## Polyol Assisted Synthesis of Copper Particles

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### Supporting Information

List of Videos:

Video S1 Motion of Au@Cu<sub>7</sub> micromotor in 1% H<sub>2</sub>O<sub>2</sub> at different UV intensities.

Video S2 Motion of  $Au@Cu_7$  micromotor in different  $H_2O_2$  concentrations without UV light.



#### Mechanism of formation Cu and CuPc in assisted polyol synthesis

Figure S1: The schematic process of formation of Cu and CuPc crystals in high-temperature solvothermal synthesis: (A) General reaction following copper acetate & phthalonitrile resulting in the synthesis of both Cu and CuPc crystals. (B) Schematic representation of the high-temperature reaction during a solvothermal method at 160 °C for 72 h. (C) The upper left image gives a visual representation of the mixture of blue (CuPc) and brownish (Cu) formed during the reaction. The SEM image indicates the formation of long crystalline rods (CuPc crystals) and spheroidal particles (metallic Cu particles). A schematic illustration of the formation of CuPc rods and Cu spheroids is shown at the center. In the right-hand part, the mechanism of formation of both CuPc (indicated in blue box) and metallic Cu (indicated in orange box) from EG is sketched. Scale bar: 1 µm.

In a high temperature and high-pressure synthesis involving copper acetate and phthalonitrile (see reaction Figure S1A), metallic Cu particles are formed along with copper phthalocyanine (CuPc) rods. This one-pot synthesis can be carried out in simple steps: mixing the reactants to form reactant solution, then stirring it to form homogeneous suspension followed by a solvothermal treatment (schematically detailed in Figure S1B). The mechanism of formation of these blue CuPc rods and brownish Cu spheroids (shown both schematically and with SEM in Figure S1C) can be explained as follows: For the formation of CuPc, the reaction is initiated by a nucleophilic attack of a monoanion of ethylene glycol (OHCH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup>) on the cyano group of one phthalonitrile moiety. An isoindolenine intermediate is formed which attacks another phthalonitrile molecule (shown in blue box in Figure S1.C.(i)). These processes result in a tetraisoindolenine structure of conjugated porphyrin ring (Figure S1.C.(ii)).<sup>1</sup> Next, the cupric ion from Cu(CH<sub>3</sub>COO)<sub>2</sub> salt forms a two-electron bond with the porphyrin ring (Figure S1.C.(iii)). The nucleophile gets regenerated again and a CuPc molecule is formed (Figure S1.C.(iv)). Finally, the CuPc molecules stack over one another by  $\pi$ - $\pi$  interaction forming a rod-like phthalocyanine crystal.<sup>2,3</sup>

The spheroidal copper is formed due to the polyol reduction of cupric ions by ethylene glycol (EG).<sup>4,5</sup> It is known from literature, that the oxidation of EG and the reduction of metal ions are facilitated by an increase in reaction temperature.<sup>6,7</sup> Similarly, in the solvothermal reaction, a high temperature and pressure environment in created, which might enhance the Cu<sup>2+</sup> reduction process by EG (see Figure S1C).

## Factors influencing the morphology and growth of copper particles formed in the presence of phthalocyanine precursors

The size of Cu particles synthesized in the presence of phthalocyanine precursors can be tuned by varying the reaction conditions. Here, we studied the morphological changes in the Cu particles by altering the reactant to solvent ratio and the time (Table S1).

The reaction was carried out in two different reactant conditions, a higher reactant to solvent ratio led to the formation of larger Cu microparticles (Cu<sub>7</sub>) (Figure S2F). When the reaction was performed at a 5 times lower reactant to solvent ratio, it resulted in smaller particles (Cu<sub>1</sub>) (Figure S2C). This variation in size can be correlated to the difference in the reactant concentration.

The size and polydispersity of Cu particles can also be tuned by varying reaction time. We studied the morphology and size distribution of formation of  $Cu_7$  and  $Cu_1$  particles in three different reaction times: 24 h, 48 h and 72 h. In case of  $Cu_1$ , a slight increase in average

particle size with increasing reaction time was observed (Figure S2A, B, and C).

Fig.	Sample	$Cu(CH_3COO)_2$	Phthalocyanine precursors		Time	Size of Cu	Polydis-
No.	ID	(M)	Phthalonitrile (M)	AMT(M)	(h)	$(\mu m)$	persity(%)
S2.A	Cu <sub>1</sub> -24	0.00125	0.005	0.00004	24	$0.79\pm0.31$	39
S2.B	$Cu_1-48$	0.00125	0.005	0.00004	48	$0.83 \pm 0.23$	28
S2.C	$Cu_1-72$	0.00125	0.005	0.00004	72	$0.96\pm0.36$	37
S2.D	Cu <sub>7</sub> -24	0.00625	0.025	0.0002	24	$1.93\pm0.44$	23
S2.E	Cu <sub>7</sub> -48	0.00625	0.025	0.0002	48	$1.95\pm0.67$	34
S2.F	Cu <sub>7</sub> -72	0.00625	0.025	0.0002	72	$6.87 \pm 1.39$	20

Table S1: Table of synthesis of Cu particles in different reactant conditions

In case of Cu<sub>7</sub> synthesis, the particle size remains similar for 24 h and 48 h (around 2 µm). A prominent increase in size is noticed at 72 h reaction time (7 µm). This can be explained by the Ostwald ripening process:<sup>8,9</sup> over the reaction time, the smaller particles dissolve and larger particles grow, at the same time the polydispersity also decreases when the reaction is carried out for 72 h (Figure S2D, E, and F).



