1 Removal of gaseous formaldehyde by portable photocatalytic air purifier equipped with bimetallic Pt@Cu-TiO₂ filter 2

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Abstract 13

In this research, a mini-scale air purifier (AP) system was built with honeycomb (HC) ceramic filters 14 coated with 1 wt% Pt@Cu/TiO₂ (HC-PCT-x, where x= 1, 2, and 3 for Pt:Cu weight ratios). The 15 photocatalytic removal of formaldehyde (FA) vapor was investigated using this AP system by controlling 16 process variables (e.g., FA concentration (0.5-5 ppm), AP-flow rate (100-160 L/min), and UV light 17 intensity (0.004-0.982 W)). Accordingly, HC-PCT-2 exhibited the highest efficacy to attain 100% removal 18 of FA (0.5 ppm) within 5 minutes at an AP-flow rate of 160 L/min and UV light intensity of 0.982 W 19 (quantum yield (QY) of 1.94E-04 molecules/photon and figure of merit (FOM) of 1.21E-06 L·mol/ (mg· 20 J·h). The in-situ DRIFTS analysis revealed the key role of Pt₂@Cu metal sites in promoting the transfer of 21 photo-induced charge carriers by TiO₂ (i.e., oxidation reaction of indoor FA vapor through the generation 22 23 of OH and O₂ radicals). The overall results of this study are expected to provide practical insights for the performance of the fabricated catalysts for the control of air quality with the aid of simple testing platforms. 24

- $\hbox{\bf 26} \qquad \hbox{\bf Keywords:} \quad \hbox{Formaldehyde;} \quad \hbox{Pt} @ Cu \quad \hbox{core-shell} \quad nanostructure; \quad \hbox{TiO}_2 \quad photocatalyst, \quad \hbox{Honeycomb} \quad \hbox{Honeycomb} \quad \hbox{Cu } a = 1, \dots, nanostructure; \quad \hbox{TiO}_2 \quad a = 1, \dots, nanostructure;$
- 27 photocatalytic filter; Indoor air purification
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30 1. Introduction

Photocatalysis is a highly effective technique for the mitigation of low-concentration volatile organic 31 32 compounds (VOCs) under ambient conditions [1-3]. In an effort to validate the effectiveness of photocatalytic systems, their performance has been assessed with different reactor configurations, such as 33 batch reactors [4-6], annular reactors [7], fluidized-bed reactors [8], honeycomb (HC) monolith reactors [9], 34 and flat-plate reactors [10, 11]. It is desirable to justify the economic and environmental feasibility of such 35 36 purification systems while addressing their high energy cost and/or toxic byproduct formation [12-14]. In 37 this respect, the great utility of photocatalytic air purifiers (APs) is successfully recognized as a sustainable way to treat indoor air pollutants through effective mineralization of the surface-adsorbed VOCs (into CO₂ 38 and H_2O) at low energy cost [15, 16]. 39

A good number of photocatalytic systems have been developed based on transition metal oxides (e.g., 40 TiO₂, Mn₂O₃, Al₂O₃, and ZnO) for the conversion of VOCs under UV/visible or solar irradiation [17-19]. 41 42 Among a plethora of photocatalytic semiconductor materials, TiO_2 has been used preferably for the 43 destruction of VOCs with multiple advantages (e.g., low-cost, commercial availability, and chemical stability) [2, 20]. Nonetheless, the utility of TiO₂ has been limited in a practical sense due to several 44 noticeable drawbacks, e.g., large bandgap ($E_g = 3.2 \text{ eV}$), fast recombination of charge carriers (electron/hole 45 pairs), poor selectivity, and low stability [21, 22]. To resolve such limitations, many strategies have been 46 proposed and validated over the years. As an example, TiO₂ was impregnated with transition/noble metal 47 nanoparticles (NPs) to increase the number of active sites (i.e., catalytic efficacy), light absorption capability, 48 49 and electron-hole separation [20, 23, 24]. Accordingly, TiO₂ impregnated with platinum NPs (Pt NPs) was recognized as a promising option to treat airborne pollutants effectively [25, 26]. The potential of bimetallic 50 core-shell nanostructures of Pt NPs with coinage metals (e.g., Cu, Ag, and Au) has also gained a great deal 51

52 of attention for such applications [27-29]. For instance, the plasmonic properties of Cu@Pt bimetallic coreshell NPs were reported to significantly enhance the light-harvesting efficiency of TiO₂ [30-32]. Such 53 54 enhancement was attributed to the strong synergistic effects between the coinage Cu metal sites and Pt NPs at the TiO₂ surface active sites which helped generate reactive oxygen species (ROS) (e.g., OH[•] and $O_2^{•}$) 55 by prolonging the partition between photoexcited electron/hole pairs. As such, the practical utility of Pt-Cu 56 bimetallic catalyst impregnated over TiO₂ has been demonstrated from many fields of applications such as 57 58 wastewater treatment [33], hydrogenation [34], fuel production [35], and combustion [36]. Despite the 59 recognition on the utility of Pt@Cu/TiO₂ photocatalysts, relatively little is known about the factors governing their performance toward air purification and gas-phase treatment (such as the effect of Pt: Cu 60 metal ratio on the photocatalytic activity) [27, 36]. 61

As a prime VOC pollutant present ubiquitously in indoor air, formaldehyde (FA) has been classified as a 62 human carcinogen (group 1) by the international agency for cancer research (IARC) [37, 38]. Therefore, in 63 64 this study, bimetallic Pt@Cu-TiO₂ composites (namely PCT-x, where x refers to Pt:Cu weight ratios of 1:1, 65 2:1, and 3:1) were prepared and deposited over a ceramic HC filter to design photocatalytic air filtration systems (HC-PCT-x) and tested for the abatement of formaldehyde (FA) as a model compound. A series of 66 photocatalytic experiments were thus carried out in a sealed chamber (17 L) fitted with an automotive AP 67 to assess the practicality of HC-PCT-x systems by controlling diverse process variables (e.g., FA 68 concentration (0.5-5 ppm), AP-flow rate (100-160 L/min), and light intensity (0.004-0.982 W)). The 69 oxidation pathway and identification of the intermediates generated during the photocatalytic process were 70 71 assessed using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). To the best of our knowledge, this is the first attempt to report the actual performance of Pt@Cu/TiO₂ filter installed in an 72 73 AP platform for the abatement of FA. The present work is expected to broaden the applicability of the bimetallic photocatalysts with the aid of a portable AP system as the practical platform for the assessment
of indoor air purification potential.

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77 2. Materials and Methods

78 2.1. Chemicals and materials used

Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, \geq 37.50% Pt basis), copper (II) nitrate pentahydrate (Cu(NO₃)₂·5H₂O, \geq 99.99% trace metals basis), titanium (IV) dioxide nanopowder (TiO₂; particle size = 21 nm (TEM), \geq 99.5%), polyvinylpyrrolidone (PVP), ascorbic acid (C₆H₈O₆), and paraformaldehyde (pFA (HO(CH₂O)_nH); 95%) were acquired from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure nitrogen (N₂; 99.99%) and air (21% O₂ and 79% N₂) gas cylinders were supplied by Green Gas Co., Ltd. (Kyeong-gi, Republic of Korea). The deionized (DI) water used for material synthesis was obtained from a water purification system (New Human RO, resistivity = 18 MΩ·cm).

86 2.2. Synthesis of mono/bimetallic Pt@Cu core-shell nanostructures

87 Bimetallic Pt@Cu core-shell nanostructures were synthesized via the co-reduction method, as described 88 in Fig. S1 (supplementary information (SI)) [39, 40]. In a 50 mL round bottom flask, an aqueous solution of Cu(NO₃)₂·5H₂O (10 mL, 3 mM) was prepared, followed by the addition of an ascorbic acid (100 mg) and 89 PVP (70 mg) mixture. The resulting solution was refluxed at 110 °C for 1 h under continuous magnetic 90 91 stirring (800 rpm). An aqueous solution of H₂PtCl₆·6H₂O (10 mL, 3 mM) was added to the above solution 92 mixture and the reaction temperature was raised and maintained at 200 °C for 1 h (Fig. S1). Three types of Pt@Cu core-shell nanostructures were synthesized by varying the Pt:Cu weight ratio and were labeled as A 93 (Pt@Cu (1:1)), B (Pt@Cu (2:1)), and C (Pt@Cu (3:1)). For further analysis, the obtained product was 94

95 centrifuged, washed (several times) with DI water, and re-dispersed in a specified volume (10 mL) of DI
96 water.

