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Journal Name

ARTICLE

Sulfuric disazo dye stabilized copper nanoparticle composite mixture: Synthesis and Characterization

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Copper nanoparticle-sulfuric disazo dye (Cu-SD1) composite was synthesized by using sol-gel method. Cu-SD1 nanocomposite formation was monitored by ultraviolet–visible spectroscopy (UV-Vis). The acquired experimental results, suggested that 8 h of reaction is needed for synthesis Cu⁰ nanoparticles. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were employed to elucidate the morphology of Cu-SD1 nanocomposite. It was found that, the diameter of particles size was in the range of 2 – 4 nm. The interaction of SD1 with the copper was confirmed by fourier transform infrared spectroscopy (FTIR). The peak shift of O-H and C-OH functional groups indicated the interaction between SD1 and copper nanoparticles. Besides that, azo group (N=N) peaks was suppressed after the formation of nanocomposite, suggesting strong linkage was formed between functional groups with copper nanoparticles. The surface composition and chemical states of as-synthesis copper nanoparticles was elucidated by X-ray photoelectron spectroscopy (XPS). Additionally, the photo switching of composites was elucidated in solution state. It was found that, Cu-SD1 nanocomposite having fast switching response compared to parent SD1 in solution.

Introduction

The synthesis of metal nanoparticles has been studied extensively in the past few decades because of their unique properties and potential applications in physical, chemical, electronic, sensors, batteries and resonance imaging fields^{1–4}. Among them, copper nanoparticles attracted enormous attention due to catalytic, optical, electrical, antifungal application and low cost^{5–8}. Different wet chemical methods have been developed for the synthesis of metal nanoparticles, such as chemical reduction, sol-gel, photochemical, hydrothermal, solvothermal, electrochemical etc^{9–12}. Sol gel method is one of the most useful methods for the synthesis of copper nanoparticles¹³, due to its simplicity ease in controlling particle size, its low temperature and cost^{6, 14, 15}. In most of the cases, a stabilizer was used to prevent particle growth and agglomeration such as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) etc. Huang and Kim¹⁶ reported shape control synthesis of gold nanoparticle using photoresponsive material as stabilizer via modified seed growth method. To the best of our knowledge, the use of azobenzene as a stabilizer in the synthesis of copper nanoparticle and its fast photoswitching

behavior has never been reported. There has been some previous work done with nanoparticles and their effect on the photoconversion of photochromes^{17, 18}. Nishi, et al.¹⁷ synthesized various sized gold nanoparticles covered with photochromic polymers consisting of diarylethenes with various structures and it was found that the gold nanoparticles covered with the photochromic polymers enhanced the rate of the photocycloreversion reaction of the chromophores through the reversible changes in localized surface plasmon resonance (LSPR) absorption around the particle. It was shown by Diaz, et al.¹⁸ that by incorporating multiple photochromic diheteroarylethene groups around the semiconductor core can be used to devise photoswitchable quantum dots (psQDs). Azobenzene, a photochromic dyes which can convert from the *trans* to the *cis* form by light of short wavelength (e.g., 380 nm) and from the *cis* to the *trans* state by light of longer wavelength (e.g., 450 nm) or by thermal relaxation. Azobenzene is very important in photonic fields as it has the fast switching property^{19–21}. Copper nanoparticle modified azobenzene might enhance the switching behavior of the composite which can be used as fast switching devices. In this context, the aim of this work is to study the formation of copper nanoparticle incorporated azo composite via *in-situ* sol-gel method at ambient condition. The formation of copper nanoparticles in azo dye was studied by using UV-Vis spectrophotometer. The composite was characterized by using, TEM, AFM, FTIR and XPS. The effect of nanoparticles on composite and on their optical properties was elucidated.

Experimental section

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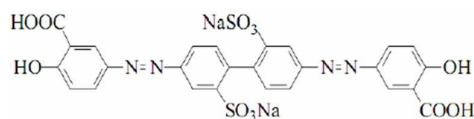
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Materials

Copper (II) chloride salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), potassium bromide (KBr), ethanol (99.9%) were obtained from Sigma-Aldrich (Malaysia) Sdn. Bhd. and used without further purification. Azo dye material, sulfuric disazo dye (SD1) was obtained from Di-Nippon Ink Japan. The molecular structure of SD1 was demonstrated at scheme 1.