Figure S2: Morphological changes of Cu particles for Cu<sub>1</sub> (lower reactant to solvent concentration) with different synthesis time: (A) 24 h (B) 48 h (C) 72 h, and for Cu<sub>7</sub> (higher reactant to solvent concentration) with different reaction time: (D) 24 h (E) 48 h (F) 72 h. The corresponding size distribution curve for each case is plotted. Scale bar: 1  $\mu$ m

## Motion study of Au@Cu<sub>7</sub> micromotors at different peroxide concentrations



Figure S3: (A) Average speed of micromotors in different peroxide concentrations in white light, without any UV light. An exemplary trajectory of a micromotor in (B) 0.5% (C) 1% and (D) 2% H<sub>2</sub>O<sub>2</sub> for 25 s is shown. The motion experiment here is conducted in just microscope light without any addition LED source.

In this study, the Au@Cu<sub>7</sub> micromotors show directed motion in visible light and the speed of the motor increases with a surge in fuel concentration which is also supported by the longer track lengths.

# UV-Visible spectroscopy of the synthesized Cu particles (Cu<sub>7</sub> and Cu<sub>0.2</sub>)

The absorption spectra of the synthesized colloidal particles are measured using a UV-Vis spectrophotometer and UV-Vis-DRS spectrometer. From both, these absorption measurements and the optical impression, we find that the optical density and the absorption intensity of the  $Cu_{0.2}$  is higher than  $Cu_7$  particles for  $1 \text{ g L}^{-1}$   $Cu_7$  and  $Cu_{0.2}$  particles dispersed

in water (Figure S4A). This can be ascribed to several origins: first, the larger particles settle down faster. Smaller copper particles ( $Cu_{0.2}$ ) show a broad absorbance in the range of 550 nm to 590 nm in both absorption graphs which could correspond to the surface-plasmon absorbance of the Cu nanoparticles.<sup>10</sup> Additionally, the smaller particles start forming networks, which drastically increases scattering (hence, the difference between S4B and C).



Figure S4: (A) UV-Visible spectrum, (B) UV-Vis diffuse reflectance spectra and (C) visual image of  $1 \text{ g L}^{-1} \text{ Cu}_7$  and  $\text{Cu}_{0.2}$  particles dispersed in water. The UV spectrum was performed using Cary 50 Scan UV-Visible spectrophotometer, UV-Vis-DRS spectra was performed using Cary 5000 absorption spectrometer with external DRA attachment using an integrated sphere.

The absorbance for wavelengths larger than 600 nm of  $\text{Cu}_{0.2}$  particles using a normal UV-Vis spectrometer is very high compared to the absorbance recorded by the UV-Vis-DRS method, this could be because our colloidal particles scatter a lot of incident light, which is only collected by the integrating sphere.

## Degradation of RhB with respect to the theoretical surface area of the particles

We calculated the theoretical surface area of  $Cu_7$  or  $Cu_{0.2}$  particles. For simplification, we considered that the particles are spherical with an average diameter of 7 µm for  $Cu_7$  particles and 0.2 µm for  $Cu_{0.2}$  particles. The theoretical density of the Cu is taken as 8.96 g cm<sup>-3</sup>. In the degradation measurement, we used 15 mg of sample and a concentration of  $1 \text{ g L}^{-1}$ , so we compared the surface areas for given amounts of sample.



Figure S5: (A) Residual concentration of dye and weight of sample taken for degradation studies as a function of particle type (Control, Cu<sub>7</sub>, Cu<sub>0.2</sub>) (B) Residual concentration of dye and total particle surface area as a function of particle type (Control, Cu<sub>7</sub>, Cu<sub>0.2</sub>). Photocatalyst concentration =  $1 \text{ g L}^{-1}$ ; Irradiation time = 30 minutes.

We found that for the same sample mass: 15 mg, the surface area of Cu<sub>7</sub> and Cu<sub>0.2</sub> particles is  $3.587 \times 10^{-4} \text{ m}^2$  and  $0.0125 \text{ m}^2$  respectively. The surface area of the smaller particles (Cu<sub>0.2</sub>) is around 35 times more than larger particles (Cu<sub>7</sub>). As the degradation of the dye depends on particle size, the residual concentration (C/C<sub>0</sub>) of the dye, the mass of the particles taken, and theoretical surface area of the given mass of particles are plotted as a function of particle size (Figure S5). As can be observed for a given mass, the Cu<sub>0.2</sub> particles with a very high surface area than Cu<sub>7</sub>, depicts better degradation.

#### Degradation of Rhodamine B in absence of UV light

As control experiment, the degradation study of RhB was also conducted under same experimental conditions, in absence of light. It can be observed that the degradation is much lower for all the cases in absence of UV light, confirming the photocatalytic behavior of the copper oxide (see Figure S6).