A similar procedure was used to fabricate monometallic Cu and Pt NPs by dissolving their corresponding salts $(Cu(NO_3)_2 \cdot 5H_2O(3 \text{ mM}) \text{ or } H_2PtCl_6 \cdot 6H_2O(3 \text{ mM}))$ in 50 mL aqueous solution containing a mixture of ascorbic acid (100 mg) and PVP (70 mg). The resulting solution was refluxed at 110 °C for 1 h under continuous magnetic stirring (800 rpm). The changes in solution color (i.e., from dark yellow to black color and from blue to brown color) indicate the formation of Pt and Cu NPs, respectively. Afterward, a specific volume of DI water (10 mL) was used to re-disperse the centrifuged end product for further analysis.

103 2.3. Fabrication of PCO-HC filter loaded with mono/bimetallic Pt@Cu-TiO2 catalysts

For the synthesis of Pt@Cu-TiO₂ composite, 500 mg of TiO₂ NPs were dispersed in DI water, followed by 104 the addition of 1 wt% of as-prepared bimetallic Pt@Cu nanostructures (with respect to TiO₂) with different 105 Pt:Cu weight ratios (1:1, 2:1, and 3:1). The resulting suspensions were stirred for 24 h using a magnetic stirrer 106 (800 rpm), centrifuged (5000 rpm), washed, and dried at 100°C. The TiO₂ impregnated with Pt@Cu 107 nanostructures with different Pt:Cu weight ratios (1:1, 2:1, and 3:1) are represented as PCT-x, where x values 108 of 1, 2, and 3 are assigned to Pt1@Cu-TiO2, Pt2@Cu-TiO2, and Pt3@Cu-TiO2, respectively. A similar 109 procedure was adopted to impregnate monometallic Pt and Cu over the TiO₂ surface. The obtained 110 mono/bimetallic Pt@Cu-TiO2 catalysts (50 mg) were dispersed in DI water and loaded onto a ceramic HC 111 filter (55 mm × 55 mm × 10 mm, Nanning Elaiter Environmental Technologies Co., Ltd, China) via a wet-112 impregnation method (Fig. S2). Afterward, the impregnated HC filters with the designed catalysts were 113 allowed to dry at 100 °C to achieve a better and more stable deposition process. 114

115 2.4. Characterization techniques

116 The absorption/optical properties of as-prepared catalysts were measured using a UV-vis spectrophotometer (Genesys 10S, EVOLUTION60, Thermo Scientific, USA). The morphologies of Pt@Cu 117 core-shell nanostructures were analyzed using transmission electron microscopy (TEM) (JEM-2100F, JEOL 118 Ltd., Tokyo, Japan) and scanning transmission electron microscopy (STEM) equipped with an energy 119 dispersive spectrometer (EDS) (Nova Nano SEM 450, FEI Co., Hillsboro, OR, USA). The crystalline 120 structure and diffraction spectra of the prepared materials were recorded on a powder X-ray diffractometer 121 (PXRD) (D8 ADVANCE, Bruker Corp., Billerica, MA, USA) using Cu Kα radiation (1.54 Å) in the 2θ range 122 of 10-80° with a scan speed and step size of 2° min⁻¹ and 0.02°, respectively. The textural features (e.g., 123 Brunauer-Emmett-Teller (BET) surface area, pore size, and pore volume) of the prepared photocatalysts were 124 assessed using N₂ adsorption-desorption isotherms at cryogenic temperature (-196 °C) using a BET surface 125 analyzer (3Flex, Micromeritics Instruments Corp., Norcross, GA, USA). X-ray photoelectron spectroscopy 126 (XPS) (Thermo Fisher Scientific Co, USA) was also utilized to assess the chemical states of elements (e.g., 127 Ti, O, Pt, and Cu) in the prepared catalysts. 128

129 2.5. Photocatalytic experimental setup

The gaseous primary standard of FA was prepared through the thermal cracking of paraformaldehyde (p-130 FA) powder [41]. In the standard procedure, a quartz tube packed with 100 mg of p-FA was inserted into a 131 thermal reactor maintained at 120 °C under continuous flow of N2 (100 mL/min) using a flowmeter 132 (ADM1000, Agilent Technologies, Santa Clara, CA, USA). A 5 L polyester aluminum (PEA) bag (obtained 133 from Top Trading Co., Seoul, Korea) was used to collect the resulting FA-rich effluent and was stored for 134 photocatalytic experiments. The concentration of FA-rich effluent was measured by the standard 2,4-135 dinitrophenylhydrazine (DNPH) method (EPA method 8215A) using high-performance liquid 136 chromatography (HPLC), as reported in our previous studies [41, 42]. Based on the quantified concentration 137

of FA, the gaseous working standards of FA (G-WS) were prepared in the range of 0.5-5 ppm by diluting theprimary FA-rich effluent with air as a background gas balance using 40 L PEA bags for gas storage.

140 For the photocatalytic study, a polypropylene rectangular sealed chamber (17 L, 340 mm × 250 mm × 200 mm) equipped with an air purifier (AP: LHS002KEK, LocknLock, Republic of Korea) and online FA sensor 141 (Model: TM-802, TENMARS Co., Ltd, Taiwan) were used to evaluate the destruction of airborne FA vapor 142 (0.5, 1, 3, and 5 ppm in the G-WS) over HC-PCT-x filters loaded with Pt_x@Cu-TiO₂ catalysts (Fig. S3 (a)). 143 In this system, the designed HC-PCT-x (x=1, 2, and 3) filters were inserted into the air purifier system. Before 144 the photocatalytic experiments, clean air was circulated using an air gas cylinder to eliminate impurities (if 145 any) in the chamber. Then, a pre-determined amount of G-WS FA vapor (relative humidity < 1%) was injected 146 into the chamber using an air-tight syringe (500 µL) (Trajan Scientific and Medical, Ringwood, Australia). 147 The chamber was sealed with parafilm tape to avoid gas leakage and was allowed to stand for 10 minutes until 148 the system stabilized. Afterward, the AP was switched on to perform catalytic oxidation of FA over HC-PCT-149 x photocatalytic systems under UV light. This system was also operated under the same conditions but in the 150 dark to obtain the control data. The online FA sensor had a detection limit of 0.5 ppm FA with $\pm 5\%$ relative 151 152 error.

The commercially available AP system (AP: LHS002KEK, LocknLock, Seoul, Republic of Korea) was capable of functioning in three distinct modes of flow rates (e.g., low (100 L/min), medium (130), and high (160 L/min)) and two light sources (e.g., UV-A (three lamps) and UV-C (one lamp), Fig. S3(b)) with power intensities in the range of 0.004 to 0.982 W. Accordingly, the photocatalytic efficiency of HC-PCT-x against FA was assessed by controlling the flow rates and AP-light source settings (Fig. S4) as defined in Table S1 (AP-O (all light sources switched on (UV-C+ 3UV-A), as purchased), AP-X (dark condition), AP-C (UV-C only), AP-C + A1 (UV-C + 1 UV-A), AP-C + A2 (for UV-C + 2 UV-A), AP-A1 (1UV-A), AP-A2 (2 UV-A),
and AP-A3 (3 UV-A)). The photocatalytic stability of the best performing HC filter (i.e., HC-PCT-2 (as
explained below)) was also evaluated for a total of five reuse cycles. For the regeneration study, the spent HCPCT-2 filter was thermally conditioned in an oven (at 100 °C) under static air conditions for 1 hour to eliminate
the moisture and adsorbed impurities prior to reuse in each cycle.

