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One-pot green synthesis of copper(I) iodide nanocrystallites using red cabbage extract and its application for the colorimetric sensing of elemental mercury vapor

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CuI nanocrystallites were synthesized via a red cabbage-mediated one-pot method at ambient temperature. Red cabbage extract functioned as reducing agent, converting Cu(II) into Cu(I) and as a capping agent stabilizing the CuI nanocrystallites. The resulting material was characterized using X-ray powder diffraction, scanning electron microscopy with energy dispersive X-ray spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, and UV-Vis spectroscopy. It was also characterized as a solid-state colorimetric sensing reagent for elemental Hg^0 vapor through a smartphone camera-based digital image analysis. The sensor exhibited a colorimetric response to Hg^0 vapor at a concentration range of 11.4–32.6 ppb_v Hg^0 with detection limit of 3.9 ppb_v Hg^0, indicating the capability of the sensor to detect the current threshold exposure limit set by the World Health Organization (6.1 ppb_v). The sensor performance characteristics confirm that the green-synthesized CuI can be a suitable colorimetric sensitive layer for detection of Hg^0 vapor.

Keywords: green chemistry, cuprous iodide, smartphone camera, colorimetric sensor, mercury vapor

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INTRODUCTION

Copper(I) iodide (CuI) has been recognized as a versatile functional material, finding applications in diverse fields, including organic electronics, optoelectronics, semiconductors, and transparent thermoelectrics [1–3]. It is also an efficient catalyst in organic synthesis [4–6], and a potential protective agent against bacterial and viral infections [7, 8]. It has likewise been employed as a solid-state chromogenic sensing material for Hg^0 vapor [9, 10].

CuI has been prepared through two basic chemical routes: iodination and precipitation reaction. Iodination is a gas-solid phase reaction, involving iodine vapor and a thin film of copper or a copper salt [11, 12]. Precipitation is usually conducted in a solution medium containing copper salt and potassium iodide, together with a reducing agent and a stabilizing agent [13, 14]. These methods are coupled with physical methods to generate nanostructured CuI.

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In order to make the synthesis of CuI cost-effective and environmental-friendly, green strategies were applied. A solvent-free approach involved a mechanochemical technique applied in an all solid state precipitation reaction [15]. Green reagents, such as plant or fruit extracts, were used as the reducing agent and the stabilizing agent in the precipitation method. Among the reagents used in the green synthesis of copper(I) iodide were sugar beet juice [16], pomegranate juice [17] and kidney bean extract [7]. Plant-derived reagents have provided green alternatives in the synthesis of nanomaterials [18].

In this study, we report a green synthesis of CuI via a red cabbage extract-mediated one-pot method. The synthesized nanocrystalline CuI was characterized and explored as a colorimetric reagent for the sensing of mercury vapor (Hg^0). The sensing reaction involved the formation of the red-orange cupro-tetraiodo-mercuriate complex when Hg reacts with CuI [19] according to Equation (1):

$$4CuI + Hg^0 \rightarrow Cu_2[HgI_4] + 2Cu^0 \qquad (1)$$

This color reaction has been previously applied to detect Hg vapor in a gas mixture, such as air [9] or Hg vapor generated from mercury species in samples such as fish, soil, sediment and gold mining residues [10]. Color measurement was realized using digital imaging devices, such as the smartphone camera. The measurement of elemental mercury vapor is of particular importance due to the inherent toxic effect of mercury to human health and the environment.

EXPERIMENTAL SECTION

One-pot synthesis. Reagent-grade $CuSO_4$ and KI were procured from Sigma-Aldrich and used without further purification. $CuSO_4$ solution (0.12 M) was slowly mixed under magnetic stirring with red cabbage extract which was prepared by boiling 100 g of cut red cabbage in 200 mL water. KI solution (0.12 M) was then added dropwise and the mixture was continuously stirred for 30 min under ambient temperature. The resulting dark gray precipitate was filtered and washed repeatedly with ultrapure water and ethanol to remove impurities. The CuI precipitate was dried in an oven at 50°C. This procedure was carried out using different volumes of red cabbage extract: 1.0, 5.0, 10.0, and 20.0 mL.