Figure S6: Residual RhB concentration  $(C/C_0)$  for control,  $Cu_7$ , and  $Cu_{0.2}$ , as a function of irradiation time is shown in absence of any external UV lamp.

#### **Rhodamine B degradation**

#### In absence of catalyst (control)

Even in absence of the catalyst, around 19% of RhB is degraded in 30 minutes. RhB undergoes a degradation in presence of UV light (see equation 1,3,4),<sup>11</sup> and this degradation is enhanced due to the photolysis of  $H_2O_2$ .<sup>12,13</sup> Hydroxyl radicals (OH<sup>•</sup>) are generated due to the photolysis of  $H_2O_2$  (see equation 2) which enrich the degradation process along with other formed radicals ( $O_2^{-\bullet}$  and  $OOH^{\bullet}$ ). These radicals help the dye degradation.<sup>11</sup>

$$RhB + h\nu \longrightarrow RhB^*$$
 (1)

$$2 \operatorname{H}_2 \operatorname{O}_2 + \mathrm{h}\nu \longrightarrow 4 \operatorname{OH}^{\bullet} \longrightarrow 2 \operatorname{H}_2 \operatorname{O} + \operatorname{O}_2$$

$$\tag{2}$$

$$\operatorname{RhB}^* + \operatorname{O}_2 \longrightarrow \operatorname{RhB}^{+\bullet} + \operatorname{O}_2^{-\bullet}$$
 (3)

 $O_2^{-\bullet} + H^+ \longrightarrow OOH^{\bullet}$  (4)

$$\operatorname{RhB}^{+\bullet} + (O_2^{-\bullet}/\operatorname{OOH}^{\bullet}/\operatorname{OH}^{\bullet}) \longrightarrow \operatorname{products}$$
(5)

#### In presence of catalyst ( $Cu_7$ or $Cu_{0.2}$ )

In the presence of catalyst, the degradation process is enhanced (around 77% for Cu<sub>7</sub> and around 88% for Cu<sub>0.2</sub>). The surface of the Cu particles oxidizes to Cu<sub>x</sub>O in presence of H<sub>2</sub>O<sub>2</sub>, which shows high photocatalytic activity (see XRD and SEM in Figure S5 and S6).<sup>14,15</sup> During the photodegradation process, the first step involves the separation of electrons and holes by light (see equation 8) followed by a reduction and oxidation process.<sup>16,17</sup> The photolysis of H<sub>2</sub>O<sub>2</sub> also takes place generating active radical species (see equation 9, 10, 11). The oxidative species such as OH<sup>•</sup>, O<sub>2</sub><sup>-•</sup>, and OOH<sup>•</sup> promote degradation of the dye.<sup>16,17</sup>

$$Cu + H_2O_2 + 2 H^+ \longrightarrow Cu^{2+} + 2 H_2O$$
(6)

$$Cu^{2+} + O_2 \longrightarrow Cu_xO$$
 (7)

$$Cu_xO + h\nu \longrightarrow Cu_xO(h^+) + Cu_xO(h^-)$$
 (8)

$$H_2O_2 + h\nu \longrightarrow 2 OH^{\bullet}$$
(9)

$$OH^{\bullet} + H_2O_2 \longrightarrow OOH^{\bullet} + H_2O$$
 (10)

$$OOH^{\bullet} + H_2O_2 \longrightarrow H_2O + OH^{\bullet} + O_2$$
(11)

$$O_2 + e^- \longrightarrow O_2^-$$
 (12)

$$H_2O + O_2^{-\bullet} \longrightarrow OOH^{\bullet} + OH^{-}$$
(13)

$$2 \operatorname{OOH}^{\bullet} \longrightarrow \operatorname{O}_2 + \operatorname{H}_2 \operatorname{O}_2 \tag{14}$$

$$H_2O + h^+ \longrightarrow OH^{\bullet} + H^+$$
 (15)

$$OH^- + h^+ \longrightarrow OH^{\bullet}$$
 (16)

$$RhB + h^+ \longrightarrow RhB^+$$
 (17)

 $RhB^{+\bullet} + (O_2^{-\bullet}/OOH^{\bullet}/OH^{\bullet}) \longrightarrow intermediate products \longrightarrow degraded products (18)$ 

# Oxidation of Cu particles to $\mathrm{Cu_xO}$ by different concentrations of $\mathrm{H_2O_2}$



Figure S7: SEM image of Cu<sub>7</sub> particles (A) without  $H_2O_2$  treatment and after exposure to (B) 1 %  $H_2O_2$  (C) 5 %  $H_2O_2$  (D) 10 %  $H_2O_2$ . Insets are the enlarged view of the corresponding SEM images. The oxidation of Cu to its oxides result in surface inhomogeneities such as the appearance of flake-like structure which increases with an increase in peroxide concentration. Scale bar: 2 µm



Figure S8: XRD pattern of pure Cu particles before and after treatment with  $10 \% H_2O_2$  indicating the formation of Cu<sub>x</sub>O.<sup>18,19</sup>

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