To assess the photocatalytic oxidation mechanism of FA over the designed PCT-2 photocatalyst, in-situ DRIFTS analysis was conducted to identify the intermediates generated during photocatalytic oxidation of FA using iS50 FT-IR (Thermo Scientific, USA) equipped with a mercury, cadmium, and telluride (MCT) detector. For this study, 50 mg of the photocatalyst was placed in the PCO reaction system under a continuous flow (100 mL min⁻¹) of FA (100 ppm) diluted with air (21% O₂ and 79% N₂) and UV-A light irradiation (8W, 365 nm) at ambient temperature (25°C).

170 2.6. Data analysis

171 The removal efficiency (R) of FA by the prepared HC-PCT-x photocatalytic filters were evaluated using172 Eq. (1).

173

174
$$R(\%) = \frac{[FA]_{it} - [FA]_{t}}{[FA]_{it}} \times 100$$
(1)

Here, [FA]_{in} and [FA]_t represents the recorded concentration of FA at the initial and at a given time (t,
min) during photocatalysis, respectively.

For commercial realization of a given photocatalyst, it is crucial to conduct performance evaluation in terms of economic viability and industrial applicability [30, 43]. The photocatalytic removal of FA depends upon the different process variables (e.g., FA concentration, catalyst dosage, light intensity, and flow rate). Accordingly, we determined the utility of key performance metrics like quantum yield (QY), space-time yield (STY), and figure of merit (FOM) to provide a more objective basis for evaluating the overall performance of the photocatalyst, as presented in Eqs. (2) to (4), respectively [30, 43, 44].

In photocatalytic reactions, QY, defined in Eq. (2), is a useful performance metric to estimate the efficiency of the photocatalyst in destroying VOC molecules, taking into account of the number of degraded VOC molecules and the total number of photons (refer to supplementary information (SI)) [45, 46].

186
$$QY = \frac{\text{Molecules/second (conversion rate)}}{\text{Photons/second (photon flux)}}$$
(2)

187 Considering the effects of photocatalyst dosage on the catalytic performance, the STY is defined in Eq.188 (3), where the QY value is normalized with respect to the amount of catalyst used for the reaction.

189
$$STY = \frac{QY \text{ (molecules/photon)}}{\text{Amount of photocatalyst (mg)}}$$
(3)

Further, the concept of the FOM metric, see Eq. (4), was developed to assess the overall performance of the photocatalyst by considering the interactive relationships between time and energy consumption involved in the photocatalytic process.

193
$$FOM = \frac{\text{Loaded pollutant volume (L)}}{\text{Catalyst dosage } (m g) \times \text{Time (h)} \times \text{Energy used } \left(W. \frac{h}{\text{mol}} \right)}$$
(4)

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195 3. Results and discussion

196 3.1. Characterization data

197 *3.1.1. Optical features*

198 The UV-Vis spectra of TiO_2 (P25) NPs impregnated with mono and bimetallic Pt@Cu core-shell 199 nanostructures and their monometallic analogues are given in Fig. 1. As seen in Fig. 1(a), monometallic Cu 200 NPs showed an intense absorption peak at 598 nm, reflecting the localized surface plasmon resonance (LSPR) effect of Cu element [40, 47]. On a comparative note, the optical spectrum of Pt NPs showcased a 201 202 relatively broad absorption peak with a feeble edge extended to the UV region at 294 nm. In the case of bimetallic Pt@Cu nanostructures (Fig. 1(a)), the absorption peak of Cu was blue-shifted to 590 nm (i.e., 203 hyperchromic shift/effect). Besides, the intensity of the Pt NPs absorption peak increased with an increase 204 in the Pt:Cu weight ratio from 1:1 to 2:1 and 3:1. These observations were attributed to an alteration in the 205 206 electron transition and optical response due to the synergistic effects in the bimetallic Pt@Cu nanostructures in reference to monometallic analogues [27, 48]. As shown in Fig. 1(b), the UV-Vis spectrum of pristine 207 P25-TiO₂ showed an absorption band edge in the UV region at 329 nm. This absorption band edge was red-208 shifted upon doping TiO₂ with mono and bimetallic nanostructures at 341, 346, 350, 358, and 389 nm for 209 PCT-1, PCT-2, PCT-3, Cu-TiO₂, and Pt-TiO₂, respectively. As such, charge transfer transition between 210 deposited metal NPs (Pt and Cu) and the TiO₂ conduction band significantly improved the light absorption 211 212 efficacy of pristine TiO₂ (329 nm) [49]. However, the lower light absorption band edge of PCT-x might be 213 attributed to the increased amount of Pt (core) content over Cu (shell), leading to the formation of larger NPs to significantly alter the light absorption efficacy of bimetallic-TiO₂ composites (e.g., relative to 214 monometallic ones) [50, 51]. Based on the Tauc plot (Fig. S5), the estimated bandgap energy of pristine 215 P25-TiO₂ decreased from 3.13 eV to 2.97, 2.93, 2.86, 2.82, and 2.77 eV upon doping with Pt NPs (Pt-TiO₂), 216 Cu NPs (Cu-TiO₂), Pt₁@Cu NPs (PCT-1), Pt₂@Cu NPs (PCT-2), and Pt₃@Cu NPs(for PCT-3), respectively. 217 Fig. S6 illustrates the photoluminescence (PL) spectra of synthesized PCT-x composites relative to the 218 219 pristine TiO₂ NPs at an excitation wavelength of 320 nm. Accordingly, the PL spectrum of pristine TiO₂ NPs consists of several emission peaks at 450, 469, 482, 492, and 537 nm due possibly to the $O_2^- \rightarrow Ti^{4+}$ 220

221 charge transfer process and surface defect (oxygen vacancy (O_v)) states [40, 52]. Notably, a considerable decrease in the PL emission intensity was observed after the impregnation of the TiO₂ surface with mono 222 223 (Pt or Cu) and bimetallic Pt@Cu) NPs. In particular, the prepared Pt-TiO₂ and Cu-TiO₂ photocatalysts showed a 4-6% decrease in the PL emission intensity relative to the pristine TiO₂. In case of the bimetallic 224 nanocomposites, an increase in the Pt: Cu weight ratios caused a higher quenching of PL intensity by 10, 225 15, and 22% for PCT-1, PCT-2, and PCT-3, respectively. This result revealed that the introduction of 226 227 bimetallic Pt@Cu onto TiO₂ efficiently served as electron traps to prolong the recombination of photo-228 induced charge carriers.

229 3.1.2. Structural and surface properties

Fig. 2 depicts the PXRD patterns of synthesized bimetallic PCT-x photocatalysts relative to commercial 230 TiO₂ (P25). The diffraction pattern of bare TiO₂ showed the intense Bragg reflections for anatase (joint 231 committee on powder diffraction standards (JCPDS) 01-084-1286) and rutile (JCPDS 01-089-0554)) phases 232 located at $2\theta = 25^{\circ}$ (101) and 27° (110), respectively. The remaining characteristic peaks observed at 2θ 233 234 values of 37°(004), 48°(200), 53°(211), 62°(204), 70°(301), and 75°(215) were attributed to the anatase phase (marked with orange stars, Fig. 2) [39, 53]. In the case of bimetallic $Pt_x@Cu/TiO_2$ photocatalysts (PCT-x, x 235 = 1, 2, and 3), the crystalline phases of anatase and rutile were detected in all patterns without shifts in the 236 peak positions. Besides, the diffraction peaks of deposited Pt@Cu nanostructures (JCPDS 00-048-1549, Pt 237 = JCPDS 03-065-5685, and Cu = JCPDS 00-035-1091) were also observed at 2 θ values of 36° (101), 41° 238 (111), 62° (204), and 70° (301), as marked with dark circles (Pt with purple and Cu with green line) in Fig. 239 240 2. As such, the impregnation of Pt@Cu onto TiO₂ surface was confirmed to be successful [47]. From the XRD patterns, the crystallite size of TiO₂ was found to be altered upon doping with bimetallic Pt@Cu 241 nanostructures as evaluated using the Debye-Scherrer equation (Eq.5) [54, 55]. 242

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{5}$$

Here, $\lambda = X$ -ray wavelength (1.54 Å), $\beta =$ full-width half maximum (FWHM) of the most intensive diffraction (101) peak, k = shape factor (0.9), and D = crystallite size.