Characterization. The synthesized CuI was characterized using a X-ray powder diffraction (XRD) analyzer (Maxima XRD-7000, Shimadzu), a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy analyzer (EDS) (JSM-5300, JEOL), a differential scanning calorimeter (DSC) (DSC 4000, Perkin Elmer), a thermal gravimetric analyzer (TGA) (TGA 4000, Perkin Elmer), and UV-Vis spectrophotometer (Lambda 35, Perkin Elmer).

Colorimetric sensing of Hg^0. The sensing characteristics of the synthesized CuI was evaluated using the procedures in a previous publication [9]. Hg^0 colorimetric paper sensor was prepared by mixing the synthesized CuI with a solution of polystyrene (PS, average MW 280,000, Sigma-Aldrich) in tetrahydrofuran (THF, RCI Labscan). The resultant emulsion was applied evenly onto a chromatography paper (Whatman, 3MM CHR) using a rolling glass rod. It was then dried at 40°C in an oven for 30 min to yield a CuI/PS sensing composite on a cellulosic substrate. It was then cut into square pieces (10×10 mm^2) and set onto a glass slide for easier handling during the experiments.

The colorimetric paper sensor was placed in a glass vial, and different volumes of standard Hg-air mixture was injected into the vial. The standard gas mixture was generated using the “bell-jar” method [20, 21]. This procedure produced in the vial a gas phase with Hg^0 vapor concentrations ranging from 3.4 to 104 ppb_v. The actual Hg^0 concentration in the vapor phase was determined using Lumex RA915M Mercury Analyzer.

The intensity of the color developed in the paper sensor was measured by capturing the digital images of the sensor using a smartphone camera (16 megapixels, Samsung S6 Edge) in a light box set up [9]. The acquired images of the paper sensors were digitized to RGB (red-green-blue) color values in a computer using ImageJ 1.49h software (National Institute of Health, USA). The sensor response was calculated as percent change (%Δ) in the R, G, or B values before and after exposure to Hg^0 of the paper sensors where X is the mean color value corresponding to R, G or B (Equation 2).

$$\%\Delta X = \frac{X_{\text{before exposure}} - X_{\text{after exposure}}}{X_{\text{before exposure}}} * 100 \qquad (2)$$

RESULTS AND DISCUSSION

Characterization of green-synthesized CuI nanocrystallites. The formation of CuI was confirmed by the X-ray diffraction pattern obtained from the synthesized product (Fig. 1). The XRD pattern corresponded to a face-centered cubic (fcc) structure of γ-CuI (JCPDS no. 06-0246, space group: F-43m) [2, 3, 15]. The absence of diffraction peaks due to impurities such as Cu or Cu oxides proved the high phase purity of the synthesized material. The average crystallite size calculated using Scherer equation [1] ranged from 85 nm to 92 nm, depending on the volume of the plant extract used. The CuI nanocrystallites obtained using 5.0 mL red cabbage extract had the largest size at 92 nm, while those obtained from 10.0 and 20.0 mL had the smallest size at 85 nm.

The SEM images of the synthesized products revealed that the CuI powder is made up mostly of triangular micro- and nanostructures that are clustered and agglomerated as shown in Fig. 2. These triangular structures were smaller in size when greater amount of red cabbage extract used during its synthesis. The EDS elemental analysis (Fig. 3) verified the presence of Cu and I as the major constituents in the synthesized products. It also revealed the presence of C and O where the atomic percentage increased as more red cabbage extract was employed in the synthesis. The identified traces of C and O could be due to the anthocyanin present in the red cabbage extract acting as capping agents for the CuI structures. Red cabbage is known to be rich in anthocyanins that can both act as a reducing agent and capping agent in the formation of CuI [3, 16]. Figure 4 illustrates the possible interaction of the anthocyanin molecules with CuI particles. A probable mechanism of CuI micro/nanostructures formation can be

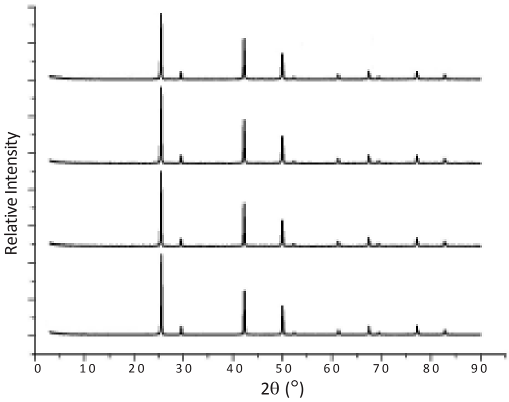

Figure 1. XRD pattern of the CuI product synthesized with 1.0, 5.0, 10.0, and 20.0 mL of red cabbage extract.

