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1 **Light harvesting hexamolybdenum cluster integrated with the 3D ordered**  
2 **semiconductor inverse opals for optoelectronic property**

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21 **ABSTRACT**

22 Solar energy-harvesting materials have significantly contributed to the development of  
23 energy-saving applications for several decades. We have mainly used a new concept  
24 composed of the electrophoretic deposition technique and photonic crystal structural  
25 engineering to understand the tunable light-absorption and electronic conduction  
26 properties. A hexamolybdenum cluster compound (denoted as the Mo<sub>6</sub> cluster) was

27 successfully functionalized on a tin pyrophosphate semiconductor integrated within an  
28 inverse opal photonic crystal. The size of the periodical pores, surface modification, and  
29 chemical composition of the infiltration material of the inverse opal film have been  
30 investigated to control the photonic bandgap in the visible range and the efficiency of the  
31 deposited Mo<sub>6</sub> cluster. The photoactive Mo<sub>6</sub> clusters act as a visible light harvester and  
32 generate an efficient photo-induced current upon light absorption that is enhanced by a  
33 slow photon effect occurring at the photonic stopband edges. The electron and proton are  
34 transferred in the inorganic-organic network via hydrogen bonds by a hopping  
35 mechanism to generate a rapid photoconductivity response during light irradiation.  
36 Specific attention focused on the role of humidity and temperature regarding the  
37 reproducibility of the experiments and the photosensitivity of the nanocomposite. The  
38 suitable tunable photo-induced conduction property in organic-inorganic materials opens  
39 a new opportunity for the applicability of cluster-based compounds in visible  
40 optoelectronic devices.

41 **KEYWORDS:** hexamolybdenum atom cluster, optical material, 3D inverse opal  
42 structure, optoelectronic, visible light harvesting, surface chemistry

## 43 1. INTRODUCTION

44 Considering the serious global warming problem, the discovery of a solar energy-  
45 converting material in the Vis-NIR domain for optoelectronic devices, such as  
46 photodetectors, light emission devices, sensors, and dye-sensitized solar cells, has  
47 occurred [1-5]. Among the nanoarchitecture nanomaterials, the  $[M_6L^i_8L^a_6]^{n-}$  cluster unit,  
48 composed of a central Mo<sub>6</sub> cluster, eight inner ligands at the face-capping position ( $L^i =$   
49 halogen or chalcogen; i for inner), and six apical ligands at the terminal positions ( $L^a =$   
50 halogen, OH<sup>-</sup>, H<sub>2</sub>O, N<sub>3</sub>, OCOC<sub>n</sub>H<sub>2n+1</sub>, etc; a for apical.), has become attractive due to the  
51 delocalization of the valence electrons on the metal centers for producing interesting  
52 photochemical and redox properties [6-7]. These metal atom clusters (MCs) exhibit  
53 luminescence properties combined with high-quantum yields, a large Stoke shift for  
54 preventing absorption loss, strong absorption in the ultraviolet (UV)-Vis domain,  
55 photostability at room temperature, and facile processing. These advanced properties  
56 have been utilized in the design of optical-related devices, phosphorescent nanocluster

57 emitters, saving-energy devices, photodetectors, photoelectrodes for DSSC, and  
58 photocatalytic electrodes for water splitting [8-14]. In addition, the tunable photo-induced  
59 electronic property of the MC with functional semiconductors has been recently  
60 investigated which will be a fascinating property for optoelectronic devices [15-17].  
61 Renaud et al. explored the potential of Mo<sub>6</sub> clusters as new nontoxic and stable inorganic  
62 sensitizers with amphoteric properties for light-emitting photoelectrodes that were  
63 achieved and integrated into solar cell devices [13]. The influence of light on the electrical  
64 properties of ionic conductors, the so-called opto-ionic property, around room  
65 temperature has become a hot topic, especially ionic conduction, which is crucial and  
66 very promising. A UV-Vis photodetector based on Mo<sub>6</sub> clusters embedded in a protonic  
67 conducting 2D material was demonstrated by Nguyen et al. It revealed that the  
68 reproducibility and stabilization of the ionic photocurrent response were verified upon  
69 light excitation at 540 nm which linearly depends on the relative humidity and  
70 temperature [12]. However, potential applications based on the cluster face many  
71 challenges due to the difficult control of a mono-dispersed cluster distribution, thermal  
72 and chemical stability, and production on a large scale. The combination of the nano-  
73 sized atom cluster with functional supporting materials; i.e., semiconductor, polymer, or  
74 hybrid, becomes an interesting solution in order to enhance the atom cluster's weakness.  
75 However, the charge transport between the cluster and the semiconductor is an important  
76 point to develop tunable photo-induced conducting properties.

77 Recently, the enhancement of the efficient photoconductivity response has been studied  
78 for visible light-harvesting materials, such as cadmium zinc telluride (CZT), cobalt-doped  
79 zinc ferrite oxide, or the use of specialized techniques, such as scalable photonic platforms  
80 based on silicon, and the band engineering of the TiO<sub>2</sub>/Si heterojunction [18-21]. As is  
81 known, artificial photonic crystal inverse opal (IO) structures can propagate the angle-  
82 dependent refractive light by using the periodic variation in the dielectric contrast or  
83 reflective index contrast within a crystal [22-23]. Light scattered or/and diffracted from  
84 the different surfaces will produce a full or partial photonic bandgap (PBG). This PBG  
85 and its manipulation ability could be deeply understood in researching different  
86 infiltration material precursors, various synthesis routes, and structural depending  
87 applications. The interesting advantages of this structure are subsequent inhibition of the

88 spontaneous emission, and the possibility to localize and enhance the emission or  
89 reflection of light. Moreover, in the 3D inverse opal photonic crystal, slow photon-  
90 induced light absorption is considered more than the photonic bandgap-induced light  
91 reflection for enhancing the generation of an electron-hole pair upon illumination [24].  
92 The 3D-ordered porous structure has been potentially developed for photodetectors,  
93 photoelectrodes for water splittings, photocatalysts, oxygen or hydrogen evolution  
94 reactions, and light-trapping parts for dye-sensitive solar cells [25-31]. In addition, the  
95 ordered porous inverse opal supplies a large area for the active site, a promising loading  
96 possibility of the active materials, necessary transmittance for the transparent conducting  
97 substrate, controllable photon absorption, etc. [29, 30]. The first goal of this study is to  
98 use the inverse opal photonic crystal to enhance the visible light absorption of the Mo<sub>6</sub>  
99 cluster.

100 The metal atom cluster exhibits an excellent photoactive property upon UV-Vis light  
101 illumination to generate electron-hole pairs, however, the excited electron will  
102 immediately recombine with the hole without transporting in the network. The second  
103 goal of this study is to select metal oxide semiconductors exhibiting high electron and  
104 ionic conductivities as a carrier for producing a high photoconductivity response. As is  
105 known, proton metallic phosphate conductors (MP<sub>2</sub>O<sub>7</sub>; M = Sn, Al, Mg, In, etc.) are  
106 potential candidates which have been studied in electrochemical device, such as  
107 intermediate-temperature proton conductors for fuel cells, batteries, gas sensors, NIR  
108 phosphor-converted light-emitting diode, etc. [32-38]. The protonic and electron-hole  
109 conductivity of SnP<sub>2</sub>O<sub>7</sub> essentially occurs in the bulk material rather than on the surface  
110 and is influenced by the structural characteristic, single cubic crystal or amorphous one  
111 [39, 40].

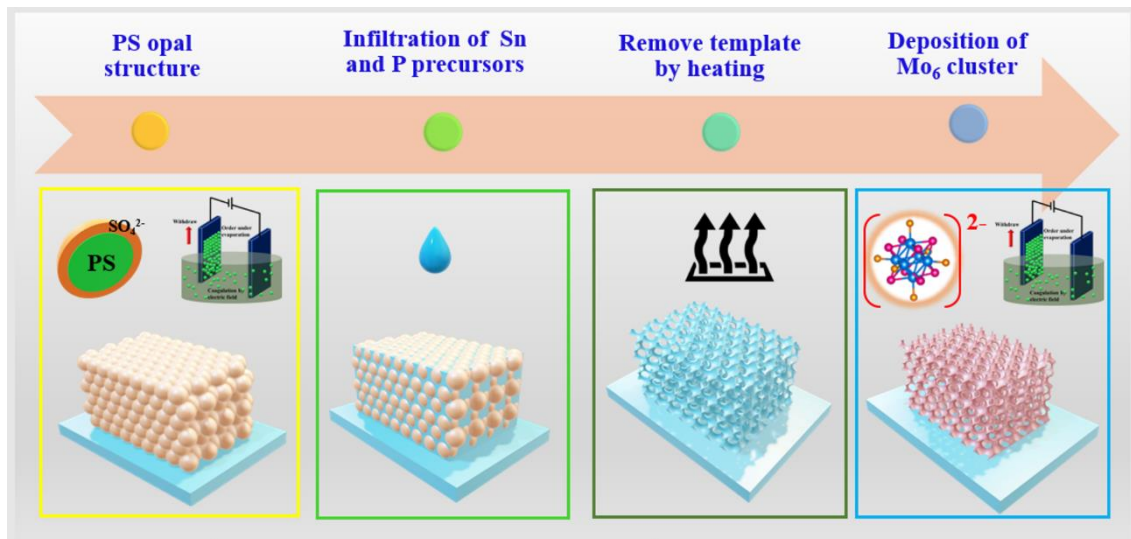
112 Until now, only one idea based on a silica opal photonic crystal and atom metal cluster  
113 has been reported with an increase in the emission intensity in the energy range of the  
114 passband [41]. For the first time, the SnP<sub>2</sub>O<sub>7</sub> proton conductor integrated with an inverse  
115 opal photonic crystal functionalized with the photoactive Mo<sub>6</sub> cluster iodide  
116 ( $\{[Mo_6I_8]I_4[H_2O]_2\}_y \cdot H_2O$ ) was successfully fabricated by using electrophoretic  
117 deposition (EPD), a short-time consuming and efficient technique. The Mo<sub>6</sub> iodide cluster

118 compound,  $\text{Cs}_2[\{\text{Mo}_6\text{I}_8\}\text{I}_6]$  (noted CMI), was selected as the cluster precursor due to its  
119 strong absorption in the visible light range and photostability under long irradiation [42].  
120 The hydrophilic surface modification of the  $\text{SnP}_2\text{O}_7$  inverse opal film by using citric acid  
121 also enhanced the loading concentration of the  $\text{Mo}_6$  cluster. The enhancement of the  
122 visible light absorption of the  $\text{Mo}_6$  cluster was obtained which is a result of the slow  
123 photon effect at the PBG edges due to the inverse opal structure. The optimizations of the  
124 pore size and ordered porous structure could control the PBG position in order to enhance  
125 the photonic energy absorption in the desired wavelength region. The photo-induced  
126 current phenomenon was investigated by the photoconductive response generated by AC  
127 and DC electric field generators upon light irradiation. The photoconductivity response  
128 upon the visible light irradiation from 400 to 580 nm is linearly dependent on temperature  
129 and humidity. This concept provided many interesting characteristics which are relevant  
130 for designing environmental sensors, a photodiode for a solar cell, or a photodetector.