It should be noted that the crystallite size (19 nm) of bare TiO₂ (P25) slightly increased to 20 nm (PCT-246 1), 21 nm (PCT-2), and 22 nm (PCT-3) upon impregnation of bimetallic Pt_x@Cu nanostructures. Besides, 247 the (101), (110), and (200) planes of TiO_2 in the PCT-x composites became more intense and sharper as the 248 Pt weight ratio in the bimetallic forms increased: $PCT-3 > PCT-2 > PCT-1 > TiO_2$ (Fig. 2). The increase in 249 250 crystallite size and improvement in phase crystallinity (in PCT-X relative to the pristine TiO₂) might be attributed to the effective interactions (i.e., Ti-Pt-Cu) or interstitial incorporation of platinum cation (ionic 251 radius = 0.52 Å into TiO₂ (0.68 Å) crystal [27, 33, 35]. Moreover, the impregnated Pt@Cu can influence 252 the defect sites (by creating vacancies e.g., O_V) or act as the nucleation sites for crystal growth to promote 253 the overall crystallinity of TiO₂ [56, 57]. 254

The N₂ adsorption-desorption isotherms of bimetallic Pt_x@Cu impregnated -TiO₂ composites (PCT-x, 255 x=1, 2, and 3) relative to the pristine TiO₂ are illustrated in Fig. 3(a). Based on the IUPAC classification, all 256 isotherms strictly followed type-IV with H3 hysteresis loops, indicating the mesoporous nature of the 257 prepared materials [58]. Based on the Barrett-Joyner-Halenda (BJH) theory, the pore size distribution of 258 prepared PCT-x samples lies in the region of 2–20 nm (Fig. 3(b)), verifying their mesoporous nature. Table 259 S2 summarizes the BET-specific surface area, total pore volume, and average pore diameter of TiO₂, PCT-260 1, PCT-2, and PCT-3 photocatalysts. As such, the BET surface area of pristine TiO₂ slightly decreased with 261 increasing Pt weight ratio: TiO₂ (47.3 m² g⁻¹) > PCT-1 (44.8 m² g⁻¹) > PCT-2 (43.4 m² g⁻¹) > PCT-3 (43.0 m²) > 262 m² g⁻¹). In compliance with this observation, a slight change in pore diameter (4.87 nm (PCT-1), 4.73 nm 263

(PCT-2), 4.69 nm (PCT-3), and 4.53 nm (TiO₂)) occurred, possibly due to internal pore strain driven by
impregnation of Pt@Cu (Fig. 3(b)) and filled vacant pore sites (Table S2) [39, 59, 60].

266 The TEM images (Fig. 4 (a-c) and Fig. S7) revealed the spherical morphology of bimetallic Pt@Cu coreshell nanostructures. The average particle size of Pt₁@Cu lies within the range of 63-75 nm and increased 267 to 112-118 nm and 141-144 nm for Pt₂@Cu and Pt₃@Cu NPs, respectively (Fig. S7). The core-shell 268 structural arrangement of Pt@Cu was further confirmed through STEM and EDS elemental mapping (Fig. 269 270 4 (d-g) and Fig. S8). Notably, the difference in reduction potential values of metals (e.g., Pt and Cu) in the 271 co-reduction method plays a key role in architecting the final structure [39, 61]. In the present case, the reduction potential difference facilitates the galvanic replacement reaction between Pt ($E^{o} = +1.2$ V) and 272 Cu ($E^{\circ} = +0.34$ V) to produce a core-shell nanostructure consisting of a Cu shell (shown in green, Fig. 4 273 (e)) and Pt core (shown in red, Fig. 4 (f)) [35, 61]. The combined EDS analysis of Pt@Cu nanostructure is 274 shown in Fig. 4 (g) and Fig. S8. Based on TEM analysis of as-prepared PCT-x photocatalysts (Fig. 5 and 275 276 Fig. S9), their d-spacing values increased relative to bare TiO_2 (d-spacing = 0.29-0.31 nm, Fig. S10) (such as 0.33-0.36 nm (PCT-1), 0.39-0.42 nm (PCT-2), and 0.48-0.56 nm (PCT-3)) to reflect the effective 277 interactions between bimetallic NPs (Pt@Cu) and TiO2. Moreover, the EDS analysis and elemental color 278 dot mapping (Fig. 5 (d-i) and Fig. S9) further confirmed the existence of Ti, O, Cu, and Pt in the as-prepared 279 PCT-x (x = 1, 2, and 3) photocatalysts. 280

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282 3.2. Photocatalytic abetment of gaseous FA

283 3.2.1. Effect of Pt:Cu weight ratio on the photocatalytic activity of HC-PCT-x filter

284 Fig. 6 presents the photocatalytic removal efficiency of different catalytic media (e.g., TiO₂, Cu-TiO₂, Pt-TiO₂, and Pt_x@Cu/TiO₂ (PCT-x: x=1, 2, and 3) composites) loaded on HC filters for the removal of 0.5 285 286 ppm FA relative to the original filter for the AP provided by the manufacturer (coded as HC-O) between under UV-light on (AP-O) and off conditions (AP-X) (Table S1). A bare HC-B filter (without loading any 287 catalyst) showcased no inherent photocatalytic activity for the removal of FA under AP-O mode (UV light 288 intensity = 0.982 W) (Fig. 6). In contrast, the HC-O filter showcased a higher ability to adsorb up to 90% 289 290 FA after 320s relative to HC-PCT-x filters (51-60% FA removal) under AP-X (light-off) conditions (Table 291 1 and Fig. 6). The high adsorption efficacy of commercial HC-O is suspected to reflect its high dosage of adsorbent components (e.g., Si, Mg, and Al) relative to HC-PCT-x filters fabricated using the Pt@Cu-TiO₂ 292 with an amount of 50 mg (Fig. S11 and S12). However, under light exposure (AP-O), all HC-PCT-x filters 293 exhibited higher photocatalytic activity relative to monometallic (Pt or Cu)-TiO₂ composites. For 10% FA 294 removal (Table 1), the time needed for filters ranked in descending order of HC-PCT-2 (13.25 s) > HC-295 296 PCT-3 (22 s) > HC-O (25 s) ≥ HC-PCT-1 (26 s) > HC-Pt-P25 (35 s) > HC-P25 (40 s) > HC-Cu-P25 (50 s). 297 As shown in Fig. 6, the overall photocatalytic removal efficiency between the catalysts ranked in the order of HC-PCT-2 (100%) = HC-PCT-3 (100%) > HC-PCT-1 (98%) > HC-O (94.3%) ≥ HC-1wt% Pt-P25 (86%) 298 > HC-1wt% Cu-P25 (80%) > HC-P25 (58.8%). As shown in Table 1, the photocatalytic reaction rate of FA 299 over the HC-PCT-2 filter was 83.52 µmol/h/g, which is 1.08 and 2.26 times higher than HC-PCT-3 (77.10 300 µmol/h/g) and HC-PCT-1 (36.85 µmol/h/g) filters, respectively. 301

To learn more about the enhanced photocatalytic activity of HC-PCT-2, the XPS analysis was carried out using PCT-2 photocatalyst (relative to bare TiO₂ photocatalyst), as seen in Fig. S13. Accordingly, the XPS survey on PCT-2 confirmed the presence of Pt, Ti, O, and Cu peaks (binding energy (BE) values of 74.57, 459.51, 530.77, and 933.4 eV, respectively), while that for bare TiO₂ only showed characteristic peaks of 306 Ti and O elements (BE values of 459.09 and 530.26, respectively). The corresponding deconvoluted spectra of Ti 2p, O 1s, Pt 4f, and Cu 2p elements are given in Fig. 7. In both samples, the C 1s signal was observed 307 308 at a BE value of 285.94 eV, which corresponds to the carbon paper used as a background during XPS analysis. For PCT-2, the core level of Ti 2p was deconvoluted into two well-resolved peaks and a shake-up 309 satellite peak centered at 459.53 (2p_{3/2}), 465.29 (2p_{1/2}), and 472.9 eV, respectively. The shake-up satellite 310 peak disappeared in the pristine TiO_2 (Fig. 7(a)). Compared with bare TiO_2 , the binding energies of Ti 2p 311 in PCT-2 were slightly blue-shifted by +0.44 eV. Further, the BE difference (ΔE_{BE}) of 5.7 eV between the 312 313 doublets of the Ti core line $(2p_{3/2} \text{ and } 2p_{1/2})$ indicates that Ti exists in the +4 oxidation state [39, 62]. However, the observed satellite peak in PCT-2 photocatalyst could be attributed to the formation of Ti³⁺ or 314 TiO_{2-x} defect sites (Ov) as a result of possible intimate contact between bimetallic Pt₂@Cu NPs and the TiO₂ 315 crystal lattice (i.e., Ti-Pt-Cu interactions) [27]. These formed Ti³⁺ or TiO_{2-x} defect sites may help promote 316 PCT-2 catalytic activity efficiently upon photon irradiation [34, 63]. 317