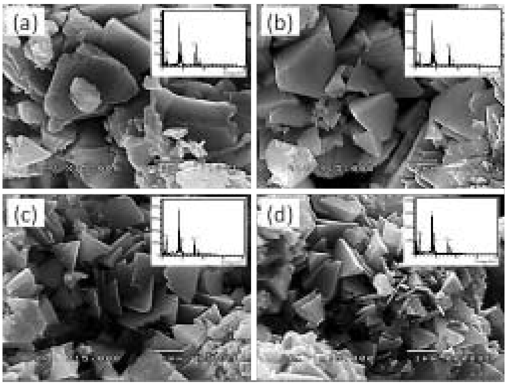

Figure 2. SEM images of the CuI products synthesized using (a) 1, (b) 5, (c) 10, and (d) 20 mL of red cabbage extract. Inset plots are the respective EDS profile of CuI products (Magnification is 15 kX).

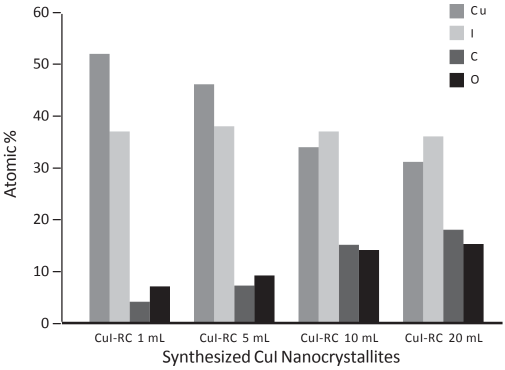

Figure 3. Summary of EDS analysis profile showing atomic percentage of Cu, I, C, and O in the synthesized products using different volumes of red cabbage extract.

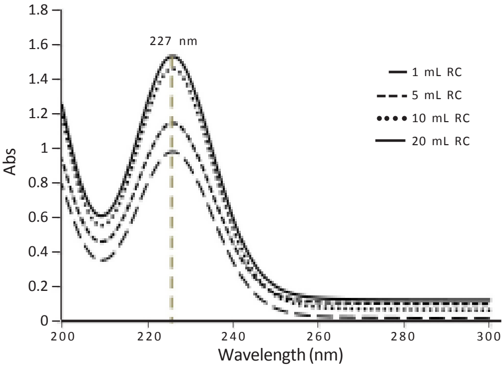

Figure 5. UV-vis spectrum of the CuI nanocrystallites synthesized with 1, 5, 10, and and 20 mL of red cabbage extract.

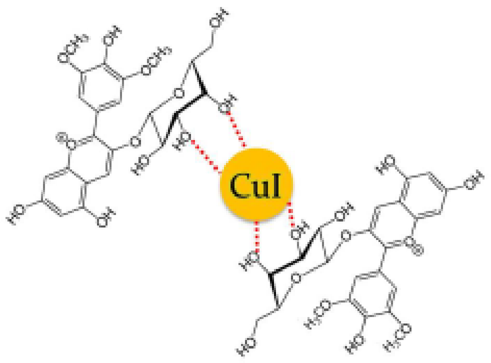

Figure 4. Illustration of the capping agent role of anthocyanin in CuI crystallite.

comparable to the proposed mechanism with glucose [22] since anthocyanin molecules contain glucose subunit [23].

The synthesized CuI nanocrystallites exhibited UV-Vis absorbance spectra which featured an absorption peaks at ~227 nm (Fig. 5). No significant difference in the absorption peak wavelength was seen among the spectra of the products which supports the comparable crystallite sizes computed from the XRD data. The absorption peak of nanoparticles is known to be influenced by the particle size, occurring at a lower wavelength for smaller particles [1]. The observed absorption maxima occurred at a wavelength higher than that observed from CuI synthesized from pomegranate juice (~210 nm), wherein smaller particles (35–50 nm) were formed [3]. It is much lower than the peak wavelength observed with bulk CuI (400 nm) [3, 16]. The absorbance of the synthesized CuI was found to increase when the amount of the red cabbage extract was increased. This behavior can be attributed to an increase in the amount of the synthesized CuI products solubilized due to the capping agent.