Scheme 1: molecular structure of SD1

Preparation of Cu-SD1 nanocomposite

The Cu-SD1 nanocomposite synthesis was performed in a two-necked round bottom flask (100 mL capacity) with magnetic stir at room temperature. Required amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and SD1 were dissolved in 45 mL deionized (DI) water. Subsequently, 5 mL of hydrazine monohydrate was injected drop-wise into the mixture, and the concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and SD1 were controlled at 200 mg/L and 2000 mg/L, respectively. The sol was continuously stirred for 12 h and the samples were withdrawn at different interval time. The sample was transferred into a 1 cm optical length quartz cuvette and analysed by UV-Vis (Hitachi U 1800 UV-visible spectrophotometer). The spectrum was recorded in the range of 400 - 800 nm.

Characterization of Cu-SD1 nanocomposite

FTIR analysis. To obtain dried nanocomposite, 50 mL sol was centrifuged at 10000 rpm for 30 min and the precipitated solid was collected and dried in vacuum dryer at 60 °C for 4 h. KBr pellet method was used to prepare SD1 and Cu-SD1 nanocomposite sample prior for spectrum recording. FTIR (Model: Spectrum 100, Brand: PerkinElmer) was used to analyze SD1 and Cu-SD1 nanocomposite. The spectrum was recorded in the range of 400 - 4000 cm^{-1} .

XPS analysis. The dried nanocomposite powder was compressed in a cylindrical mold with a pressure of 1 MPa to obtain disc specimen. XPS data were acquired using a PerkinElmer PHI 5400 X-ray photoelectron spectrometer. This system was equipped with a Mg X-ray source operated at 300 W (15 kV, 20 mA). The carbon (C 1s) line at 285.0 eV was used as the reference line.

TEM and AFM analysis. The particle sizes were determined by TEM using a LEO 912 AB EFTEM operating at 100 kV. The sample for TEM analysis was obtained by dispersing dried nanocomposite into 99.9% ethanol and then placing a drop of the ethanol solution on a copper grid and evaporating it in air at room temperature. Furthermore, AFM analysis of

nanocomposite was conducted using NT-MDT AFM in close contact mode.

Photo switching analysis

The dried nanocomposite powder was dissolved in the DI water and the liquid was transferred into 1 cm optical length quartz cuvette for the UV-Vis spectrum recording. The UV-Vis absorption spectrum and photo switching times were measured using Ocean Optics (HR2000+) spectrophotometer equipped with 365 nm filter.

Results and Discussion

Cu-SD1 nanocomposite formation

The formation of SD1 stabilized Cu nanoparticle was monitored by using UV-Vis spectrophotometer. Fig. 1a represents UV-Vis absorption spectra of aqueous solution of SD1 and CuCl_2 -SD1. SD1 showed the maximum absorbance at 475 nm which was shifted to 487 nm after CuCl_2 was dissolved in SD1 solution. The shift indicates the formation of Cu(II)-SD1 complex.

Fig. 1b demonstrated the UV-visible spectrum of the sol at different time of its formation. The 0 h refers to the addition of hydrazine in the precursor solution and a pale yellowish solution was observed. It can be seen that, the intensity of Cu(II)-SD1 complex peak (487 nm) was reduced with reaction progressed and it diminished after 2 h of reaction. A new peak at 520 nm after 3 h of reaction and the colour of sol turned into red, corresponding to the formation of copper nanoparticle^{6, 8, 22, 23}. The characteristic Cu^0 plasmon peak intensity was increased as the reaction time extended. The absorbance at 520 nm for all reaction times was normalized with respect to the absorbance at 8 h and plotted against time as shown in Fig. 1c. A sharp increase in the rate of copper nanoparticle formation was observed after 3 h of reaction and reached a plateau after 7 h of reaction. The concentration of copper nanoparticle was slightly dropped after 10 h of reaction and sol colour turned to deep red. This might be due to the formation of CuO. The chemical transformation of Cu^{2+} to Cu^0 appeared to be completed at 8 h of reaction time.