318 As shown in Fig. 7(b), the core-level of O 1s for PCT-2 can be deconvoluted into three peaks for lattice oxide ions: O²⁻ (530.75 eV), O-H binding (532.80 eV), and O₂ (surface adsorbed oxygen: 534.42 eV) [64, 319 65]. It is noted that the lattice oxygen and O-H peaks in the PCT-2 displayed a red-shift of +0.49 and +1.38 320 compared to bare TiO₂ (as O^{2-} (530.75 eV) and OH (531.42 eV)) [36, 66]. The above finding can be 321 accounted for by the alteration in the electronic environment due to (i) the electron exchange between TiO₂ 322 and bimetallic NPs (Pt and Cu) and (ii) the formation of surface defect sites (i.e., Ov) after the deposition 323 of bimetallic Pt@Cu over TiO₂ [34, 63]. Besides, the deconvolution spectrum of Cu 2p (Fig. 7(c)) showed 324 325 the presence of typical doublets in its core line at BE values of 933.41 (metallic (Cu⁰) 2p2/3) and 953.16 eV for (cationic Cu^+ (Cu_2O) 2p1/2) [40, 67]. Similarly, the core-level spectra of Pt 4f confirmed the presence 326 of metallic Pt^0 (BE= 71.49 eV) and Pt^{2+} cations (as PtO with two deconvoluted peaks at BE values of 75.18 327

328 and 77.2 eV, respectively) (Fig. 7(d)) [68, 69]. Notably, the metallic states of Cu and Pt are the dominant components in the synthesized bimetallic Pt₂@Cu NPs due to the use of ascorbic acid (as a reducing agent) 329 330 in their preparation [63]. However, both of them underwent partial oxidation in the environment due to the higher electronic transitions between Pt and Cu deposited over the surface of TiO₂, owing to the difference 331 in their electronegativity values (e.g., Pt (2.28) and Cu (1.9)) [34, 68, 69]. Additionally, the impregnated Pt 332 metal sites can increase the number of weak acid sites on the catalyst surface and strengthen the adsorption 333 334 between the FA molecules and the PCT-2 catalyst surface because of the electronic density of states and 335 high work function (5.93 eV for the 111 crystal plane) of Pt [70]. This phenomenon, in turn, helped enhance the photocatalytic oxidation process due to enhanced interactions between adsorbed FA molecules and the 336 active oxygen species (O*) and oxygen associated with Cu-O over the HC-PCT-2 surface [27]. 337

Compared with PCT-2 photocatalyst, the lower surface area of PCT-3 photocatalyst (Table S1) exhibited low metal dispersion with large Pt₃@Cu NPs. As such, PCT-3 showed fewer active surface sites available for interaction with FA molecules. Moreover, the higher Pt content can favorably induce the "shielding effect" while lowering the light-harvesting efficiency of TiO₂ (i.e., suppression of photogeneration of e^{-}/h^{+} pairs) [33, 71]. It is thus suggested that the HC-PCT-2 photocatalyst with Pt:Cu weight ratio (about 2:1) possesses abundant active sites and electronic trap to improve the photocatalytic activity of TiO₂ against polar FA vapor with the aid of the suppressed recombination of photoinduced charge carriers.

345

346 *3.2.2. Effect of photocatalytic reaction variables*

To learn more about the effect of process variables on the photocatalytic activity, the photocatalytic efficiency of HC-PCT-2 (as the best performing photocatalytic filter) for FA removal has been assessed under varying operation conditions (e.g., FA concentration level (e.g., 0.5, 1, 3, and 5 ppm) and AP-flow 350 rate (100-160 L/min)) (Fig. 8). It can be seen from Fig. 8(a) that HC-PCT-2 filter has the capability to remove gaseous FA under both AP-X and AP-O conditions, as the designed HC-PCT-2 filter has the 351 352 capability to induce sequential adsorption/catalytic reactions at room temperature. However, the removal efficiency of FA by a HC-PCT-2 filter under UV light-illumination (AP-O) was about 2 to 3 folds higher 353 than that in dark (AP-X) conditions. Under UV light (AP-O) illumination, the as-prepared HC-PCT-2 filter 354 was able to achieve 100% removal of FA after 300 s (0.5 ppm), 380 s (1 ppm), 420 s (3 ppm), and 480 s (5 355 356 ppm) with photocatalytic reaction rates of 83.52, 125.28, 349.62, and 522 µmol/h/g, respectively (Table 2). 357 The above finding can be explained by the fact that the higher gas phase concentration corresponding to a higher adsorbate concentration (according to the equilibrium considerations). Therefore, a greater number 358 of FA molecules can interact with catalysts (HC-PCT-2) (i.e., increase effective collisions) at higher FA 359 concentration, resulting in higher reaction/removal rate [72-74]. Comparatively, under light off (AP-X) 360 conditions, only 50% FA removal was observed after 235 to 580 s at inlet FA feed concentration of 0.5 and 361 362 5 ppm, respectively. As shown in Table 2, the reaction rate over HC-PCT-2 filter under AP-X condition (at 363 each feeding FA concentration) was computed as 53.31 (0.5 ppm), 104.40 (1 ppm), 234.90 (3 ppm), and 216 µmol/h/g (5 ppm). The lower reaction rate of HC-PCT-2 at the highest 5 ppm FA might be accounted 364 for by the possible blocking of active catalytic sites (or deactivation) with the increasing FA mass adsorbed 365 at the highest inlet FA concentration under AP-X condition [43, 75]. 366

Fig. 8 (b) shows the effect of AP flow rate (100 (low), 130 (medium), and 160 (high) L/min) on the photocatalytic removal efficiency of 0.5 ppm FA by a HC-PCT-2 filter as a function of reaction time between light on and off conditions. The result reveals that the HC-PCT-2 photocatalytic filter was able to remove FA at a faster pace under high AP-flow rate condition. At a constant inlet FA concentration (0.5 ppm), the increase in the AP flow rate from 100 to 160 L/min slightly shortened the time need to achieve 372 100% FA removal from 320 to 300 s (Fig. 8 (b)), with the corresponding photocatalytic rate of 73.52 to 83.52 µmol/h/g respectively (Table 3). In dark (AP-X) conditions, the HC-PCT-2 was able to achieve a 373 374 maximum 50% (after 235 s) removal of FA at the highest flow rate (160 L/min), with a removal rate of 53.31 µmol/h/g (Table 3). A decrease in the AP flow rate to 130 and 100 L/min led to a significant decline 375 in the removal efficiency of the HC-PCT-2 filter for FA to 44% and 36%, respectively. This observation 376 can be explained by considering the increased movement cycles of FA molecules (more than 9 cycles/min) 377 378 through the HC-PCT-2 filter in the confined photocatalytic reaction chamber (capacity = 17 L) with the rise 379 of AP flow rate.