## 131 **2. EXPERIMENTAL**

### 132 **2.1 Preparation of $\text{SnP}_2\text{O}_7$ IO films and citric acid-modified $\text{SnP}_2\text{O}_7$ IO films**

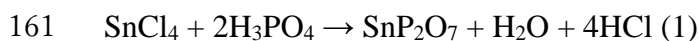
133 **Figure 1** shows a schematic diagram of the simple methods to prepare the  $\text{SnP}_2\text{O}_7$  IO  
134 films. Aqueous solutions containing 8 wt% of monodispersed polystyrene (PS) beads  
135 were prepared by the standard emulsion polymerization method [43]. The average sizes  
136 (240, 288, and 308 nm) of the PS beads were measured from a scanning electron  
137 microscope image. The anodic EPD was used to fabricate the PS-based photonic crystal  
138 film with the periodic arranged face-centered cubic lattice. The simple EPD system  
139 included two electrodes; i.e., indium tin oxide-coated glass (ITO) (Geomatec Co., Ltd.,  
140 Tokyo, Japan; 6.15-7.27 Ohm/sq) with a surface area of  $2 \times 3 \text{ cm}^2$  treated in ethanol and  
141 stainless steel with a surface area of  $2 \times 3 \text{ cm}^2$  treated in ethanol. The distance between the  
142 electrodes was fixed at 0.5 cm. The electrodes were connected to a Source Meter  
143 (Keithley Model 2400, Ohio, USA) as an electric field generator. The aqueous 8wt% PS  
144 solution was diluted by ethanol (99.5%, Nacalai Tesque Co., Ltd.) at the volume ratio of  
145 15/85 which is an optimized ratio to obtain a good periodic structure<sup>44</sup>. The EPD opal  
146 films were optimally prepared at 10 or 12 V for 1 minute.



147

148 Figure 1. Schematic diagram of the fabrication process of Mo<sub>6</sub> cluster-deposited SnP<sub>2</sub>O<sub>7</sub>  
 149 IO nanostructure using a PS-bead template and electrophoretic deposition (EPD).

150 The precursor solutions for the infiltration process were prepared by dissolving tin  
 151 tetrachloride (SnCl<sub>4</sub>·5H<sub>2</sub>O, 98%, Nacalai Tesque Co., Ltd.) into ethanol: H<sub>2</sub>O (volume  
 152 ratio of 10:1) at the concentration of 10%. The molar ratio between P (0.5 ml) from  
 153 phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%, Nacalai Tesque Co., Ltd.) and Sn precursors (1 g) was 2.6.  
 154 The mixture was stirred for 3h under ambient conditions. Five drops of the solution  
 155 mixture were then infiltrated into the PS-based photonic crystal film with an area of 5  
 156 cm<sup>2</sup>, then slowly dried for 24 h. The SnP<sub>2</sub>O<sub>7</sub> IO film was then fabricated by a thermal  
 157 treatment program including 2 steps; i.e., fast heating to temperature T1 (500, 550, or  
 158 600°C) and slow heating from temperature T1 to temperature T2 (550, 600, or 650°C) for  
 159 reducing cracking because of complete decomposition of the PS. The performance of  
 160 SnP<sub>2</sub>O<sub>7</sub> is illustrated following reaction (1) at high temperatures.



162 The porous SnP<sub>2</sub>O<sub>7</sub> IO film was then immersed in citric acid (98%, FUJIFILM Wako  
 163 Pure Chemical Corporation) with a concentration of 52 mM for 10 minutes at 90°C, then  
 164 heated at 100°C for 24 h in air. The acid-modified SnP<sub>2</sub>O<sub>7</sub> IO film was stored at 50°C in  
 165 air for the next fabrication process.

166 **2.2 Preparation of the Mo<sub>6</sub> cluster-deposited SnP<sub>2</sub>O<sub>7</sub> IO films**

167 The hexamolybdenum cluster compound  $Cs_2[\{Mo_6I_8\}I_6]$  was synthesized by the  
168 reaction of CsI (Alfa Aesar 99.9 %) and  $MoI_2$  at a high temperature ( $700^\circ C$ ) following  
169 the procedure reported in a previous study [6]. The CMI powder was dissolved in acetone  
170 at the concentration of 1g/L by ultrasonication for 1h, then magnetic stirring for 72 h. The  
171 use of EPD to deposit the  $Mo_6$  cluster in the porous  $SnP_2O_7$  IO films was optimally  
172 studied at a voltage of 15 V and a deposition time of 2 minutes with a deposition area of  
173  $5\text{ cm}^2$ . The obtained films were dried at  $100^\circ C$  for 24 h to eliminate the residual solvent  
174 before the characterization and photocurrent response measurements. An abbreviated  
175 representation of the sample is SnPO IO<sub>x</sub>ca-MI, where ‘SnPO’ is  $SnP_2O_7$ , ‘x’ is the PS  
176 bead size (240, 288, 308 nm), ‘ca’ is citric acid, and the ‘MI’ is the hexamolybdenum  
177 iodine cluster.

### 178 **2.3 Measurement of photocurrent response**

179 A cell containing ITO glass coated by SnPO-IO<sub>x</sub>, SnPO-IO<sub>x</sub>ca, SnPO-IO<sub>x</sub>ca-MI films (x  
180 = 240, 288, and 308 nm, the average size of PS bead) and a blank ITO glass with a  
181 measured area of  $1.2 \times 2\text{ cm}^2$  connected to a micrometer. The film thickness was measured  
182 by a scanning electron microscope. The different UV-Vis light illuminations were  
183 generated by a 300 W compact Xenon light source (MAX-303, Asahi Spectra Co., Ltd.).  
184 A monochromator combined with an optical filter (transmittance ~ 80 %) was used to  
185 generate monochromatic light with a bandwidth of 10 nm, centered respectively on 350,  
186 370, 410, 440, 540, and 580 nm. The real intensity of the photon energy arriving at the  
187 surface of the material film corresponded to almost 80% in the UV-Vis light range (350  
188 nm – 600 nm) as revealed by the manufacturer. A source meter (VSP300, Potentiostat,  
189 BioLogic) was used to measure the DC photocurrent response of the films at a bias of 0.5  
190 V with active area of  $2.4\text{ cm}^2$ . The AC conductivity of the films was measured by a 1260A  
191 impedance analyzer (Solartron analytical, AMETEK Scientific Instruments) at a bias of  
192 500 mV in the frequency range between  $10^1\text{ Hz}$  and  $10^7\text{ Hz}$ . All measurements were  
193 performed under controlled environmental conditions. The electrical conductivity was  
194 expressed by the following **Eq. 1**:

$$195 \quad \sigma = I / (R.A) \quad (1)$$



196 where  $\sigma$  is the electrical conductivity,  $l$  is the thickness of the film,  $A$  is the area of the  
197 sample ( $1 \times 1 \text{ cm}^2$ ), and  $R$  is the total resistance measured by Electrochemical Impedance  
198 Spectroscopy (EIS).

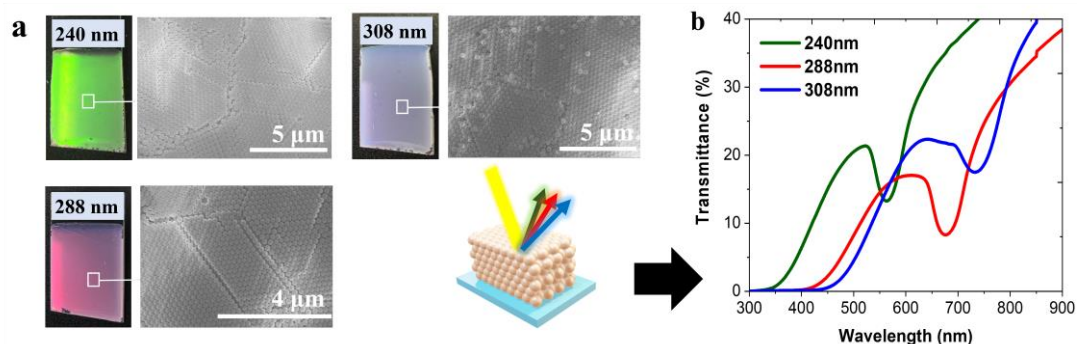
## 199 **2.4 Characterization**

200 The morphology characteristics were analyzed by field emission scanning electron  
201 microscopy (FE-SEM, SU8000, Hitachi High-Technologies Corp.) at 10 kV coupled with  
202 an energy-dispersive X-ray (EDX) analysis device. High-resolution (HR) observations of  
203 the powder were performed by an HR-transmission electron microscope (HR-TEM)  
204 (JEOL JEM 2100F) equipped with an EDX analysis device. The X-ray powder diffraction  
205 (XRD) patterns were recorded at room temperature at the 2-theta angle in the range of  
206  $10^\circ$  and  $60^\circ$  using a SmartLab diffractometer (RIGAKU, 40 kV and 30 mA) with Cu  $K\alpha$   
207 radiation ( $\lambda = 1.54 \text{ \AA}$ ), a step size of  $0.02^\circ$  and a scan speed of  $1^\circ/\text{min}$ . Le Bail fittings  
208 were performed using the FullProf program included in the WinPLOTR software [44,  
209 45]. The zero-point shift, asymmetry parameters, lattice parameters, and  $\beta$  angle were  
210 systematically refined, and the background contribution was manually estimated (**Tab.**  
211 **SI1**). The typical chemical vibration of the powder was recorded by Fourier transform  
212 infrared spectroscopy (FTIR) (Thermo Scientific Nicolet 4700) in the wavenumber range  
213 from  $4000$  to  $400 \text{ cm}^{-1}$  using a KBr pellet. The transmittance spectra of the IO films were  
214 measured by UV-Vis-NIR spectroscopy (V570, Jasco Corp.) in the wavelength range of  
215  $200$  to  $2000 \text{ nm}$  at the scan rate of  $400 \text{ nm}/\text{min}$ . The specular reflectance spectra of the  
216 films were measured at the incidence angle of  $5$  degrees in the wavelength range of  $200$   
217 to  $2000 \text{ nm}$  by using a UV-Vis-NIR spectrophotometer (Solidspec-3700, Shimadzu  
218 Corp.). The luminescent emitting spectra of the films were measured by high-  
219 performance fluorescence spectroscopy (JASCO FP8500) connected to a Xenon lamp at  
220 the scan rate of  $500 \text{ nm}/\text{min}$ . The electron binding energy spectra were measured by X-  
221 ray photoelectron spectroscopy (XPS) (PHI Quantera SXM (ULVAC-PHI)) using Al  $K\alpha$   
222 radiation at  $20 \text{ kV}$  and  $5 \text{ mA}$  and taken-off angle of  $45^\circ$ . All the binding energies were  
223 calibrated concerning the C 1s peak of the adventitious carbon at  $285 \text{ eV}$ .

## 224 **3. RESULTS AND DISCUSSION**

### 225 3.1 Characterization of SnP<sub>2</sub>O<sub>7</sub> IO film

226 Recently, the growth of photonic crystals by colloidal assembly routes has been  
227 particularly done but their potential in real-world applications still faces many challenges.  
228 The difficulties in controlling the external forces of suspension, solvent evaporation rate,  
229 withdrawal rate, and template concentration inhibited obtaining the chemical and thermal  
230 stability and well-ordered 3D porous structure [22]. EPD is a good technique that shows  
231 the flexibility of the substrate sizes and templates, short-time consumption, and uniform  
232 structure in comparison to the conventional methods [46]. FE-SEM images from **Fig. 2a**  
233 show the surface characteristic of the crystal opal films that were successfully fabricated  
234 using the anodic EPD at 10 V for 1 minute. The PS beads with the average sizes of 240  
235 nm, 288 nm, and 308 nm were arranged to form well-ordered hexagonally packed  
236 photonic crystals that result in reflectance of green, red, and slight red colors as seen in  
237 the next photographs. The cross-section images of the films also showed good  
238 organization in a face-centered cubic (fcc) structure. The thickness of the different-sized  
239 opal films was recorded in the range of 5 to 10  $\mu\text{m}$  (**Fig. S11**) depending on the PS bead  
240 size with similar EPD parameters. The optical and photonic bandgaps were based on the  
241 UV-Vis transmittance spectra. The transmittance spectra from **Fig. 2b** show specific  
242 peaks centered at wavelengths of 563, 677, and 732 nm which indicated the partial  
243 photonic band gaps (PBGs) of the opal films corresponding to the 240, 288, and 308 nm-  
244 sized PS-bead templates, respectively. The PS spheres are well known without absorption  
245 in the blue/violet range. It means that the transmittance at 0 in this range comes from the  
246 scattering by the polystyrene spheres. For a larger PS bead size, the scattering appears  
247 stronger.  
248



249  
 250 Figure 2. (a) Photographs of observed color and FE-SEM images of the opal films  
 251 prepared by EPD (10 V, 1 minute) using different PS-bead sizes. (b) UV-Vis  
 252 transmittance spectra and schematic image of the opal films.