The DSC curves (Fig. 6A) of the synthesized CuI nanocrystallites displayed two distinct sharp peaks centered at ~380°C and ~403°C which can be assigned for the phase transition of γ-CuI to β-CuI and β-CuI to α-CuI phases, respectively [1, 13, 24]. These DSC peaks of the synthesized CuI products referring to phase transitions are comparable to that obtained from the bulk CuI [13, 25]. TGA curves of the synthesized CuI (Fig. 6B) showed major weight loss occurring beyond 568–592°C, which corresponds to the melting temperature of CuI [26]. These major weight loss zones which extend up to 745–776°C can be associated with the loss of iodine in the samples [1, 12].

Hg^0 vapor-sensing performance of CuI nanocrystallites. The colorimetric sensing reaction for gaseous elemental mercury using

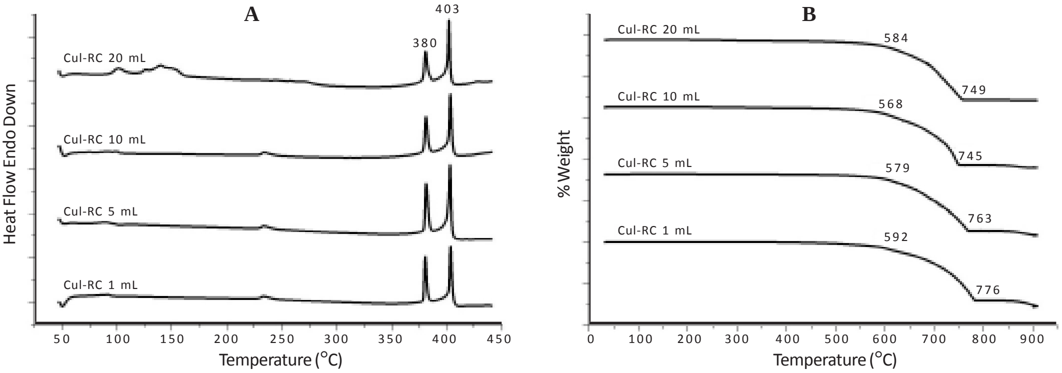

Figure 6. DSC (A) and TGA (B) curves of the synthesized CuI with different volumes of red cabbage extract.

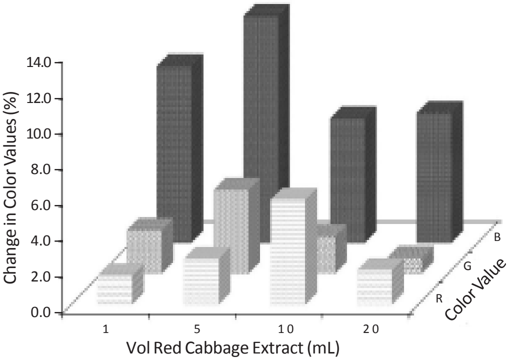

Figure 7. Sensor response in percent change RGB values for the synthesized CuI nanocrystallites with different volumes of red cabbage extract.

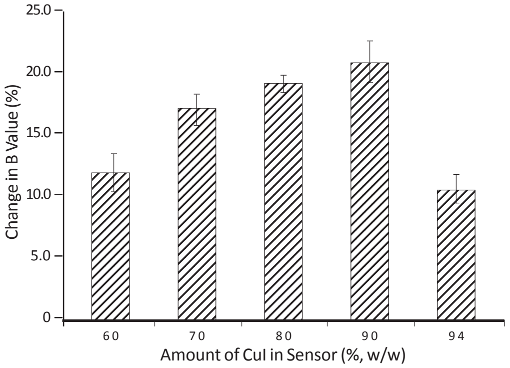

Figure 8. Effect of the amount of CuI in the colorimetric paper sensing reagent phase on the change in blue response to 45 ppb$_v$ Hg^0 vapor. Standard error bars indicate three replicate.