Fig. 9 shows the effect of UV light source (UV-A and UV-C) intensity (0.004 to 0.982 W) on the 380 photocatalytic efficiency of the HC-PCT-2 under 0.5 ppm FA and a 160 L/min AP flow rate. Accordingly, 381 the illumination time required to achieve 100% FA removal increased with decreasing light intensity and 382 different combination of UV-A and UV-C light sources as follows: 300 s (AP-O, 0.982 W), 340 s (AP-A3, 383 384 0.972 W), 360 s (AP-A2, 0.571 W), 400 s (AP-C + A2, 0.577 W), 560 s (AP-A1, 0.392 W), and 580 s (AP-C + A1, 0.393W). However, it should be noted that the removal efficiency for FA (about 60%) under the 385 lowest AP-C light intensity (0.004 W) was still higher than that of the light-off condition (51% FA removal) 386 (Table 4). The improved photocatalytic activity of HC-PCT-2 with increasing incident UV light intensity 387 should be attributable to the increased number of photons reaching the catalyst surface. As a result, the 388 formation of surface active radicals (e.g., OH' and O₂[•]) increased, improving the removal efficiency of FA. 389 In line with general expectation, the total number of photons absorbed by the catalyst surface under AP-O 390 391 condition (1.06E+21 photons) were found to be 1.45, 3.15, and 150 times higher than photons absorbed under AP-A1, AP-A2, and AP-C light conditions, respectively. Hence, it is projected that the rate of 392 photocatalytic degradation of FA over the HC-PCT-2 filter is directly proportional to UV light intensity 393

(first-order kinetic). As a result, the generation of photo-induced charge carriers (e^-h^+ pairs) considerably improved when PCT-2 (bandgap: 2.82 eV) was exposed to a higher UV light intensity (i.e., AP-O condition). Upon UV excitation, the difference in electronegativity values of Pt (2.28) and Cu (1.9) can favorably enhance the charge separation efficiency of PCT-2 photocatalyst (by suppressing the recombination of charge carries) [76, 77]. This, in turn, should help accelerate the production of ROS radicals (e.g., OH[•] and O₂^{•-} radicals, Fig. 9) responsible for the control over the oxidation reaction rate of FA on HC-PCT-2 filter under UV light illumination [78, 79].

401

402 3.3. Performance comparison

To properly assess the practical feasibility of the designed $Pt_x@Cu-TiO_2$ photocatalytic system, its 403 performance was evaluated in reference to other TiO2-based composites reported previously for 404 photocatalytic removal of FA under batch mode conditions (i.e., a fixed concentration of pollutant confined 405 406 in a chamber or reactor) in terms of key performance metrics (e.g., QY, STY, and FOM). For QY and FOM 407 computation, the wavelength of incident light was assumed to be 365 and 420 nm for UV and visible light, respectively, if such information was not mentioned explicitly in the corresponding literature [30, 78]. The 408 results of this comparison are summarized in Table 5. In certain cases, such metrics were not computed due 409 to the lack of basic data in the reported literature. 410

The top five performers, if compiled in terms of QY (molecules/photon), were found as: HC-PCT-2 (1.94E-04, this study) > $Zr_xTi_{1-x}O_2$ (2.95E-06) > TiO_2 -diatomite (8.91E-07) > Pt-TiO_2 (3.09E-10) > Cy35 (2.17E-09) (Table 5). Under UV light exposure, the synergistic interactions between Pt@Cu and TiO_2 (HC-PCT-2) facilitated the migration of photo-induced e⁻ from TiO_2 to Pt@Cu to boost the formation of ROS species for FA degradation while suppressing the recombination of e⁻/h⁺ pairs. Based on the STY metric 416 (molecules/photon·mg), the relative ordering of top five performer photocatalysts was slightly altered such as HC-PCT-2 (3.88E-06) > Pt-TiO₂ (1.55E-08) > $Zr_xTi_{1-x}O_2$ (7.37E-09) > TiO₂-diatomite (8.91E-10) > 417 418 Cy35 (2.17E-11). The STY-based ranking still supports the superiority of HC-PCT-2 even at a low catalyst dosage (50 mg). Also, the high surface area of PCT-2 (43.41 m²g⁻¹) was advantageous to further boosted up 419 the degradation efficiency against FA. Likewise, in terms of the FOM (L·mol/(mg·J·h)), the photocatalytic 420 performance of the top five photocatalysts were ranked in the order of HC-PCT-2 (1.21E-06) > $Zr_xTi_{1-x}O_2$ 421 422 $(1.42E-12) > TiO_2$ -diatomite $(2.26E-13) > Pt-TiO_2$ (9.49E-15) > Cy35 (7.99E-19). Note that most catalytic 423 systems (e.g., Zr_xTi_{1-x}O₂, TiO₂-diatomite, and Pt-TiO₂) studied in previous studies have been developed using high power sources (18-250 W), high catalyst dosage (100-1000 mg), and long reaction time (1-4 h) 424 (Table 5). In contrast, our HC-PCT-2 operated more efficiently through combination of a low power source 425 (0.982 W) and short reaction time (0.166 h), making it the top performer in all computation metrics. 426

To further evaluate the feasibility of the designed photocatalytic filter for real-world applications, the 427 428 reusability of the HC-PCT-2 filter was investigated for FA removal over five successive cycles under AP-429 O condition, as shown in Fig. S14. Accordingly, the FA removal efficiency remained constant, showing 100% efficiency over five consecutive cycles. Based on the above analysis, Pt2@Cu-TiO2 (HC-PCT-2) has 430 excellent potential for field applications. Generally, the utilization of powdered photocatalysts is not 431 recommended for indoor air purification due to the potential inhalation risk [80]. In light of such limitations, 432 the loading of TiO_2 -based photocatalysts over a ceramic honeycomb (HC) filter can be as an ideal strategy 433 to improve the efficacy of air purification. [81, 82]. The extensive network of interconnected channels in 434 435 the HC ceramic filter is advantageous to bestow good contact between the filter and gas streams. Such distinctive structures should be beneficial for the application of HC ceramic filters as catalytic supports [12]. 436

437 3.4. Photocatalytic oxidation pathway of FA

438 To study the possible photocatalytic oxidation mechanism of FA by the catalytic system developed in this work, the photocatalytic reaction of FA onto PCT-2 photocatalyst under UV light (in reference to dark) 439 440 conditions was evaluated using in-situ DRIFTS analysis (Fig. 10). Apparently, several characteristic bands were observed during the photocatalytic reaction of FA over the HC-PCT-2 filter (e.g., 2955, 2916, 2858, 441 2759, and 1580 cm⁻¹). These are attributed to the symmetric (v_s)/asymmetric (v_{as}) stretching vibrations 442 (υ (CH) or δ (CH), υ_{as} (COO⁻), and υ_{s} (COO⁻)) of formate species, respectively [83, 84]. Also, the peaks 443 observed at 1169, 1102, and 1059 cm⁻¹ were assigned to the $\delta(CH_2)$ and $\upsilon(CO)$ of the dioxymethylene (DOM) 444 445 species. As such, formate or DOM species were the dominant intermediate for the FA degradation pathway over HC-PCT-2 filter under UV illumination [83]. Additional bands also observed at 1409, 1365, and 1306 446 cm⁻¹ should be associated with the carbonate species [83, 84]. Moreover, the peaks observed at 2377, 2342, 447 and 2301 cm⁻¹ were attributed to CO₂, while the peak at 2088 was assigned to CO generation. Based on 448 these results, It can thus be inferred that the mineralization of FA molecules should proceed through the 449 450 photocatalytic reaction over the HC-PCT-2 filter [83, 85]. Notably, the intensity of OH absorption bands (at 3686, 3643, 3486, and 1657 cm⁻¹) increased gradually under UV light conditions. This observation 451 indicates that the formation of ROS species should occur actively to contribute to the photocatalytic 452 degradation of FA molecules [83]. 453

Based on these findings, the UV light-assisted degradation mechanism of gaseous FA over Pt@Cu-TiO₂ may be illustrated as depicted in Fig. 11. Under the exposure of UV light, the photo-excited electrons move toward the conduction band (CB) to leave positive holes (h⁺) in the valence band (VB) of TiO₂, see Eq. (6) [78, 86]. The impregnated Pt@Cu NPs over TiO₂ can serve as trapping sites for the photo-induced e⁻ to suppress the recombination of charge carriers (e⁻-h⁺ pairs) (Fig. 11) [87]. Additionally, the formation of surface defect sites (e.g., Ti³⁺ or TiO_{2-x} and Ov) in the doped Pt@Cu-TiO₂ catalyst should have facilitated 460 the charge transfer mechanism across the Pt@Cu-TiO2 interface under UV light illumination, as verified by optical analysis (refer to Section 3.1.1). As such, the photo-induced electron and hole (e^-h^+) pairs can help 461 462 promote the formation of radical oxidative species (ROS: OH' and O2') for enhanced degradation of FA molecules (e.g., mineralization into CO_2 and H_2O , as expressed in Eqs. (7) to (9)) [87]. 463