253 For the first time, the  $\text{SnP}_2\text{O}_7$  inverse opal structure was directly prepared by using the tin  
 254 chloride precursor and phosphoric acid with the initial P: Sn molar ratio of 2.6. In this  
 255 study, an annealing critical temperature of  $600^\circ\text{C}$  was effective to produce the cubic  
 256  $\text{SnP}_2\text{O}_7$  structure and ordered porous inverse opal structure for the PBGs. The major  
 257 reflections in the XRD pattern of the referenced  $\text{SnP}_2\text{O}_7$  powder synthesized under the  
 258 same conditions can be observed at specific 2-theta angles centered at  $19.4^\circ$  (111),  $22.4^\circ$   
 259 (200),  $31.8^\circ$  (200),  $37.6^\circ$  (311),  $50.1^\circ$  (331),  $51.5^\circ$  (420), and  $56.8^\circ$  (422) (**Fig. SI2**). A Le  
 260 Bail refinement of the whole samples has been performed and reasonably reliable factors  
 261 have been obtained to confirm a space group of cubic  $P a-3$  ( $a = b = c$ ,  $\beta \approx 90^\circ$ ) (**Tab.**  
 262 **SI1**). A similar pattern was verified for the  $\text{SnP}_2\text{O}_7$  inverse opal film ( $\text{SnPO-IO}_{288}$ ) with a  
 263 weak intensity of crystallinity because of the porous structure (**Fig. 3a**).  $\text{SnP}_2\text{O}_7$  has a  
 264 cubic structure that shows corner-sharing  $\text{SnO}_6$  octahedra and  $\text{PO}_4$  tetrahedra containing  
 265 the oxygen lattice ion on the surface as seen in **Fig. 3b** [47]. The FT-IR spectrum provides  
 266 evidence for the symmetric and asymmetric stretching vibrations of the P-O bonds of the  
 267  $\text{PO}_4$  groups at the wavenumbers of  $1120\text{ cm}^{-1}$  and  $960\text{ cm}^{-1}$  (**Fig. 3b**). The vibration band  
 268 assigned to the Sn-O bonds was recorded at  $498\text{ cm}^{-1}$ . This characteristic peak is in  
 269 agreement with previous reports [48].

270 The UV-Vis transmittance spectra from **Fig. 3c** and **Fig. SI3** show the optical and PBGs  
 271 of the  $\text{SnPO-IO}_x$  ( $x = 240, 288, 308$ ) films annealed at different temperatures and  
 272 ethanol/ $\text{H}_2\text{O}$  volume ratios fixed at 10/1. The  $\text{SnP}_2\text{O}_7$  powder almost shows a low

273 transmittance under 300 nm due to its absorbance in this range. The initial molar ratio of  
274 P: Sn is more than 2 and the heat-treating temperature is higher than 500°C which should  
275 be applied to definitely obtain the single cubic phase structure of SnP<sub>2</sub>O<sub>7</sub> [49]. By the  
276 thermal treatment up to 550°C, the SnP<sub>2</sub>O<sub>7</sub> phase is performed and the IO film starts to  
277 form PBGs but their width is broad and asymmetric (**Fig. S13**). This can be a reason for  
278 the impurity of the SnO<sub>2</sub> phase which is not completely transferred to SnP<sub>2</sub>O<sub>7</sub> [49]. As is  
279 known, the existence of the SnO<sub>2</sub> impurity with a high refractive index can expand the  
280 width of the stopband peak. However, at treatment temperatures up to 600°C, the SnP<sub>2</sub>O<sub>7</sub>  
281 IO films definitely show symmetrical PBGs at the wavelengths of 379, 457, and 502 nm,  
282 respectively, originating from the 240, 288, and 308 nm-sized PS beads (**Fig. 3c**).  
283 Although the single cubic phase structure of SnP<sub>2</sub>O<sub>7</sub> was definitely created at 650°C, the  
284 high-heating temperature can create much cracking and then destroy the ordered  
285 macropore structure. The low transmittance around the stopband positions in **Fig. 3c**  
286 (upper) possibly comes from the reflection, scattering, and refraction of the light caused  
287 by the inverse opal film. In order to clearly identify these inverse opal PBGs originating  
288 from the contribution of reflective light, the spectacular reflectance spectra were obtained  
289 at an incident angle of 5 degrees that show similar stopband peaks with a reflective light  
290 percentage lower than 15% (**Fig. 3c** under).

291 From **Fig. 3d**, these photographs of the SnPO-IO<sub>x</sub> (x= 240, 288, 308) films having pore  
292 sizes of about 223, 267, and 294 nm, respectively, are in agreement with the reflectance  
293 of the visual violet (379 nm), blue (457 nm), and cyan (502 nm) color (**Fig. 3c** under).  
294 The obtained pore size was reduced from 5 to 7 % compared to the initial size of the PS  
295 bead as seen in the FE-SEM image. It can be influenced by the shrinkage of PS during  
296 the thermal treatment before the SnP<sub>2</sub>O<sub>7</sub> crystal was formed. In addition, the low  
297 shrinkage also indicated a high SnP<sub>2</sub>O<sub>7</sub> condensate. On the other hand, the thickness of  
298 the IO film was reduced by less than 10% from 5 to 10 μm while retaining the periodic  
299 structure (**Fig. 3d**). The role of water in this step contributes to the association of the Sn  
300 precursor that supports their transport in the voids between the PS beads. The pore size  
301 and inverse opal structure were confirmed in the STEM images (**Figs. 3e**). The elemental  
302 composition of tin pyrophosphate was confirmed to contain O, Sn, and P from the STEM-  
303 EDX mapping (**Fig. 3f**). By using the EPD technique, a SnP<sub>2</sub>O<sub>7</sub> inverse opal photonic

304 crystal film showing the typical PBG was efficiently prepared in a short time, with a  
305 flexible thickness and active area on the TCO substrate. The thermal treatments at  
306 temperature T1 of 550°C and temperature T2 of 600°C with different heating rates were  
307 fixed to efficiently fabricate the SnPO-IO<sub>x</sub> (x = 240, 288, 308) films for the next steps.

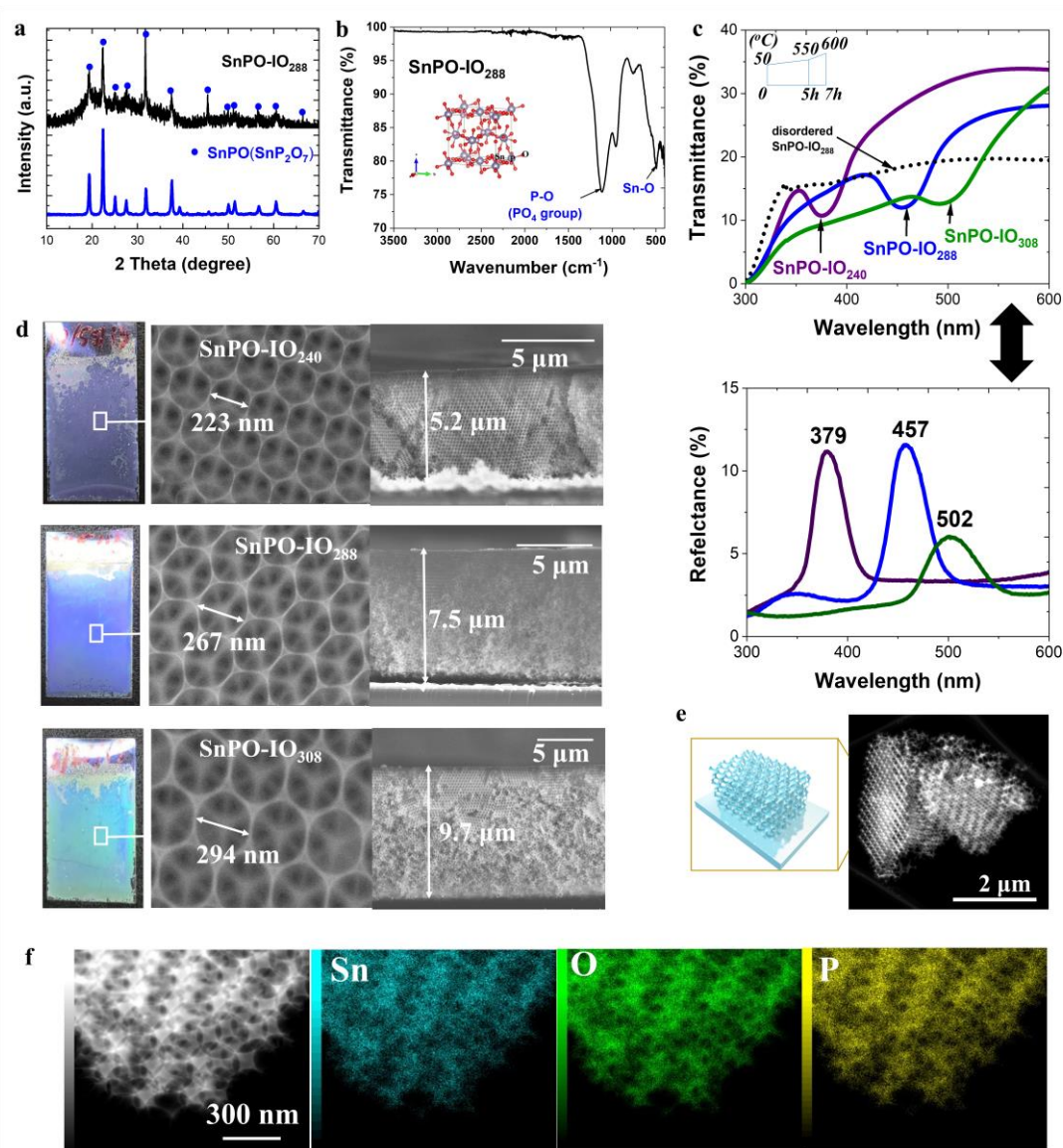
308

309 The approximate stopband position of the inverse opal can be calculated by a modification  
310 of Bragg's law taking into account Snell's law of refraction that is expressed in **Eq. 2**  
311 [50]:

$$312 \quad \lambda_{\max} = 2D \sqrt{\frac{2}{3} \sqrt{fn_1^2 + (1-f)n_2^2} - \sin^2\theta} \quad (2)$$

313 Where,  $\lambda$  is the stopband position for the first-order Bragg diffraction, D is the PS bead  
314 size of the PhCs or pore size of IO,  $n_1 = 1$  for air and  $n_2 = 1.59$  for PS or  $n_1 = 1$  for air and  
315  $n_2 \sim 1.65$  for SnP<sub>2</sub>O<sub>7</sub> are the refractive indices, and  $\theta$  is the incidence angle of the light  
316 which is 5° in this measurement. Depending on the face-centered cubic (fcc) structure of  
317 the photonic crystals, the volume percentage (f) of the air and PS is 0.26 and 0.76,  
318 respectively. Based on **Eq.2**, the PS bead sizes of 240, 288, and 308 nm sizes confirmed  
319 by the FE-SEM images were used to calculate the PBGs which result in the wavelengths  
320 of 571, 685, and 732 nm, respectively. However, the experimental PBGs resulted in a  
321 small difference which was taken at 563, 677, and 732 nm as seen in **Table SI2**. The  
322 volume fraction of air was calculated from the measured data as more than 0.26 which is  
323 taken at the average fraction of  $0.36 \pm 0.02$ . The performance of the well-organized face-  
324 centered cubic structure is not completely preferred for a small PS bead size. In the case  
325 of the inverse opal structure, refractive indices of 1.65 for SnP<sub>2</sub>O<sub>7</sub>, the measured pore  
326 diameters (223, 267, and 294 nm), and stopband positions (379, 457 and 502 nm) were  
327 used to calculate the volume fraction of SnP<sub>2</sub>O<sub>7</sub> based on **Eq. 2 (Table SI2)**. It can be  
328 seen that the filling factors (f) of air in the SnP<sub>2</sub>O<sub>7</sub> inverse opals almost reached more than  
329 94%. As the result, the solid filling fractions of the inverse opal skeleton are 5, 6, and 6  
330 % for the SnPO-IO<sub>x</sub> (x= 240, 288, 308) films, respectively. In order to achieve a perfect  
331 inverse opal structure with a filling fraction close to 26% corresponding to a perfect fcc

332 structure, the filling quantity of the precursor solution, infiltration operation, and heating  
 333 rate of the annealing should be appropriate.