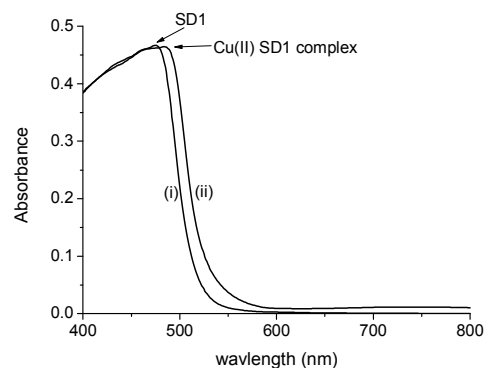


Figure 1a. UV-Vis absorbance spectra of SD1 (i), CuCl_2 in SD1 (ii).

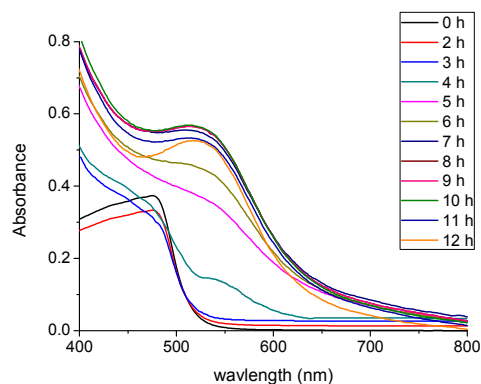


Figure 1b. UV-Vis absorbance spectra of Cu-SD1 nanocomposite in solution at various reaction times.

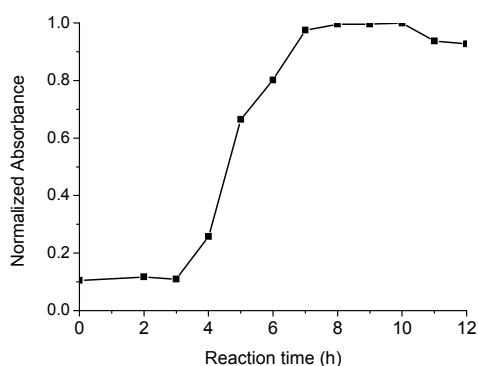


Fig 1c: Normalized absorbance of peak at ■ 520 nm.

FTIR analysis

Fig. 2a illustrates the FTIR spectra of parent SD1 and Cu-SD1 nanocomposite, recorded as the transmittance (%) versus frequency in the range of 4000-400 cm^{-1} . The spectra in Fig. 2a, demonstrate a number of absorption peaks, representing the multi-functional groups of the samples. The FTIR spectrum analysis displayed broad bands at 3700-3100 cm^{-1} , which corresponds to the hydrogen bonded O-H groups²⁴⁻³². The absorption band at 1574 cm^{-1} and 1077 cm^{-1} corresponded to phenyl ring³³⁻³⁵ and S=O²⁷ groups, respectively. Besides that, azo group (N=N) in SD1 was detected at $\sim 1460 \text{ cm}^{-1}$ region^{27, 29, 36} and C-OH group was appeared in the range of 1300-1000 cm^{-1} ²⁷. The absorption band of O-H groups of SD1 appeared at 3433 cm^{-1} and 3441 cm^{-1} before and after nanocomposite formation, respectively, showing 8 units red shift of this polar group. This shift of frequency indicates that SD1 molecules assist in coordination with copper⁷. Besides that, C-OH of SD1 at 1186 cm^{-1} was shifted to 1166 cm^{-1} after nanocomposite formed. This amount of shift indicated the coordination of copper with SD1. Such coordination might be due to the electrostatic attraction between SD1 and copper³⁷. Additionally, azo group (N=N) in SD1 intensity was drastically decreased after formation of nanocomposite which suggested the interaction of the azo group with copper nanoparticles.