464
$$Pt@Cu - TiO_2 + h\nu \rightarrow e^- + h^+$$
 (6)

$$t(a)Cu - TiO_2 + hv \rightarrow e + h'$$
(6)

(7)

$$e^- + O_2 \rightarrow O_2^{--} \tag{7}$$

466
$$h^+ + H_2 0 \to O H^-$$
 (8)

468

4. Conclusion 469

In this work, bimetallic Pt@Cu core-shell NPs (at three weight ratios of Pt:Cu) supported over the TiO₂ 470 surface were synthesized via the galvanic interaction method. The prepared $Pt_x(a)Cu-TiO_2$ (PCT-x, where x 471 = 1, 2, and 3 related to Pt:Cu ratios) photocatalysts were then impregnated (at 1 wt.%) over a honeycomb 472 (HC) air filter for the operation of mini-scale AP to treat formaldehyde (FA) based on sequential adsorption 473 and photocatalysis. Using this AP system in a sealed chamber (17 L), its photocatalytic performance was 474 assessed in various respects. Among the designed bimetallic forms, HC-PCT-2 (1 wt% Pt₂@Cu-TiO₂) 475 outperformed all other catalysts for photocatalytic abatement of FA (0.5-5ppm) when operated at a high 476 477 AP-flow rate (160 L/min) and AP-O light (intensity= 0.982 W). The photocatalytic activity of HC-PCT-2 (bandgap of 2.82 eV and surface area of 43.4 m^2/g) showcased a directly proportional relationship to the 478 light intensity and AP flow rate while declining with increasing FA inlet concentration (under AP-X 479 condition). 480

481 Based on the in-situ DRIFTS analysis, the synergistic interactions between Pt (as electron trapping sites) and Cu (LSPR effect) efficiently promote the generation of ROS radicals (e.g., OH' and O2') for FA 482 483 degradation while suppressing the recombination of e⁻/h⁺ pairs within the TiO₂ crystal lattice under UV light exposure. The reusability tests also verified the good photocatalytic stability of HC-PCT-2 toward removal 484 of 100% FA under UV irradiation, without loss in its efficiency over five reuse cycles. To further assess the 485 practical viability of our photocatalytic system, the overall performance of $Pt_2@Cu-TiO_2$ (PCT-2) was 486 487 compared with previously reported TiO₂-based composites for photocatalytic removal of FA in terms of key 488 performance metrics (e.g., QY, STY, and FOM). The HC filter loaded with PCT-2 was found to be the most effective photocatalytic system against FA (0.5 ppm) over short reaction time (0.166 h) under the conditions 489 of (a) low catalyst dosage (50 mg) and (b) low power consumption (0.982 W) Therefore, the present work 490 is expected to open a new pathway in the fabrication of bimetallic NPs-based photocatalysts and broaden 491 their applicability for air purification under real world conditions. 492

493

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499

500 Declaration of Competing Interest

501 The authors declare no competing interests with the publication of this manuscript.

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Table 1. Performance evaluation of the photocatalytic system developed in this work against 0.5 ppm FA in terms of elapsed time, removal efficiency, and reaction

kinetic rate.

						Remo	val (%)			
	IIV light			R10%		R50%	1	R90%		R100%
Order	condition	Filter type	Time (s)	Reaction rate (µmol/h/g)						
1		HC-PCT-1	30.40	58.18	223.33	56.10	478.00	47.18	680.00	36.85
2		HC-PCT-2	5.89	623.50	54.00	214.77	227.00	135.03	300.00	83.52
3		HC-PCT-3	15.25	164.30	80.00	156.60	276.00	78.21	420.00	77.10
4	UV-light on (AP-O)	HC-1 wt% Pt-P25	18	556.8	145	200.45	NA	NA	NA	NA
5	. ,	HC-1 wt% Cu-P25	22	303.71	167	121.31	NA	NA	NA	NA
6		HC-P25	31	162.71	355	117.17	NA	NA	NA	NA
7		HC-O	16.63	NA	36.67	NA	274.00	NA	NA	NA
8		HC-PCT-1	26.00	96.37	430.00	29.14				
9		HC-PCT-2	13.25	189.15	235.00	53.31				
10	LIV-light off	HC-PCT-3	22.00	113.89	350.00	35.79	NA	NΔ		
11	(AP-X)	HC-1 wt% Pt-P25	35	71.59	NA	NA		NA	NA	NA
12	() () ()	HC-1 wt% Cu-P25	50	50.11	NA	NA				
13		HC-P25	40	62.64	NA	NA				
14		HC-O	25.00	NA	65.00	NA	320.00			

Table 2. Performance of HC-PCT-2 filter for varying concentrations of FA (0.5, 1, 3, and 5 ppm).

			Removal (%)									
		FA concentration (ppm)		R10%		R50%		R90%	F	k100%		
Order	UV light condition		Time (s)	Reaction rate (µmol/h/g)	Time (s)	Reaction rate (µmol/h/g)	Time (s)	Reaction rate (µmol/h/g)	Time (s)	Reaction rate (µmol/h/g)		
1		0.5	5.89	623.50	54	214.77	227	135.03	300	83.52		
2	UV-light on	1	11.67	411.64	66.25	414.61	233	193.29	380	125.28		
3	(AP-O)	3	17.45	861.41	68.79	1193.44	237	572.62	420	349.62		
4		5	21.28	1127.02	70.20	1784.62	242.78	928.85	480	522.00		
5		0.5	13.25	189.15	235	53.31						
6	UV-light off	1	14.86	337.29	240	104.40	NA	NA	NA	NA		
7	(AP-X)	3	15.25	985.82	320	234.90						
8		5	17.21	1455.54	580	216.00						

774	Table 3. Eff	fect of flow rate	e (low, medium	i, and high) o	of the AP system	on the performance	of an HC-PCT-2
					2	1	

	UV light condition	AP flow rate (L/min)		Removal (%)									
			R10%		R50%			R90%		R100%			
Ord er			Time (s)	Reaction rate (µmol/h/g)									
1		Low	27.29	91.83	72.86	171.95	237.00	113.89	320.00	73.52			
2	UV-light on (AP-O)	Medium	26.14	95.84	70.00	178.97	230.00	120.59	310.00	81.45			
3	011 (7 % 0)	High	5.89	623.50	54.00	214.77	227.00	135.03	300.00	83.52			
4		Low	35.00	71.59	NA	NA							
5	UV-light off (AP-X)	Medium	30.67	97.42	NA	NA	NA	NA	NA	NA			
6	off (AP-X) High		13.25	189.15	235.00	53.31							

775 AP Flow rates: low (100 L/min), medium (130 L/min), and high (160 L/min).

filter.

Table 4. The elapsed time and kinetic rate of HC-PCT-2 filter against 0.5 ppm FA under different intensities of UV light.