334

335 Figure 3. (a) X-ray diffraction diagrams of synthesized SnP<sub>2</sub>O<sub>7</sub> powder and SnPO IO<sub>288</sub>  
 336 film, (b) Schematic illustration of the cubic SnP<sub>2</sub>O<sub>7</sub> unit, and the FT-IR spectrum of  
 337 SnPO-IO<sub>288</sub>. (c) UV-Vis transmittance spectra and the specular reflectance spectra at the  
 338 5 degree incident angle of the SnPO-IO<sub>x</sub> films (x= 240, 288, 308) with thermal treatment  
 339 at T1 = 550°C and T2 =600°C. (d) Visual photographs and FE-SEM images (left) and  
 340 cross-section SEM images of the SnPO-IO<sub>x</sub> (x= 240, 288, 308) films. (e) HR-

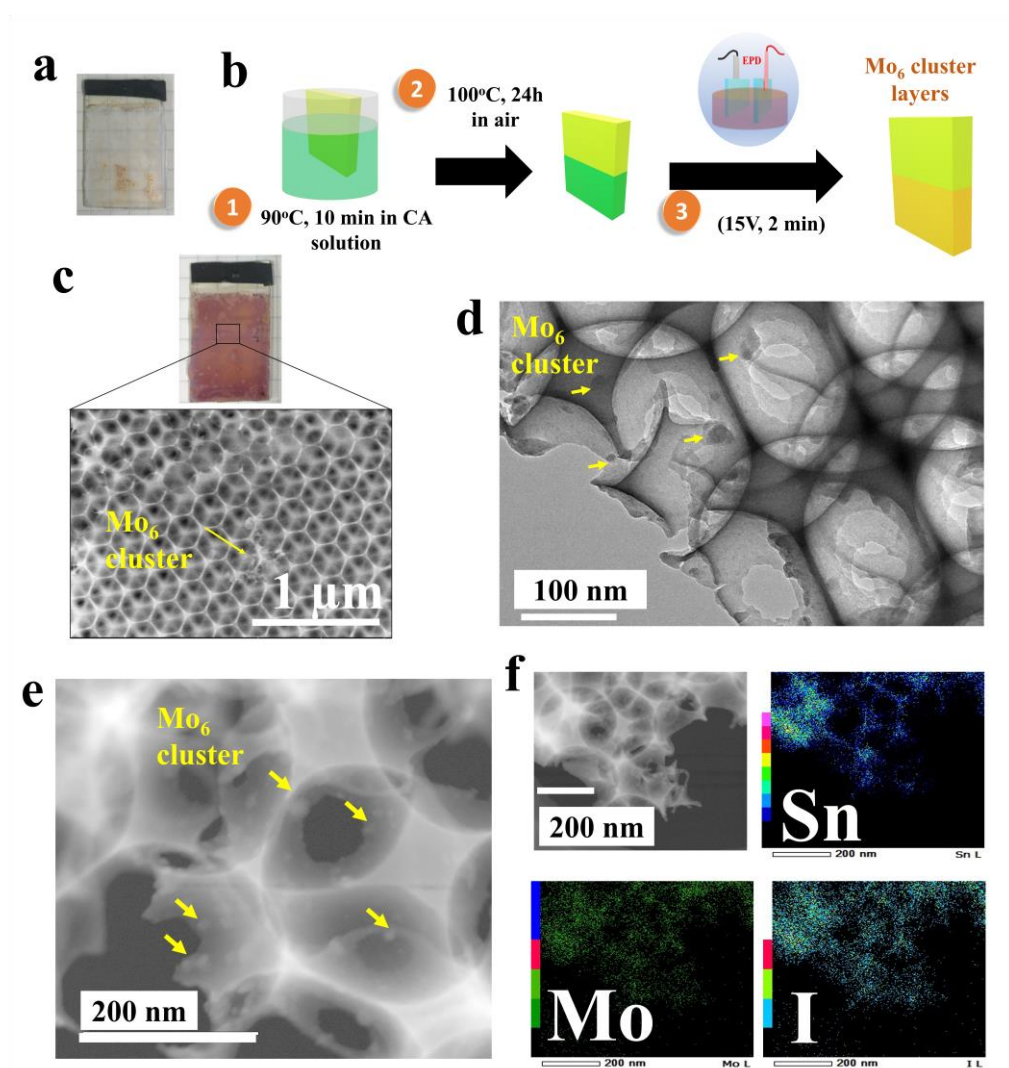
341 TEM, (h) STEM and schematic image, and (f) STEM-EDX mapping of the SnPO-IO<sub>288</sub>  
342 films.

### 343 **3.2 Characteristics and optical properties of Mo<sub>6</sub> cluster-deposited SnP<sub>2</sub>O<sub>7</sub> IO films**

344 The CMI presents the efficiency of the visible light absorbing characteristics, which could  
345 be functionalized with an ionic conducting layer of a double hydroxide for tuning the  
346 photoconductivity response [12]. The obtained result showed a good photoconductivity  
347 response; however, the photosensitivity and photostability needed to be improved. The  
348 elimination of the apical iodide ligands of the Mo<sub>6</sub> cluster during the fabrication was also  
349 a reason for a reduction of the visible light absorption efficiency. In this study, the  
350 anhydrous proton conductor of tin pyrophosphate (SnP<sub>2</sub>O<sub>7</sub>) was chosen to be combined  
351 with the [Mo<sub>6</sub>I<sub>14</sub>]<sup>2-</sup> cluster unit precursor. As is known, the Cs<sub>2</sub>[{Mo<sub>6</sub>I<sub>8</sub>}I<sub>6</sub><sup>a</sup>] solid-state  
352 compound is fully dissociated to form the Cs<sup>2+</sup> cation and [{Mo<sub>6</sub>I<sub>8</sub>}I<sub>6</sub><sup>a</sup>]<sup>2-</sup> cluster anion in  
353 solution. During EPD, hydronium and hydroxide ions, which were generated by the  
354 hydrolysis reaction of water in the dispersing medium, will replace some apical ligands  
355 to form the [{Mo<sub>6</sub>I<sub>8</sub>}I<sub>6-x</sub><sup>a</sup> [OH]<sub>x</sub><sup>a</sup>]<sup>2-</sup> (0 ≤ x ≤ 6) cluster anion in solution which possibly  
356 works in the EPD. However, **Fig. 4a** shows a photograph of the SnPO-IO<sub>288</sub> deposited  
357 MI without modification by citric acid with the poor deposition of MI by using the EPD  
358 at 15 V for 2 minutes. Surface functionalization of the SnPO-IO<sub>x</sub> (x = 240, 288, 308)  
359 films was then performed with two treatment steps in a citric acid solution at 90°C for 10  
360 minutes and in air at 100°C for 24 hours (**Fig. 4b**). The dried SnP<sub>2</sub>O<sub>7</sub> containing  
361 negatively-charged oxygen lattice ions can cause an opposite electrostatic interaction with  
362 the [{Mo<sub>6</sub>I<sub>8</sub>}I<sub>6-x</sub><sup>a</sup> [OH]<sub>x</sub><sup>a</sup>]<sup>2-</sup> (0 ≤ x ≤ 6) cluster anion. For this reason, the citric acid  
363 involving three carboxylic acid groups will generate the acidic surface and then becomes  
364 a bridge in order to make a second electrostatic interaction with the [{Mo<sub>6</sub>I<sub>8</sub>}I<sub>6-x</sub><sup>a</sup>  
365 [OH]<sub>x</sub><sup>a</sup>]<sup>2-</sup> (0 ≤ x ≤ 6) cluster anion. These bridges will create hydrogen bonds that are  
366 efficient to immobile MI on SnP<sub>2</sub>O<sub>7</sub>. Moreover, the functionalization by acid groups can  
367 improve the interface charge collection efficiency, which is important to carry the electron  
368 or ion transport in optoelectronic devices [51]. The deposition of MI on the SnPO-IO<sub>288</sub>  
369 film was significantly improved as seen in the photograph with a homogeneous red color  
370 which was assigned to the MI nanocluster (**Fig. 4c**). Small cluster aggregates were also

371 observed on the surface of the SnPO-IO<sub>288ca</sub> film. TEM and STEM were then used to  
372 confirm the distribution of MI that exists inside the pores of SnPO-IO<sub>288ca</sub>-MI (**Fig. 4d**,  
373 **e**). STEM-EDX mapping indicated the composition elements of Sn, Mo, and I that  
374 confirmed MI nanoparticles with sizes less than 30 nm existing inside the pores (**Fig. 4f**).  
375 **Fig. S14** presents the element composition spectrum of Sn, I, and Mo with a poor  
376 observation of Cs. As is known, MI is synthesized at high temperatures with a crystal  
377 shape. The size of the aggregates of MI was confirmed in the range between 15 and 30  
378 nm by the SEM image (**Fig. S15**) which can deposit in the pore size of 267 nm from the  
379 SnPO-IO<sub>288ca</sub>. The concentration and incomplete dissolution of MI in a solvent medium  
380 can create small nanoparticles composed of many 2 nm-sized MI clusters with the charge  
381 on the surface coming from the MI cluster unit. Only EPD can deposit the  $[\text{OH}]^a_x]^{2-}$  ( $0 \leq$   
382  $x \leq 6$ ) cluster anion without a counter cation which is an essential part of light harvesting.





383

384 Figure 4. a) Photograph image of SnPO-IO<sub>288</sub>-MI without citric acid modification. b)  
 385 Schematic diagram of the fabrication process photos of SnPO-IO<sub>x</sub>ca and SnPO-IO<sub>x</sub>ca-MI  
 386 films (x = 240, 288, 308). c) Photograph images and FE-SEM images of SnPO-IO<sub>288</sub>ca-  
 387 MI with citric acid modification. (d) TEM, (e) STEM, and (f) STEM-EDX mapping  
 388 images of SnPO-IO<sub>288</sub>ca-MI.