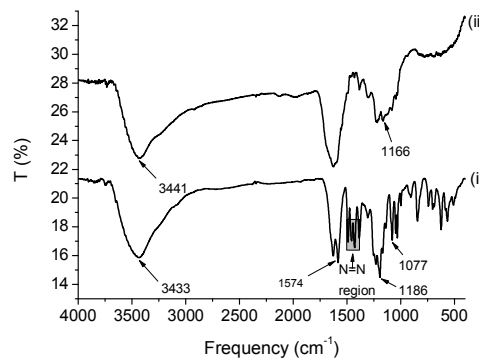
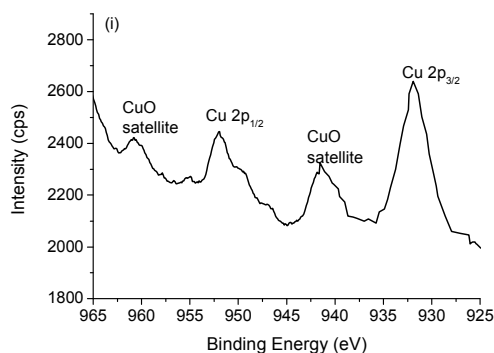


Figure 2a. FTIR spectrum of parent SD1 (i) and Cu-SD1 nanocomposite (ii).

XPS analysis

A typical XPS spectrum of Cu-SD1 nanocomposite was measured and the core level spectrum of Cu 2p is depicted in Fig. 2b-i. XPS is an effective approach for the investigation of the surface composition and chemical states of solid samples³⁸ including oxidation states of metals^{8, 23, 39, 40}. The core level spectrum and shake-up satellite line of copper (2p_{3/2} and 2p_{1/2}) were illustrated in Fig. 2b-i where the Cu 2p_{3/2} and 2p_{1/2} were assigned at ca. 932.0 and 951.9 eV, respectively, these findings were also consistent with other researchers^{41, 42}. In order to acquire a more precise knowledge of these environments, the spectrum of Cu 2p_{3/2} was fitted using a Gaussian/Lorentzian mixed function and presented in Fig. 2b-ii. The Cu 2p_{3/2} peak was fitted to a single peak at 932 eV which related to Cu⁰⁴³. At satellite regions, 2 CuO (BE 942.35 and 940.85 eV)⁴⁴ peaks were contributed. The binding energy, FWHM and area of Cu 2p_{3/2} are summarized in Table 1.



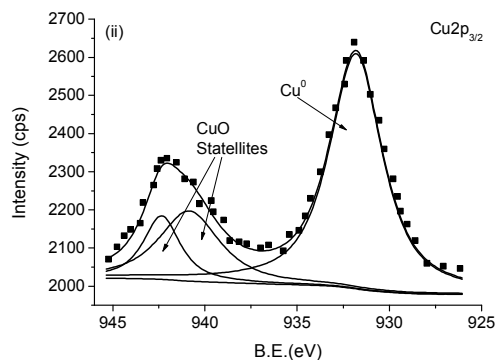


Figure 2b. XPS spectra of Cu-SD1 nanocomposite in core level regions: (i) deconvolution of Cu 2p, (ii) Gaussian/Lorentzian fitted profile of Cu $2p_{3/2}$.

Table 1. The results of deconvolution of XPS Cu $2p_{3/2}$ peaks

Binding energy (eV)	Cu phase	FWHM	Area	Percentage (%)
932.0	Cu	3.40	3083.346	65
940.85	CuO	3.90	1054.291	22
942.35	CuO	2.36	579.304	13

Morphology analysis

The morphology of Cu-SD1 nanocomposite was investigated using TEM and AFM techniques. Figs. 3a and b demonstrated the surface roughness and thickness Cu-SD1 nanocomposite in 2D and 3D topographs. It can be seen that, Cu-SD1 nanocomposite was homogeneous distributed and thickness of the sample was 16 nm, indicating the formation of multi-layer of the composite. In order further determined the size of particle, TEM technique was employed. TEM image of the Cu-SD1 nanocomposite is shown in Fig. 4. In Fig. 4a, nanocomposite was observed where nanoparticles were agglomerates on SD1 molecules. At high magnification section (Fig. 4b), fine and spherical shape copper nanoparticles were clearly seen and the diameter of particle was in the range of 2 – 4 nm.