								Removal (%)			
	UV light		FA	Flow	R10	%	R5	0%	R9	0%	R1	00%
Order	intensity (W)	UV light source	concentratio n (ppm)	rate (L/min)	Time (s)	Reaction rate (µmol/h/g)						
1	0.004	AP-C			27.75	90.29	270.00	46.40	NA	NA	NA	NA
2	0.393	AP-C + A1			24.00	104.40	100.00	125.28	300.00	75.17	580.00	43.20
3	0.577	AP-C + A2			6.63	378.21	72.50	188.45	234.00	96.37	400.00	62.64
4	0.982	AP-O	0.5	160	5.89	623.50	39.09	214.77	147.00	135.03	300.00	83.52
5	0.392	AP-A1	0.5	(high)	24.44	102.50	96.00	130.50	300.00	75.17	560.00	44.74
6	0.571	AP-A2			15.33	163.41	80.00	156.60	216.00	104.40	360.00	69.60
7	0.972	AP-A3			13.60	184.24	35.00	357.94	212.00	106.37	340.00	73.69
8	Dark	AP-X			13.25	189.15	235.00	53.31	NA	NA	NA	NA

Order	Photocatalyst	Light source	Reactor	Mass of catalyst (mg)	Concent ration (ppm)	Irradiation Time (h)	Chamber volume (L)	Conversion (%)	Quantum yield (molecules/ph oton)*	Space time yield (molecules/ photon*mg)	FOM* (L·mol/(mg·J ·h)	Reference
1	TiO ₂ -diatomite	250 W UV lamp	batch reactor	1000	0.79	3	250	90.9	8.91E-07	8.91E-10	2.26E-13	[88]
2	Zr _x Ti _{1-x} O ₂	45 W UV– Vis light	airtight reactor	400	0.81	4	220	92	2.95E-06	7.37E-09	1.42E-12	[89]
3	rGO−TiO₂	xenon lamp	stainless steel reactor	500	0.5	4	0.45	88.3	3.21E-10	6.43E-13	2.54E-19	[90]
4	Pt-TiO ₂	visible light source	batch reactor	100	400	1	_	93.8	NA	NA	NA	[91]
5	Cy25 (Ag/F/N/W doped TiO ₂)	HR 16 blue light emitting diode	20 mL tubular borosilicate glass	100	2	2	0.02	35	8.65E-10	8.65E-12	3.18E-19	[92]
6	Су35	HR 16 blue light emitting diode	20 mL tubular borosilicate glass	100	2	2	0.02	88	2.17E-09	2.17E-11	7.99E-19	[92]
7	Су45	HR 16 blue light emitting diode	20 mL tubular borosilicate glass	100	2	2	0.02	55	1.36E-09	1.36E-11	4.99E-19	[92]

Table 5. Performance comparison of TiO₂-based composites employed for photocatalytic removal of FA between studies.

8	Pt@TiO₂	18 W daylight lamp	reaction chamber	20	10	4	0.7	98.3	3.09E-07	1.55E-08	9.49E-15	[93]
9	1 wt% Pt/TiO2	18 W daylight Iamp	reaction chamber	20	10	4	0.7	85.6	2.69E-07	1.35E-08	8.26E-15	[93]
10	HC-PCT-1	UV light air purifier (0.982 W)	rectangular sealed chamber	50	0.5	0.166	17	70.6	1.37E-04	2.74E-06	8.56E-07	This study
11	HC-PCT-2	UV light air purifier (0.982 W)	rectangular sealed chamber	50	0.5	0.166	17	100	1.94E-04	3.88E-06	1.21E-06	This study
12	HC-PCT-3	UV light air purifier (0.982 W)	rectangular sealed chamber	50	0.5	0.166	17	92.3	1.79E-04	3.58E-06	1.12E-06	This study
799 * 1 800 and	The QY, STY, and I d 365 nm were used	FOM values we to represent v	ere calculated ba	ased upon UV light c	the peak wa conditions, r	avelength of the espectively.	light source re	ported in the give	en paper. For refe	rence without spe	ecific wavelength	information, 420

> (b) (a) Absorbance Intensity (a.u.) Cu NPs Absorbance intensity (a.u.) 389 nm Bare TiO, Pt NPs 350 nm Cu-TiO₂ C (Pt@Cu (3:1)) B (Pt@Cu (2:1)) A (Pt@Cu (1:1)) Pt-TiO₂ 329 nm PCT-3 346 nm PCT-2 PCT-1 598 nm 341 nm 500 800 250 300 350 400 450 200 300 400 600 700 500 550 600 650 700 Wavelength (nm) Wavelength (nm)

Fig. 1. The UV-visible spectra of synthesized nanomaterials: (a) mono/bimetallic Pt@Cu nanoparticles
(NPs) (b) after their impregnation onto TiO₂.

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- 807
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Fig. 3. BET surface analysis of synthesized PCT-x photocatalysts in reference to the pristine TiO₂: (a) N₂
adsorption-desorption isotherms and (b) pore size distribution.





856 Pt@Cu (2:1) core-shell nanostructure.





Fig. 6. Performance of HC-filters loaded with different photocatalytic material (50 mg) against 0.5 ppm FA
under UV-light on (AP-O) and off (AP-X) conditions at high AP-flow rate (160 L/min): (a) removal
efficiency as function of time and (b) maximum removal efficiency achieved by different HC filters in
maximum operation time (10 minutes).











1011 Supplementary Information

- 1012 **Table S1.** Specification of different air purifier (AP) filters and its diverse irradiation conditions tested for the removal of
- 1013 gaseous FA.

	A. Type of filters prepared to load on AP system								
Order	Filter code	Filter type	Major components of filter	Loaded mass (mg)					
1	HC-O	Commercial	Ti, O, Si, Al, and Mg.	Unknown					
2	HC-PCT-1	Coated	Pt ₁ @Cu-TiO ₂	50					
3	HC-PCT-2	Coated	Pt ₂ @Cu-TiO ₂	50					
4	HC-PCT-3	Coated	Pt₃@Cu-TiO₂	50					
5	HC-1 wt% Pt-P25	Coated	1 wt% Pt-TiO ₂	50					
6	HC-1 wt% Cu-P25	Coated	1 wt% Cu-TiO ₂	50					
7	HC-P25	Coated	Pristine TiO ₂ (P25)	50					
B. AP system with different light irradiation conditions									

	AP code	Light irradiation conditions*
8	AP-X	no UV-light source
9	AP-O	all UV-light sources
10	AP-A1	1 UV-A source
11	AP-A2	2 UV-A sources
12	AP-A3	3 UV-A sources
13	AP-C	only UV-C source
14	AP-C + A1	1 UV-A and 1 UV-C sources
15	AP-C + A2	2 UV-A and 1 UV-C sources

* Light sources: An AP system is built with one UV-C and three identical UV-A sources.

		NF (11	BET surface area	Pore volume	Average pore
	Order	Material	(m^2g^{-1})	(cm ³ g ⁻¹)	diameter (nm)
	1	TiO ₂	47.3	0.065	4.53
	2	PCT-1	44.8	0.075	4.87
	3	PCT-2	43.4	0.072	4.73
	4	PCT-3	43.0	0.071	4.69
1017					
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Table S2. Surface properties of bare and bimetallic Pt@Cu modified TiO₂ photocatalysts.





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Fig. S3. Schematic of photocatalytic removal system for FA: (a) experimental setup using AP in a closed
chamber (17 L) and (b) AP light source and filter position .

1090	AP-C+A1 (UV-C+1UV-A)	(a) AP-C+A2 (UV-C + 2 UV-A)	(b) AP-O (UV-C + 3 UV-A, as purchased) (C)
1091	Little marks		Commission (
1092	1000		
1093	ATT-		
1094	AP-A1 (1 UV-A)	(d) AP-A1 (2 UV-A)	(e) AP-A3 (3 UV-A) (f)
1095			
1096			N.T.
1097	ALCONC.		
1098	AP-C (UV-C only)		
1099			
1100	CORS-		
1101			

Fig. S4. The AP system used to examine the photocatalytic activity of HC-PCT-2 photocatalyst under
different UV light sources.







1172 Fig. S7. TEM images and EDS analysis of bimetallic nanostructures with different Pt:Cu weight ratios: (a-













Fig. S11. The morphological characteristics of material loaded over commercial HC-O filter: (a-c) TEM
images and (d) EDS analysis.





Fig. S12. The color mapping of different elements presents in the material loaded over commercial HC-O
filter: (a) selected area, (b) Ti, (c) O, (d) Mg, (e) Si, and (f) Al.





Fig. S14. The reusability test of HC-PCT-2 photocatalyst (50 mg) against FA (0.5 ppm)condition.

- 1334 Estimation of total number of photons
- 1335 The total number of photons were calculated theoretically by considering the power of light source used,
- 1336 wavelength of light, and experiment time as follow:
- 1337 Photon energy $(J) = hc/\lambda$ (1)
- 1338 $h = Plank's constant, c = speed of light, and <math>\lambda = wavelength$
- 1339 Photons per second = photon energy $(J)/lamp power (J.s^{-1})$ (2)
- 1340 [3] Total number of photons = photons per second (photons s^{-1}) * reaction or experiment time (s^{-1}) (3)