389

390 **Fig. SI6** summarizes the XPS spectra of SnPO-IO<sub>288</sub> and SnPO-IO<sub>288</sub>ca-MI. The binding  
 391 energy spectra of the Sn3d, P2p, C1s, O1s, Mo 3d, and I 3d regions were measured as  
 392 seen in **Table. SI3**. All binding energies were calibrated concerning the C1s peak of the  
 393 adventitious carbon at 285 eV. **Table 1** shows the atomic percentages of the elements of

394 SnPO-IO<sub>288</sub> and SnPO-IO<sub>288ca</sub>-MI. The atomic ratio of P and Sn is about 1.77. This ratio  
 395 is almost unchanged after the EPD (~ 1.73) which indicates the chemical stability of the  
 396 SnP<sub>2</sub>O<sub>7</sub> inorganic IO film during the hydrolysis reaction. In the SnPO-IO<sub>288ca</sub>-MI film,  
 397 the concentration of carbon atoms increased 2.5 times due to the introduction of citric  
 398 acid in comparison to SnPO-IO<sub>288</sub> without acid treatment. The binding energies assigned  
 399 to Sn 3d<sup>5/2</sup> and Sn 3d<sup>3/2</sup> of SnPO-IO<sub>288</sub> were recognized at 487 eV and 495.5 eV,  
 400 respectively, with the spin-orbit splitting of the doublet peaks of 8.5±0.1 eV (**Fig. 5a**).  
 401 This binding energy confirms the existence of the Sn<sup>4+</sup> cation in SnP<sub>2</sub>O<sub>7</sub>[34]. The binding  
 402 energies assigned to the Sn 3d<sup>5/2</sup> and Sn 3d<sup>3/2</sup> regions show a slight change at 486.7 eV  
 403 and 495.1 eV for SnPO-IO<sub>288ca</sub>-MI. The binding energy spectrum of the P 2p region  
 404 assigned for P from the PO<sub>4</sub> tetrahedra shows a similar slight shift of the peak from 133.5  
 405 eV for SnPO-IO<sub>288</sub> to 133.3 eV for SnPO-IO<sub>288ca</sub>-MI (**Fig. 5b**). It can be predicted that  
 406 the citric acid can protonate the surface via oxygen in the SnP<sub>2</sub>O<sub>7</sub> lattice, as discussed in  
 407 detail in the next part. The spectrum of the C1s region shows a strong peak at 284 eV  
 408 assigned to the C=C bonding which comes from the decomposed products of polystyrene  
 409 existing in SnPO-IO<sub>288</sub> (**Fig. SI6**). The same result was analyzed for the binding energy  
 410 of the O 1s region with a peak at 531 eV from the O-P bonding in both films, and extra  
 411 peaks at 533 eV assigned to the O-C and O-H bonds for SnPO-IO<sub>288ca</sub>-MI in the  
 412 convolution spectrum (**Fig. SI6 and Tab. SI5**). The Cs<sup>+</sup> cation was almost not observed  
 413 in the XPS spectrum of SnPO-IO<sub>288ca</sub>-MI which confirmed the separation of the counter-  
 414 cation from the cluster by using EPD. The binding energy spectrum of Mo 3d includes  
 415 two specific peaks at 228.7eV (3d<sup>5/2</sup>) and 231.8 eV (3d<sup>3/2</sup>) which are assigned to the Mo-  
 416 I bonding (**Fig. 5c**). The binding energy peak assigned to Mo-O (235.1) was not observed  
 417 which means that the Mo<sub>6</sub> cluster does not oxidize or no valence bonding occurs between  
 418 the cluster and other compositions [52]. The deconvolution spectra of I3d are presented  
 419 in **Fig. 5d** that shows the peaks assigned to the inner iodine (I<sup>i</sup>) at 620.1 eV (3d<sup>5/2</sup>) and  
 420 631.6 eV (3d<sup>3/2</sup>) and apical iodine (I<sup>a</sup>) at 618.4 eV (3d<sup>5/2</sup>) and 629.9 eV (3d<sup>3/2</sup>). The  
 421 average atomic ratio of I<sup>i</sup> and I<sup>a</sup> is 8 and 4 which was calculated from the deconvolution  
 422 spectra of I3d (**Tab. SI6**). Based on the XPS analysis, the [{Mo<sub>6</sub>I<sub>8</sub>}I<sup>a</sup><sub>4</sub>[OH]<sup>a</sup><sub>2</sub>]<sup>-2</sup> cluster  
 423 anions were suggested to move to the anode and be neutralized by the hydronium cation  
 424 to form [H<sub>3</sub>O<sup>+</sup>]<sub>2</sub>[{Mo<sub>6</sub>I<sub>8</sub>}I<sup>a</sup><sub>4</sub>[OH]<sup>a</sup><sub>2</sub>] or [{Mo<sub>6</sub>I<sub>8</sub>}I<sup>a</sup><sub>4</sub>[H<sub>2</sub>O]<sup>a</sup><sub>2</sub>].yH<sub>2</sub>O cluster compounds as

425 reported earlier [16]. Depending on the total Mo/I atomic ratio of 6/13.6 (theoretical index  
 426 is 6:14), the separated iodine anions from the initial cluster were also deposited on an  
 427 anode to form the iodide-enriched deposition. A similar conclusion has been revealed  
 428 regarding the exchange of two apical ligands and the performance of the  
 429  $[\{\text{Mo}_6\text{Br}^{\text{i}}_8\}\text{Br}^{\text{a}}_4[\text{H}_2\text{O}]^{\text{a}_2}]\cdot y\text{H}_2\text{O}$  film enriched Br anion layers which were prepared by  
 430 EPD [53]. In summary, the acid modification successfully protonated the  $\text{SnP}_2\text{O}_7$  lattice  
 431 by hydrogen bonding that produced a slight shift in the binding energy of the Sn3d and  
 432 P2p regions to the lower range. In addition, the general formula of the cluster in the film  
 433 suggested being  $[\{\text{Mo}_6\text{I}^{\text{i}}_8\}\text{I}^{\text{a}}_4[\text{H}_2\text{O}]^{\text{a}_2}]\cdot y\text{H}_2\text{O}$ , possibly generating an interaction with the  
 434 citric acid or  $\text{SnP}_2\text{O}_7$  through the apical water ligands. This suggestion would support the  
 435 electronic conducting transport in the material.

436 Based on the FT-IR spectrum of citric acid (**curve 1**), the absorption peaks of the carbonyl  
 437 (C=O) stretching vibration centered at 1759 and 1695  $\text{cm}^{-1}$  shift to lower wavenumbers  
 438 when citric acid is grafted on the  $\text{SnP}_2\text{O}_7$  surface as shown in the spectrum of SnPO-  
 439  $\text{IO}_{288\text{ca}}$  (**curve 3**) (**Fig. 5e**). The covalent bond between a carboxylic group of the acid  
 440 and oxygen on the surface of the  $\text{SnP}_2\text{O}_7$  lattice can possibly be created by a thermal  
 441 treatment, resulting in a shift of the absorption band of the carbonyl (C=O) stretching  
 442 vibration. Besides, the wide absorption band in the 1700 and 1000  $\text{cm}^{-1}$  range assigned to  
 443 the O-H, C-O, C-OH, and C-C vibrations of the citric acid as well as the absorption  
 444 bands in the 1300 and 400  $\text{cm}^{-1}$  range assigned to the P-O and Sn-O vibration from the  
 445 phosphate group (**curve 2**) in SnPO- $\text{IO}_{288\text{ca}}$  were verified (**curve 3**). Once the MI is  
 446 immobilized on the IO film, the signal of C=O from the acid in SnPO- $\text{IO}_{288\text{ca}}$  has an  
 447 unchanged absorption band. It is suggested that the interaction that occurred between  
 448  $[\{\text{Mo}_6\text{I}^{\text{i}}_8\}\text{I}^{\text{a}}_4[\text{H}_2\text{O}]^{\text{a}_2}]$  clusters and citric acid is hydrogen bonds (H-O...H) without  
 449 covalent bonding. The chemical structure of MI has not changed after fabrication which  
 450 can assure the retainment of the optical absorption characteristic in the visible domain.

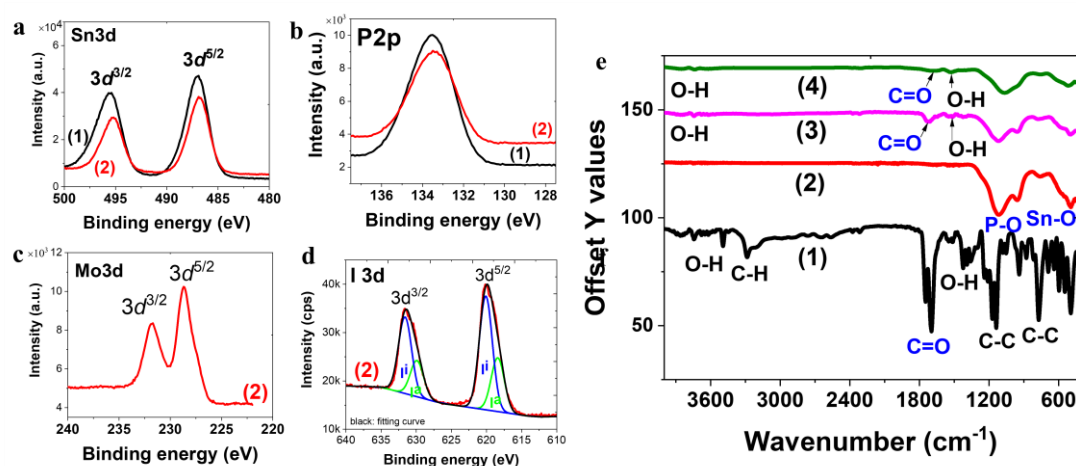
451 **Table 1.** The atomic concentration of the elements of SnPO- $\text{IO}_{288}$  and SnPO- $\text{IO}_{288\text{ca}}$ -MI  
 452 by the peak analysis of the XPS measurements.

Sn	O	C	P	Cs	Mo	I
----	---	---	---	----	----	---

	% at.							
<b>SnPO-IO<sub>288</sub></b>	8.32	66.79	4.62	14.75	-	-	-	454
<b>SnPO-IO<sub>288ca-MI</sub></b>	8.86	56.91	10.67	14.51	-	2.91	6.56	455
								456

457

458



459

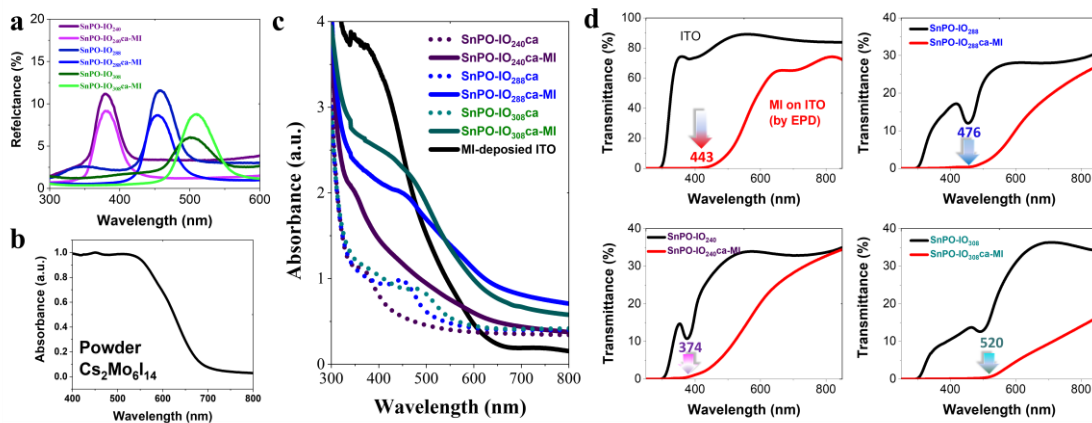
460 Figure 5. XPS binding energy (eV) spectra of SnPO-IO<sub>288</sub> (1) and SnPO-IO<sub>288ca-MI</sub> (2)  
 461 including (a) Sn3d region, (b) P2p region, (c) Mo3d region, and (d) I3d region. (e) FTIR  
 462 spectra of citric acid (1), SnPO-IO<sub>288</sub> (2), SnPO-IO<sub>288ca</sub> (3), and SnPO-IO<sub>288ca-MI</sub> (4).