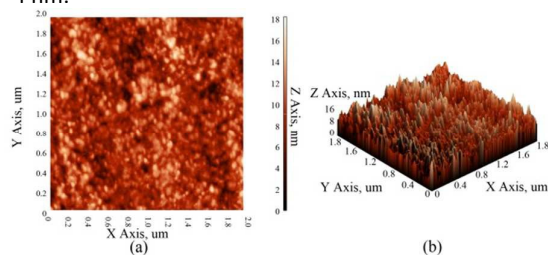


Figure 3. AFM 2D phase diagram (a) and 3D surface topography (b) of Cu-SD1 nanocomposite.

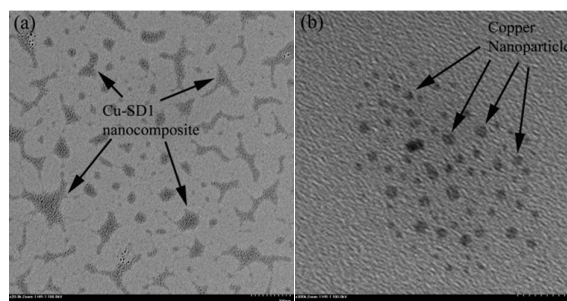


Figure 4. TEM micrograph of Cu-SD1 nanocomposite at low magnification (a), and high magnification (b).

Effect of photoswitching

Effect of photoswitching was compared between composite mixture and the parent SD1 in solution. To our surprise inclusion of copper nanoparticles makes the switching faster as compared with the SD1 in solution as shown in Fig. 5a. Initially the solutions were kept in dark. When UV light of wavelength 365 nm was passed through the solution, immediately the molecules of the light sensitive materials reoriented in the solution which can be observed through the sharp change in absorbance leading to a saturation value. When light is turned off, the molecules came back to original position faster than expected (see supplementary figure S1) and the time required for the SD1 and nanoparticle modified SD1 photoconversion lifetime were 31 s and 3 s, respectively. Cu-SD1 nanocomposite having 10 times faster response as compared to parent SD1. This might be due to the hydrogen bonding between copper nanoparticle and –COOH and –OH (electron donating or withdrawing groups) in Cu-SD1 nanocomposite that enhanced the electron transports which leads faster reconversion molecular structure⁴⁵.

To check the stability of the composite mixture few cycles were repeated as shown in Fig. 5b. One can see that on and off times remains the same throughout the cycles emphasizing the stability of the system. Figure 5c shows the UV on times recorded as a function of different intensity. It is obvious that as intensity increases UV ON time becomes faster which makes them suitable candidates for fast photoswitching devices. Grey area corresponds to the UV ON. One can also see the similar behavior on UV Off data where molecules return back to the original configuration faster than expected (See supplementary figure S2). Figure 5d is extracted from Fig. 5c where one can see similar values for UV ON with respect to different UV intensities. One can conclude from this graph that Cu nanoparticles enabled SD1 shows faster photoconversion time as we increase the intensity and after the saturation there is no effect of intensity on them.

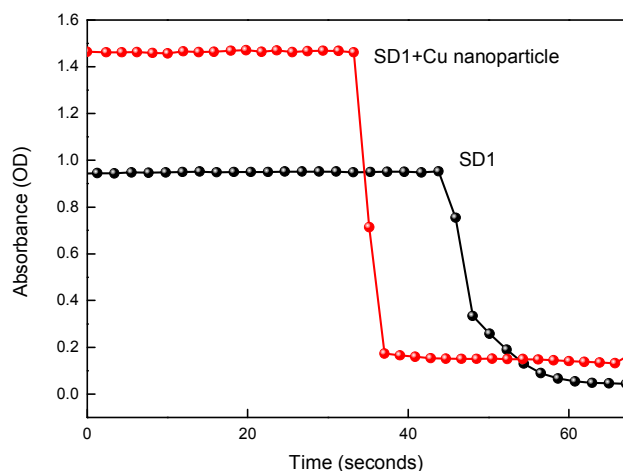


Figure 5a. UV On effect of Cu-SD1 nanocomposite and parent SD1.

