br 3d was observed during the experiment, indicating that the state of bromine was not influenced during these treatments.

**Figure S11.** Photographs of M$_{213}$-B$_{326}$-T$_{317}$-CuBr(7.4%) thin films (2 cm × 2 cm × 0.1 mm) after exposure to HCl vapor for different time intervals.

**Figure S12.** Photographs of M$_{200}$-b-(B$_{378}$T$_{248}$)-CuBr(6.6%) thin films (2 cm × 2 cm × 0.1 mm) after emerged into H$_2$O$_2$ (3% wt) solution for different time intervals.
**Figure S13.** Photographs of $M_{213}$-B$_{326}$-T$_{317}$-CuBr(7.4%) thin films (2 cm × 2 cm × 0.1 mm) after emerged into H$_2$O$_2$ (3% wt) solution for different time intervals.

**Figure S14.** Photographs of $M_{200}$-b-(B$_{378}$T$_{248}$)-CuBr(6.6%) sticks (3 cm × 0.3 cm × 0.05 cm) after immersed in H$_2$O$_2$ solution (0.3% by weight) for different time intervals.

**Figure S15.** $^1$H NMR spectrum for $M_{200}$-b-(B$_{378}$T$_{248}$)-CuBr(6.6%) after treating with H$_2$O$_2$. Part of the thioether groups are oxidized into sulfoxides as shown in the $^1$H NMR spectrum. The partially oxidized polymers became slightly soluble in water.
Figure S16. IR spectra for M₂₀₀⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻┅┅┅┅┅┅┅┅┅┅┅┅.DataGridViewTextBoxColumn 3000 2500 2000 1500 1000 500

Transmittance (a.u.)
Wavenumbers (cm⁻¹)
S=O

Figure S17. XPS spectrum of Cu 2p for (A) M₂₀₀⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻┅┅┅众所周’s for (B) Polymers treated by H₂O₂ (3% wt) solution (Red curve). Peaks at 934 eV and satellite peaks at 943, 963 eV matched with typical XPS spectrum of CuO.
Figure S18. The mixture of CuBr and H₂O₂ solution (3% by weight). Brown color was immediately observed when adding H₂O₂.

References