463 The specular reflectance spectra at the 5-degree incident angle of the SnPO-IO<sub>x</sub>ca films  
 464 (x= 240, 288, 308 nm) from **Fig. SI7** confirm the stability of the ordered porous IO  
 465 structure after the citric acid treatment, showing relatively similar stopband peaks. In  
 466 order to confirm the different PBGs of the IO films before and after introducing the MI  
 467 cluster, the specular reflectance spectra of the IO films were performed (**Fig. 6a**). In **Figs.**  
 468 **4d and e**, the MI nanoparticles were anchored on the pore surface, and cluster  
 469 concentration was not enough to completely infiltrate the pores or make a thicker SnP<sub>2</sub>O<sub>7</sub>  
 470 wall. For this reason, the stop band peak for the SnPO-IO<sub>x</sub>ca (x = 240, 288, 308 nm) films  
 471 still remains at a similar position to the original band structure after depositing the Mo<sub>6</sub>  
 472 cluster. In general, the UV-Vis absorption spectrum of MI shows a strong UV-Vis light

473 absorption in the range between 300 and 550 nm and gradually reduces to 670 nm (**Fig.**  
474 **6b**). The efficiency of the optical absorption of MI significantly linearly reduces from 400  
475 and 600 nm after the MI deposited ITO substrate in comparison to the original powder  
476 (**Fig. 6c**). Besides the loss of Cs<sup>+</sup> cations, the exchange of iodine apical ligands during  
477 deposition from  $[\{\text{Mo}_6\text{I}_8\}\text{I}_6]^{2-}$  to  $[\{\text{Mo}_6\text{I}_8\}\text{I}_4[\text{H}_2\text{O}]_2]_y \cdot \text{H}_2\text{O}$  also caused the reduction  
478 of visible light absorption of the Mo<sub>6</sub> cluster. The weak photoluminescence measured for  
479 the nanocomposite film shows a difference in comparison to that of the CMI powder (**Fig.**  
480 **SI8**). MI appeared to undergo a strong photoluminescence with an emission peak at 700  
481 nm after creating a Mo-O covalent bonding with glycine and the layer double hydroxide  
482 as reported in a previous study [12]. In this study, the unchanged binding energy of Mo3d  
483 proves that the Mo atom of  $[\{\text{Mo}_6\text{I}_8\}\text{I}_4[\text{H}_2\text{O}]_2]_y \cdot \text{H}_2\text{O}$  does not create any covalent  
484 bonds with other compositions. However, it is well known that hydrolysis of the apical  
485 ligands of such a cluster complex leads to a small change in the luminescence spectra  
486 [54]. Although the composition modification occurred during fabrication, the CMI  
487 powder and MI-deposited ITO film still show the same optical absorption in the range  
488 from 400 to 600 nm with a different efficiency, resulting in a similar energy bandgap at  
489 1.9 eV which is in agreement with the previous study [16].

490 The absorbance contribution of SnP<sub>2</sub>O<sub>7</sub> in the visible light range is zero as seen in the  
491 disordered IO powder (dot line) from the transmittance spectrum of **Fig. 3c**. Therefore,  
492 the absorbance properties in the visible light of SnPO-IO<sub>x</sub>ca (x = 240, 288, 308) films  
493 will mainly assume the contributions of MI. (**Figs. 6c**). However, the cluster's visible light  
494 absorbing range of the Mo<sub>6</sub> cluster in the IO film is expanded to a higher wavelength than  
495 the MI-deposited ITO glass. The expansion wavelength range depends on the position of  
496 the stopband of the PBGs. The transmittance spectra also confirm the effect of the inverse  
497 opal which synergistically improves the light absorption around the original stopband  
498 (**Fig. 6d**). The SnPO-IO<sub>x</sub>ca-MI (x = 240, 288, 308) films show a transmittance of zero at  
499 various wavelengths which overlaps with the stop band from the IO structure of SnPO-  
500 IO<sub>x</sub> even though there is no difference in the EPD parameter, substrate, and MI solution.  
501 The size of the MI nanoparticle is an average of 30 nm which is possible to be totally  
502 introduced inside 223, 267, and 294 nm-sized pores. The fact that the PBGs in the inverse  
503 opal structure are not able to enhance the light absorption because these photons will be

504 reflected in this frequency range. However, a slow photon effect that occurs on the  
 505 stopband edges properly enhances the absorption of the material, leading to generating  
 506 electron-hole pairs upon irradiation in these wavelength regions [24, 55]. Curti and  
 507 colleagues have explained the behavior of the stopband and slow photons at different  
 508 positions corresponding to the absorbance region of the material. Depending on their  
 509 suggestion, PBGs at 379 nm and the slow photon effect are inactive because their  
 510 wavelength is located within the region of the strong absorption of the Mo<sub>6</sub> cluster. In this  
 511 case, there is no enhancement of photons for generating electron-hole pairs. On the other  
 512 hand, the PBGs at 457 and 502 nm are inactive and their slow photon effects are active.  
 513 When the stopband overlaps with the strong absorption region, the reflection will be  
 514 avoided and the stopband band edges in the poor absorption region will enhance the light  
 515 absorption in this range by slow photon effects. These phenomena are verified by an  
 516 enhanced absorption part at higher wavelength ranges in **Fig. 6c**. The enhanced photon in  
 517 the absorption region will be scattered inside the pore and absorbed by MI deposited  
 518 within the IO structure to generate electron-hole pairs. In summary, the light utilization  
 519 capability in the IO structure is improved due to slow photon-induced light absorption  
 520 more reasonable than the photonic bandgap-induced light reflection. A few studies also  
 521 reported that slow photons of the 3D inverse opal photonic crystals could promote light  
 522 absorption of ZnO and TiO<sub>2</sub>-Au-CdS for visible photocatalytic activity enhancement [55-  
 523 57].

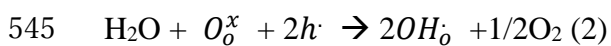


524  
 525 **Figure 6.** a) UV-vis absorbance spectra of CMI, b) the specular reflectance spectra at the  
 526 5-degree incident angle, c) UV-vis absorbance spectra and d) the transmittance spectra of

527 ITO glass, MI deposited on ITO glass and SnPO-IO<sub>x</sub>ca, and SnPO-IO<sub>x</sub>ca-MI (x = 240,  
528 288, 308) films.

### 529 **3.3 Effect of inverse opal structure on the photoconductivity response of Mo<sub>6</sub> cluster-** 530 **functionalized SnP<sub>2</sub>O<sub>7</sub> IO film**

531 To understand the electrochemically kinetic information as well as the charge transport  
532 on the surface of the SnP<sub>2</sub>O<sub>7</sub> bulk and MI cluster units, an illustration of the EIS  
533 measurement is presented in **Fig. SI9a**. The experiments were employed for the SnPO-  
534 IO<sub>288</sub>, SnPO-IO<sub>288</sub>ca, and SnPO-IO<sub>288</sub>ca-MI films in the humidity and temperature-  
535 controlled chamber. The light will directly irradiate the cluster deposited IO film. The  
536 interfacial charge transfer resistance ( $R_{ct}$ ) of the IO films measured at 298 K and 60 %RH  
537 was calculated from the fitted value by using a Randles equivalent circuit as depicted in  
538 **Fig. SI9b**. The charge transfer resistance ( $R_{ct}$ ) of SnPO-IO<sub>288</sub>ca was observed to be lower  
539 than that of SnPO-IO<sub>288</sub> corresponding to the smaller semicircle from the Nyquist plots  
540 in **Fig. 7a**. In general, SnP<sub>2</sub>O<sub>7</sub> nominally does not contain protons in the bulk which is  
541 proved by the disappearance of the O-H vibration as seen in the FT-IR spectra in the range  
542 between 3500 and 3000 cm<sup>-1</sup> (**Fig. 3b**). However, SnP<sub>2</sub>O<sub>7</sub> has been reported to exhibit a  
543 mixed proton and electron-hole conduction [39,40]. Therefore, the protonation process of  
544 SnP<sub>2</sub>O<sub>7</sub> during modification in water has been discovered from reaction (2):

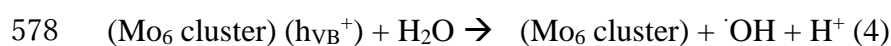
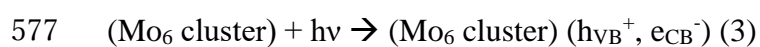


546 Where,  $\text{O}_o^x$ ,  $h \cdot$  and  $\text{OH}_o$  denote a lattice oxide ion, an electron-hole, and a protonated  
547 lattice oxide ion, respectively.

548 The appearance of new protons with a high concentration in the SnP<sub>2</sub>O<sub>7</sub> bulk was proved  
549 by the <sup>1</sup>H MAS NMR spectra reported by Shen et al. [32]. In addition, it was reported that  
550 protons migrate via dissociation of the O-H bond (hopping mechanism) [39]. At the  
551 humidity of 60% RH, protons coming from the water will interact with lattice oxide ions  
552 following reaction (2) to form a protonated lattice oxide ion on the surface of the SnP<sub>2</sub>O<sub>7</sub>  
553 bulk. The introduction of citric acid supports the charge transport on the interface of the  
554 conducting IO film by a covalent bond with a protonated lattice oxide ion. It has been  
555 claimed that carboxylic acid self-assembled monolayers can reduce the band gap of the

556 initial work function that improves the device performance by aligning the energy levels  
 557 in organic optoelectronic devices [51]. Moreover, citric acid contains two another  
 558 carboxylic groups for generating hydrogen bonds on the SnP<sub>2</sub>O<sub>7</sub> bulk surface which can  
 559 accelerate the charge ion transport. As the result, the interfacial charge transport is  
 560 improved in SnPO-IO<sub>288ca</sub>. However, the deposition of  $[\{\text{Mo}_6\text{I}_8\}\text{I}_4[\text{H}_2\text{O}]^a_2]_y\text{H}_2\text{O}$   
 561 limited the transport of charge on the surface of the SnP<sub>2</sub>O<sub>7</sub> bulk by blocking the hydroxyl  
 562 groups by the hydrogen bond and made a significant increase in the interfacial charge  
 563 transport resistance ( $R_{ct}$ ) of more than 100 times.

564 However, only the SnPO-IO<sub>288ca</sub>-MI interestingly shows the AC photoconductivity  
 565 response with the photosensitivity of about  $0.05 \pm 0.01$  nS/cm and  $0.10 \pm 0.01$  nS/cm during  
 566 the irradiation at fixed wavelengths in the UV range (350 and 370 nm) and visible range  
 567 (410, 440, 540 and 580 nm), respectively (**Fig. 7b**). The photosensitivity in the visible  
 568 light range (400-600 nm) is more efficient than in ultraviolet light. It can be explained  
 569 that the photoconductivity response comes from the  $[\{\text{Mo}_6\text{I}_8\}\text{I}_4[\text{H}_2\text{O}]^a_2]_y\text{H}_2\text{O}$  clusters  
 570 which strongly absorb in the visible range from 400 to 600 nm and generate photoexcited  
 571 clusters containing an electron and a hole as already reported [16]. As is known, the  
 572  $[\{\text{Mo}_6\text{X}_8\}\text{X}^a_6]^{2-}$  (X = halogen) cluster possesses a closed 24 valence electron shell. Some  
 573 studies have demonstrated a reversible one-electron oxidation that leads to 23-electron  
 574 complexes [58]. On the other hand, during the irradiation of photon energy, the MI cluster  
 575 units will generate electron/hole pairs following reaction (3). A hole on the photoexcited  
 576 cluster will then react with water to form a proton followed by reaction (4) [12,59].



579 A schematic representation of the proton and electron conducting mechanism is  
 580 illustrated in **Fig. 7c**. The Mo<sub>6</sub> clusters with apical water are anchored on the surface of  
 581 SnP<sub>2</sub>O<sub>7</sub> by a hydrogen bond with citric acid which is directly immobilized on SnP<sub>2</sub>O<sub>7</sub>.  
 582 The separated electrons will move from the valence band to the conduction band and are  
 583 collected by O-H bonding to move forward to SnP<sub>2</sub>O<sub>7</sub> while the generated proton will  
 584 continue to move inside the conducting SnP<sub>2</sub>O<sub>7</sub> by hydrogen bonds and citric acid bridge.