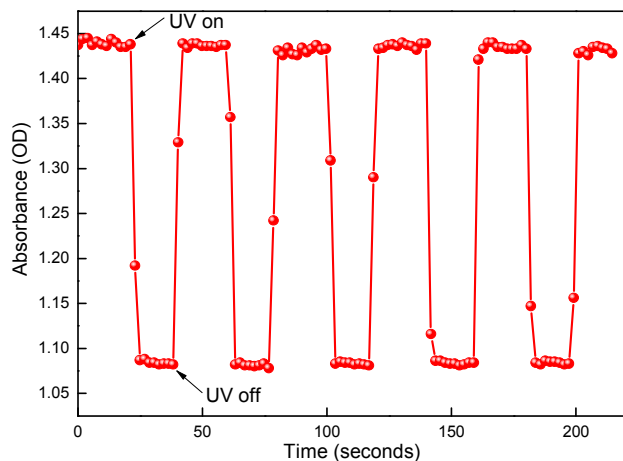


Figure 5b. Stability of Cu-SD1 nanocomposite with several on and off cycles.

Although one can't predict the exact behavior for this result but we speculate the following as shown in Scheme 2. It can be observed that, after the UV light shine, the SD1 compound was transformed into *cis*-isomer (scheme 2-(i)). The shape of the molecule was slightly reoriented therefore after the UV off it can return to *trans*-isomer in short time. As seen in scheme 2-(ii), nanoparticle is bonded to SD1 compound through hydrogen bond as suggested by FTIR results (Fig. 2a). The additional of the nanoparticle around the SD1 structure induced the shape of molecule and after UV shine it was almost unchanged, in other words shape is just slightly reoriented. This phenomenon explained that, the fast switching behavior of modified SD1 is shorter than the parent SD1.

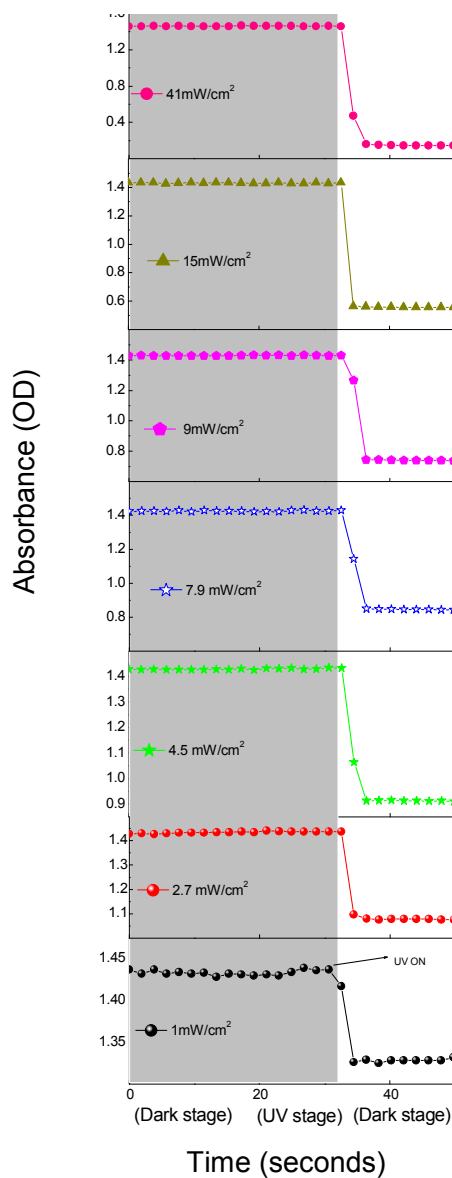


Figure 5c. UV on time at different UV intensity.