CuI can be conducted only in the gas-solid phase, since the reactants are not soluble in the common aqueous medium. Following our previous work on colorimetric sensing of Hg^0 vapor [9], the green-synthesized CuI nanocrystallites was immobilized using a polystyrene binder and supported on a cellulosic substrate. Polystyrene has been proven to be an effective binder for CuI-based colorimetric paper sensor, showing the highest sensor response compared with other polymer binders.

When exposed to Hg^0 vapor, the immobilized CuI nanocrystallites exhibited a color variation from very pale gray to red-orange. This color change was measured using digital image colorimetry based on a smartphone camera. The digital image captured by the camera was analyzed in the RGB color space. The exposure of the paper sensor to Hg^0 vapor produced distinction in the color values of R, G, and B channels generated from digital image analysis using Image J. The greatest sensitivity to the color change was observed in the B value (Fig. 7) which was consequently used as the sensor response. The color change was found to vary with the amount of red cabbage extract used in the synthesis of CuI. Highest sensor response (in the B value scale) was observed with the sensor prepared from CuI nanocrystallites synthesized with 5 mL red cabbage extract.

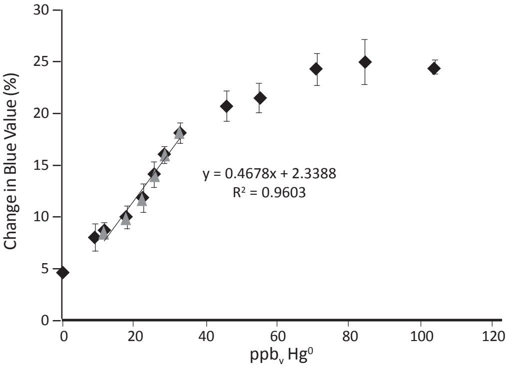

Figure 9. Change in the blue-based response of CuI nanocrystallites-based colorimetric sensor as a function of the mercury vapor concentration.

Recovery tests on Hg^0 in air samples (n = 5)

Sample	Added concentration (ppb_v Hg^0)	Recovered concentration (ppb_v Hg^0, mean ± S.D.)	Mean percent recovery
1	20.8	21.4 ± 1.8	103 ± 8.6
2	22.9	22.6 ± 1.4	99 ± 6.0
3	30.8	31.1 ± 1.1	101 ± 4.2

The sensor response was also dependent on the percentage of CuI in the sensing reagent phase. The maximum sensitivity was obtained from a 90% CuI composition (w/w, CuI:polystyrene) (Fig. 8). The high concentration of CuI nanocrystallites in the reagent phase favored the formation of a colored $Cu_2[HgI_4]$ complex subsequently producing high color intensity in the colorimetric sensing paper. The observed decrease in the sensor response at 94% CuI was due to the unstable sensing phase which cracked upon drying.

The sensor response varied with concentration of Hg^0 vapor. As seen in Fig. 9, the best linear behavior (r^2 = 0.9603) was established in the concentration range of 11.4–32.6 ppb_v Hg^0 vapor. Beyond this range, there was only a small variation in the response which caused a lower sensitivity. The sensor exhibited very good reproducibility, showing a relative standard deviation ranging from 5.1% to 10.0%. The limit of detection was calculated based on $3sd_{blank}$/slope to be 3.9 ppb_v Hg^0.

The sensor exhibited a highly satisfactory analytical performance in recovery tests using spiked air samples (Table). The performance of the sensor indicates the promising sensor application for the green-synthesized CuI, particularly for an environmentally importance such as Hg^0 vapor.

CONCLUSION

Triangular nanocyrstallites of γ-CuI was synthesized using a one-pot method at ambient temperature. The red cabbage extract functioned as reducing agent and capping agent in the formation of the nanocrystallites products. XRD data confirmed the formation of CuI, and calculations showed that the sizes of the nanoparticles ranged from 85 nm to 92 nm. The synthesis was environment-friendly since it solvent-free, straightforward, and one-pot. The synthesized CuI could be used as a colorimetric sensor for Hg^0 vapor concentrations as low as 3.9 ppb_v. CuI was immobilized on a cellulosic substrate using polystyrene as binder, and a smartphone camera was used to quantify the variation of the color upon exposure to Hg^0 vapor. This sensing technique can be applied for monitoring exposure levels to Hg^0 vapor, since the threshold exposure limit set by the World Health Organization is 6.1 ppb_v [27].

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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