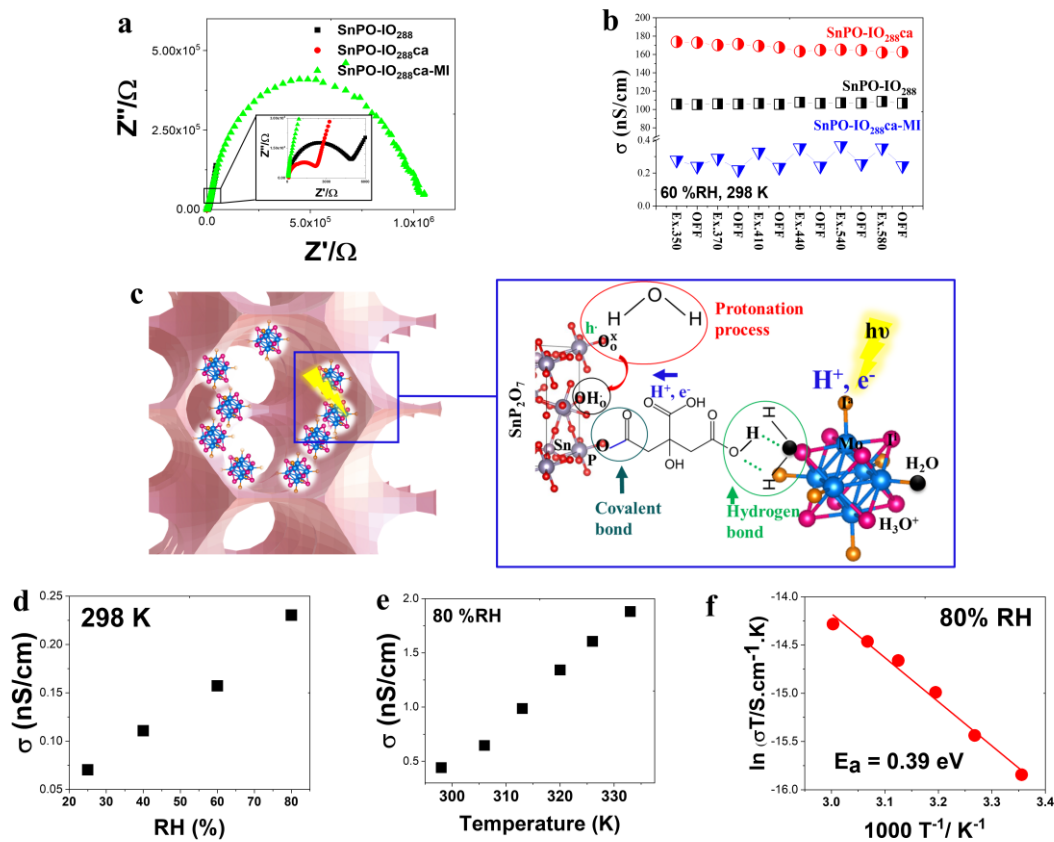


585 Both electrons and protons, which result in a photoconductivity response, will add to the  
586 total conductivity by transporting via the O-H bonds and protonated SnP<sub>2</sub>O<sub>7</sub> bulk towards  
587 the electrodes. When the illumination was switched off, the electron returned to the Mo<sub>6</sub>  
588 cluster and OH<sup>•</sup> to form OH<sup>-</sup> at the surface of SnP<sub>2</sub>O<sub>7</sub>. The conductivity of the MI film  
589 prepared by EPD could not be measured due to the extremely low conductivity coming  
590 from MI. As a result, the obtained conductivity of SnPO-IO<sub>288ca</sub>-MI was essentially  
591 contributed by SnP<sub>2</sub>O<sub>7</sub> IO and the additive photocurrent comes from the contribution of  
592 MI.

593 As is discussed, the protonic conductivity of SnP<sub>2</sub>O<sub>7</sub> will be distributed by the water  
594 concentration as seen in reaction (2). **Figs. 7d and e**, respectively, present the dependence  
595 of the conductivity on the relative humidity (RH) at 298K and the temperature at 80%  
596 RH. The deposition of the Mo<sub>6</sub> cluster units does not influence the linear dependence of  
597 the protonic and electrical conductivities on the environmental conditions. The activation  
598 energy (E<sub>a</sub>) was calculated from the relation with the ionic conductivity by Eq. 3:

$$599 \sigma T = A \cdot \exp(-E_a/RT) \quad (3)$$

600 where A is a constant, T is the temperature, R is the gas constant, and E<sub>a</sub> is the activation  
601 energy. The slope of the fitted Arrhenius plots, wherein the value of the natural logarithm  
602 of (σT) is linear versus the temperature (1/K), was used to calculate the activation energy  
603 (**Fig. 7f**). The activation energy of SnPO-IO<sub>288ca</sub>-MI is 0.39 eV that confirms the hopping  
604 conduction mechanism [60].



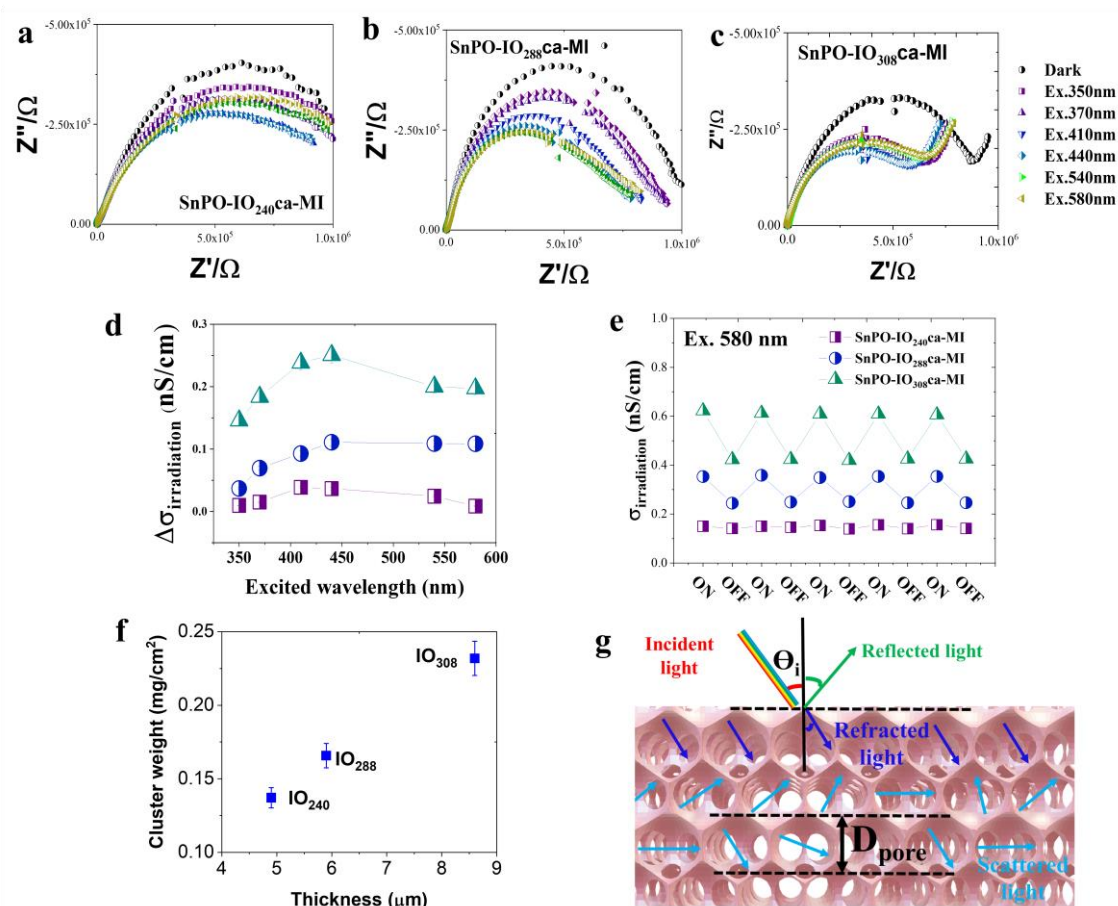
605

606 Figure 7. a) Nyquist plots of SnPO-IO<sub>288</sub>, SnPO-IO<sub>288ca</sub>, and SnPO-IO<sub>288ca-MI</sub> at 298K  
 607 and 60 %RH. (b) The AC photoconductivity response of the films at different irradiation  
 608 wavelengths. (c) Schematic representation of the proton and electron conducting  
 609 mechanism between SnP<sub>2</sub>O<sub>7</sub> and Mo<sub>6</sub> cluster. (d) The dependence of the electrical  
 610 conductivity vs. the relative humidity at 298 K, (e) The dependence of the electrical  
 611 conductivity vs. the temperatures at 80% RH, and (f) Linear fits of the plots of ln(σT)  
 612 versus T<sup>-1</sup> of the thin films at different temperatures and humidities.

613 The IO structure with various pore sizes results in a different interfacial charge transport  
 614 resistance (R<sub>ct</sub>) during irradiation of different fixed wavelengths as seen in **Figs. 8 a,b,**  
 615 **and c**. The thicknesses of the SnPO-IO<sub>240ca-MI</sub>, SnPO-IO<sub>288ca-MI</sub>, and SnPO-IO<sub>308ca-</sub>  
 616 **MI** films were respectively measured to be 4.9, 5.9, and 8.6 μm (**Fig. S110**). It can be seen  
 617 that R<sub>ct</sub> decreases with a similar tendency for the films irradiated at wavelengths in the  
 618 visible domain. SnPO-IO<sub>308ca-MI</sub> has the lowest R<sub>ct</sub> which means it produces the best  
 619 photocurrent based on **Eq. 1**. The thickness and pore size will contribute to the humidity

620 absorption and the concentration of MI which influences the photocurrent. The increasing  
621 photoconductivity of the SnPO-IO<sub>x</sub>ca-MI (x = 240, 288, 308) films irradiated at the fixed  
622 wavelengths of 350, 370, 410, 440, 540, and 580 nm was calculated from **Eq. 1 (Fig. 8d)**.  
623 All the films show the best increase in the photoconductivity response at the wavelengths  
624 of 410 and 440 nm, then a slight decrease at the wavelength of 580 nm. Several reasons  
625 have been considered for the photocurrent result such as i) the transmittance of the ITO  
626 glass in the UV range (70%) is lower than that in the visible range (>80%), and ii) the  
627 photon energy in the UV range is partially adsorbed by SnP<sub>2</sub>O<sub>7</sub> (**Fig. 3c**). The  
628 reproducibility and photosensitization of the photoconductivity are important points for  
629 use in optical-related devices. The AC photocurrents of the films irradiated at the fixed  
630 wavelength of 580 nm were measured for 5 cycles with every measurement performed  
631 for 3 minutes without stopping (**Figs. 8e**). The photosensitization of SnPO-IO<sub>240</sub>ca-MI,  
632 SnPO-IO<sub>288</sub>ca-MI, and SnPO-IO<sub>308</sub>ca-MI was, respectively, 0.034, 0.11, and 0.19 nS/cm  
633 irradiated at the wavelength of 580 nm. All the films obtained a good reproducibility of  
634 the photocurrent after 5 cycles of the EIS measurement. As seen in Fig. 8f, the deposited  
635 Mo<sub>6</sub> concentration is proportional to the thickness of the films which are determined by  
636 0.14, 0.17, and 0.23 mg/cm<sup>2</sup> corresponding to the thickness value at 4.9, 5.9, and 8.6 μm,  
637 respectively, for SnPO-IO<sub>240</sub>, SnPO-IO<sub>288</sub>, and SnPO-IO<sub>308</sub>. For the same EPD  
638 parameters, the bigger the PS bead size, the larger the pore size, and the thicker the IO  
639 film. During EPD, the charged PS particles smoothly move toward the IO electrode within  
640 a greater pore volume, resulting in more Mo<sub>6</sub> clusters in thicker IO film. Moreover, the  
641 incidence light will be reflected at the stopband while the absorption light will be  
642 enhanced at the stopband edges by an impact of slow photons which occur for the poor  
643 absorption region. As is discussed in **Fig. 6**, only the films which show the PBGs at 457  
644 and 502 nm can activate a low photon effect. The enhanced absorbance light will be  
645 mostly scattered within the pore and adsorbed by the Mo<sub>6</sub> cluster (**Fig. 8g**). Moreover,  
646 the scattering light will be proportionally enhanced with the increase in the macropore  
647 size. As the result, the IO film containing PBG at 502 nm that its stopband edge overlaps  
648 with to excitation wavelength at 580 nm can show the highest ability to generate electron-  
649 hole pairs for increasing the photocurrent upon illumination at this wavelength. In  
650 summary, the baseline current will be affected by the thickness of SnP<sub>2</sub>O<sub>7</sub>, while the

651 photocurrent depends on the MI concentration controlled by the thickness, active porous  
 652 areas, and the slow photon effect in the stopband edges.