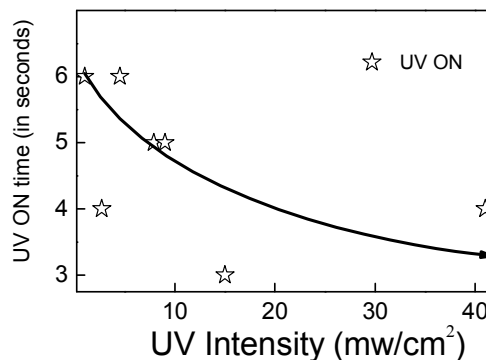
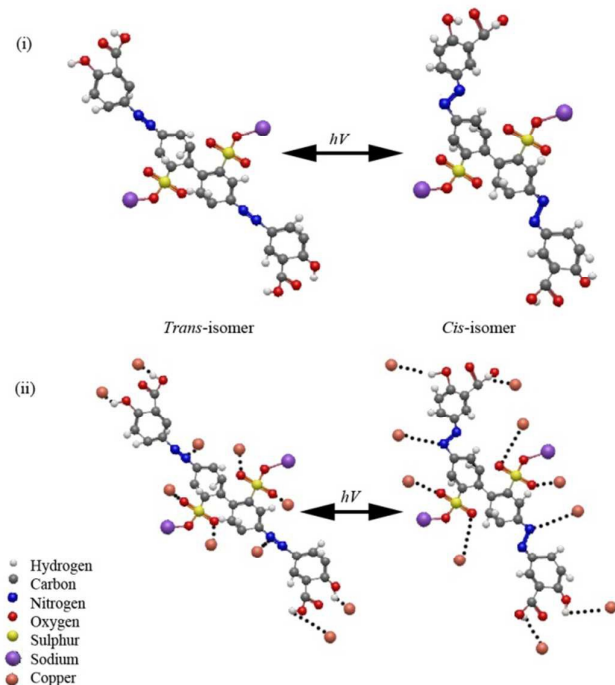


Figure 5d. Effect of UV intensity on UV on time extracted from Figure 5c.

Present study elucidate that the nanoparticle incorporated light sensitive molecules might be used in fast photoswitching applications in near future due to their advantage in bringing the molecules back to the original configuration (*trans-cis-trans*) quickly. Study concerning the solid surface is underway and will be reported in due course.



Scheme 2. Re-orientation of *trans-cis-trans* of Cu-SD1 nanocomposite before and after UV shine.

Conclusions

The sulfuric disazo dye stabilized copper nanocomposite was prepared via sol gel method. The formation of nanocomposite was monitored by UV-Vis spectrophotometer and it was found that 8 h of reaction is needed to synthesis Cu⁰ nanocomposite. Copper and copper oxide phases were found in the nanocomposite via XPS techniques. Furthermore, XPS reveal the composition inside the composite powder, it was found that 65% is copper species and the rest is copper oxide species. FTIR results indicates that, copper nanoparticles having chemical interaction with surface functional groups of SD1 such as phenyl ring, S=O, -OH, C-OH and N=N groups. The size of the nanoparticles was visualized by TEM and the diameter of the particle was in the range of 2 – 4 nm. The on-off effect of Cu-SD1 nanocomposite was elucidated and Cu-SD1 nanocomposite having faster switching performance compared to parent SD1. The mechanism model of the *trans-cis-trans* molecule re-orientation of Cu-SD1 nanocomposite was proposed.

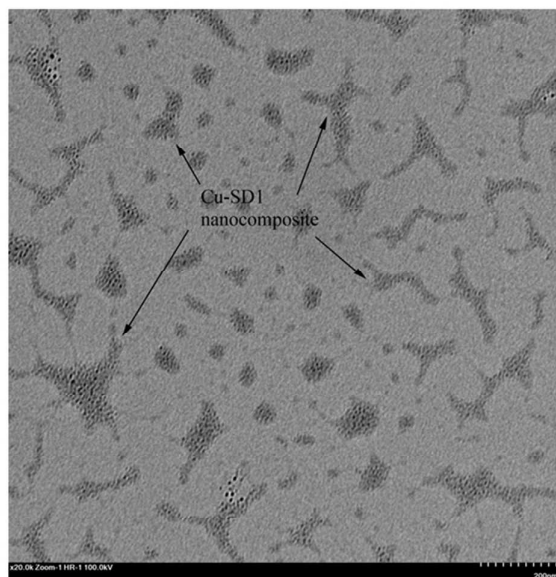
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Graphical abstract**Cu-SD1 Nanocomposite**