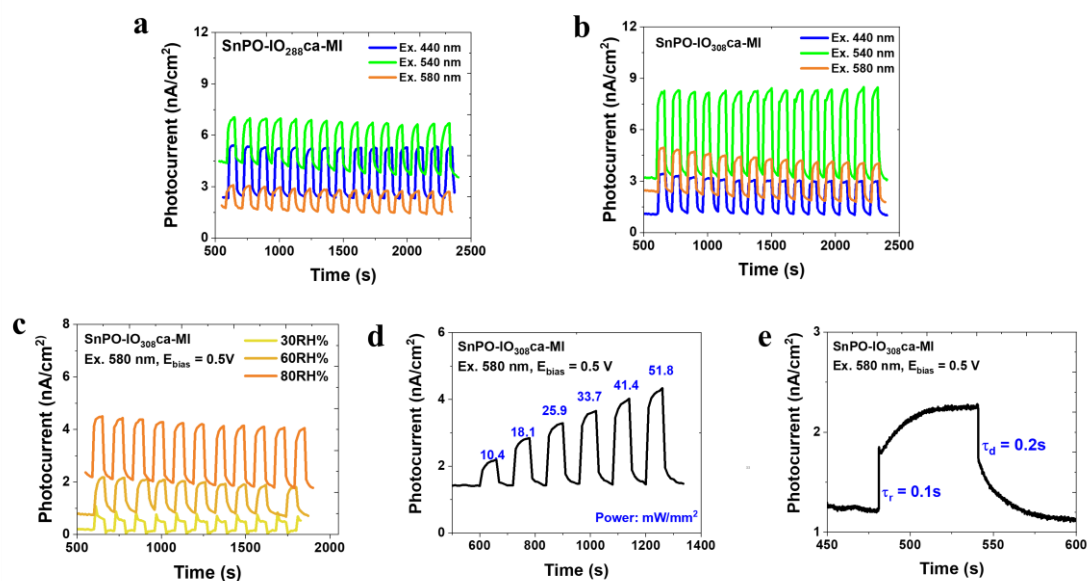


653

654 Figure 8. Nyquist plots of (a) SnPO-IO<sub>240</sub>-ca-MI, (b) SnPO-IO<sub>288</sub>-ca-MI, and (c) SnPO-  
 655 IO<sub>308</sub>-ca-MI films. d) The AC photoconductivity response of SnPO-IO<sub>x</sub>-ca-MI (x = 240,  
 656 288, 308) films at different excitation wavelengths at 297K and RH 60%. e) Repeatability  
 657 of photoconductivity response of SnPO-IO<sub>x</sub>-ca-MI (x = 240, 288, 308) films irradiated at  
 658 the fixed wavelength of 580 nm. f) Schematic illustration of the absorption light scattered  
 659 by the IO structure.

660 The reproducible on/off switching curves of the DC photocurrent at the bias voltage of  
 661 the 0.5 V of SnPO-IO<sub>x</sub>-ca-MI (x = 288, and 308) films are presented in **Figs. 9a and b**,  
 662 respectively. The measurement of SnPO-IO<sub>240</sub>-ca-MI was skipped in this experiment  
 663 because the slow photon effect does not occur at the stopband edge of PBG. It is noted  
 664 that the DC photoconductivity responses depend on light illumination at the wavelengths

665 of 440, 540, and 580 nm at the relative humidity (RH) of 80% and 298 K. The  
666 photocurrents from various excitation wavelengths have different baselines due to  
667 currents that are not stable after a continual and long measurement time. The excitation  
668 light at wavelengths, which overlapped with the stopband edges of PBG results in a  
669 leading light absorption in these wavelengths. This would explain the highest observed  
670 photocurrents; the slow photon effect occurs around PBG at 453 nm of the SnPO-IO<sub>288</sub>ca-  
671 MI which is near the irradiation light of 440 nm (Fig. 9a), whereas SnPO-IO<sub>308</sub>ca-MI  
672 shows a slow photon somewhere closer to 540 nm (Fig. 9b). Both films with different  
673 pore sizes result in a stable photocurrent reproducibility after 15 cycles. Reproducible  
674 on/off switching curves at the 580 nm illumination of the nanocomposite films measured  
675 at different humidities and 298 K are shown in **Fig. 9c and Fig. SI11**. The photocurrent  
676 response is proportional to the relative humidity which agreed with **Fig. 7d** following the  
677 hopping conduction mechanism. At the temperature of 298K and RHs of 30%, 60%, and  
678 80%, the photosensitive of SnPO-IO<sub>308</sub>ca-MI was recognized to be about 0.11, 1.29, and  
679 2.41 nA/cm<sup>2</sup> during the irradiation of the fixed wavelengths at 580 nm, respectively.  
680 Humidity plays an essential role to provide a water carrier that accelerates the movement  
681 of ions and electrons. In addition, the photocurrent also shows a linear dependence on the  
682 illumination power (**Fig. 9d**). The rising and decaying photocurrent responses ( $\tau$ ) were  
683 measured at 0.1 and 0.2 s, indicating a rapid photoresponse characteristic (**Fig. 9e**). The  
684 reproductivity of the photoconductivity was also obtained in a short time that improved  
685 in comparison to the layer double hydroxides functionalized by MI clusters in a previous  
686 report [12]. This result is more interesting for the application of environmental sensors or  
687 visible photodetectors.



688

689 Figure 9. Reproducible on/off switching curves of DC photocurrent at a bias voltage of  
 690 0.5 V of a) the SnPO-IO<sub>288</sub>ca-MI film and b) SnPO-IO<sub>308</sub>ca-MI film during the  
 691 illumination by different light wavelengths measured at RH of 80 % and 298 K versus  
 692 the time, and c) SnPO-IO<sub>308</sub>ca-MI film during the illumination by the wavelengths of 580  
 693 nm measured at different humidities and 298 K versus the time. d) The DC photocurrent  
 694 of the SnPO-IO<sub>308</sub>ca-MI film during the illumination by the wavelengths of 580 nm  
 695 measured at the RH of 80%, 298 K, and different powers versus irradiation power. e)  
 696 Enlarged rising and decaying edges of the photocurrent response of the SnPO-IO<sub>308</sub>ca-  
 697 MI film (298 K, 80 %RH) during the illumination of power at the 51.8 mW/mm<sup>2</sup>.

698 A good photosensitization and reproducibility depend on the interfacial charge transport  
 699 which is contributed by the protonic and electrical conductivities coming from the Mo<sub>6</sub>  
 700 cluster, SnP<sub>2</sub>O<sub>7</sub>, and an acid bridge between them. The proton conductivity of three  
 701 molybdenum cluster-based materials as building blocks, (H)<sub>4</sub>[Mo<sub>6</sub>Br<sub>6</sub>S<sub>2</sub>(OH)<sub>6</sub>]-12H<sub>2</sub>O  
 702 and (H)<sub>2</sub>[Mo<sub>6</sub>X<sub>8</sub>(OH)<sub>6</sub>]-12H<sub>2</sub>O (X = Cl, Br), was reported for the first time with the good  
 703 conductivity of  $1.4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$  under wet conditions for (H)<sub>2</sub>[Mo<sub>6</sub>Cl<sub>8</sub>(OH)<sub>6</sub>]-12H<sub>2</sub>O  
 704 (X = Cl, Br) [61]. It is possibly claimed that concerted proton transfers through the  
 705 hydrogen-bond network and vehicular (or diffusion) transport probably occur within the  
 706 materials. During the irradiation, it was proved that the excited electron enhanced the  
 707 charge on the surface of the Mo<sub>6</sub> cluster and was easily transported in the network [15].

708 The covalent and hydrogen bonds generated between the Mo<sub>6</sub> cluster with graphene  
709 oxide, silica oxide, hexagonal boron nitride, and layered double hydroxide have been  
710 reported that achieved an excellent photooxidation for a catalyst and photocurrent for  
711 optoelectronic materials [12, 62-64]. Hence, the strategy for the improvement of this  
712 material in the future is to find a new approach for improving the photon and electrical  
713 photoconductivity of the SnP<sub>2</sub>O<sub>7</sub> IO films by doping some different metals, such as In,  
714 Al, and Mg elements, and creating covalent bonding with the Mo<sub>6</sub> cluster.

#### 715 **4. CONCLUSIONS**

716 For the first time, the 3D SnP<sub>2</sub>O<sub>7</sub> conducting inverse opals with different pore size  
717 intergrated Mo<sub>6</sub> clusters were successfully fabricated by electrophoretic deposition and  
718 thermal treatment. The acid surface modification of the SnP<sub>2</sub>O<sub>7</sub> IO films results in an  
719 improvement of the deposited concentration of the Mo<sub>6</sub> cluster. The covalent bonding  
720 was recognized between the citric acid and SnP<sub>2</sub>O<sub>7</sub> IO films by FTIR and XPS. The  
721 [ $\{\text{Mo}_6\text{I}_8\}\text{I}_4[\text{H}_2\text{O}]^a_2\}.y\text{H}_2\text{O}$ ] cluster compound still retained the octahedral structure with  
722 a poor existence of Cs<sup>+</sup> counter-cations and exchanging of the two apical iodide ligands  
723 compared to the Cs<sub>2</sub>[ $\{\text{Mo}_6\text{I}_8\}\text{I}_6$ ] precursor. The SnP<sub>2</sub>O<sub>7</sub> IO films exhibited PBG at 379,  
724 457, and 502 nm, and their stopband edges activated the slow photon effect to enhance  
725 the optical adsorbing property of the Mo<sub>6</sub> cluster. Interestingly, the photocurrent response  
726 during the irradiation of visible light with a high photosensitivity efficiency comes from  
727 the Mo<sub>6</sub> cluster-functionalized SnP<sub>2</sub>O<sub>7</sub> IO films. The protons and electrons conducting  
728 mechanism of the SnP<sub>2</sub>O<sub>7</sub> IO films combines the proton and electrical conductivities via  
729 hydrogen bonding (a vehicular mechanism). The reproducibility and photostability of the  
730 nanocomposite were confirmed by both EIS measurement and DC measurement. This  
731 study will contribute to the achievement of the nanocomposite family that can show an  
732 efficient photoconductivity response in the visible domain, an important characteristic of  
733 materials for applications of water splitting, photodetectors, and photoelectrodes for dye-  
734 sensitized solar cells.

#### 735 **AUTHOR CONTRIBUTIONS**

736 Thi Kim Ngan Nguyen conceived and designed the experiments; performed the  
737 experiments, analyzed and interpreted the data, and drafted the article. Fabien Grasset and  
738 Stephane Cordier analyzed and interpreted the data; and drafted the article. Noee Dumait  
739 performed the experiments. Satoshi Ishii, Hiroshi Fudouzi, and Tetsuo Uchikoshi  
740 critically revised to improve the intellectual content.

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#### 747 **APPENDIX A. SUPPLEMENTARY MATERIAL**

748 Supplementary data to this article can be found online at

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