Novel graphene based photocatalyst glass coating for organic removal under solar light

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Abstract

A novel hybrid multifunctional nanocomposite (GO-COOH-CuS-Ag) was synthesized by integrating carboxylic acid functionalised graphene oxide (GO-COOH) sheets, silver (Ag) nanoparticles and copper sulfide (CuS) nanoflakes via a facile method at room temperature. The crystal phase, optical properties and morphology of obtained composite were characterized using transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and UV-vis diffuse reflectance spectra (DRS). The as-synthesized GO-COOH-CuS-Ag nanocomposites were transformed and applied on glass via glass coating method aiming to facilitate their practical applications on photodegradation of emerging organic contaminants (EOCs) under solar light irradiation. Results demonstrated that the glass coatings had excellent photodegradation and antibacterial performance with good stability and repeatability. It was also found that synergistic reaction existed among CuS, Ag and

GO-COOH. This study concludes that the immobilization of multifunctional GO-COOH-CuS-Ag nanocomposite can be a promising technology for organic matter removal due to its highly efficient performance and non-recycling issue.

Keywords: GO-COOH-CuS-Ag nanocomposite; glass coating; photodegradation and antibacterial performance

Introduction

Recently, semiconductor-mediated heterogeneous photocatalysis has gained its recognition as an effective treatment method for the emerging organic contaminant (EOCs) removal from wastewater. The advantages of such technology include higher reaction rate for pollutant removal, complete mineralisation of the contaminants into harmless substances, e.g. water and carbon dioxide, and most importantly employment of non-hazardous and economical materials – semiconductors[1]. These photocatalysts are commonly applied in fine-powder form for various environmental applications[1, 2]. The problem associated with such application lies in propensity of powdered nano-particles to cluster and agglomerate as suspension in aqueous solution[3], which may reduce the efficiency of photo-catalytic performance and induce the difficulty in recovery, recycling and isolating these nanoparticles. Coating those fine-powder nanoparticles onto common glass slides is a method to solve this problem[4, 5]. Moreover, the coating industry has been driven to seek new technologies and materials to improve the efficiency of coatings by economic benefits and growing environmental concerns.

Coating is usually used to improve the surface properties of a substrate, corrosion resistance, wettability and adhesion[6], for example, Prasai et al. (2012) have demonstrated that using graphene as a corrosive protective coating can inhibit or control the rate of corrosion between a metal and a corrosive environment[7]. In addition, researchers have paid more attention on the photocatalytic ability improvement using coating. For example, Wang et al. (2012) have shown that the TiO_2-graphene coated culture dishes had enhanced photocatalytic ability for gas-phase acetone degradation under UV light irradiation[8] and Kamegawa et al (2010) have studied theat graphene coating of TiO_2 can enhance the decomposition of 2-propanol in water compared with unmodified samples[9].

As a narrow band gap new semiconductor, hexagonal CuS has an effective catalytic property under visible light[10]. Graphene and its derivatives can enhance the electron transfer rate, so materials like GO-COOH-CuS, RGO-CuS, and G-ZnS/CuS can all show excellent photocatalytic abilities[11] [12, 13]. It is hypothesized in this study that the performance and stability of GO-COOH-CuS can be enhanced with glass coating technology thus facilitate its practical application in wastewater treatment.

In short, this study synthesized a hybrid multifunctional nanocomposite (GO-COOH-CuS-Ag) glass coating via a facile method by integrating copper sulfide (CuS) nanoflakes, carboxylic acid functionalised graphene oxide (GO-COOH) sheets, and silver (Ag) nanoparticles, with an aim to enhance their EOCs photodegradation under solar light irradiation.

Material and methods

1 Materials

Natural graphite (SPI) was purchased from Bay Carbon Company (USA). Sodium nitrate ($NaNO_3$, 99%) potassium permanganate ($KMnO_4$, 99%), hydrogen peroxide (H_2O_2, 35%), concentrated sulfuric acid (36.5%), hydrochloric acid (35%), nitric acid (HNO_3), chloroacetic acid (CH_3COOCl, 99%), sodium hydroxide, copper ethyl xanthate [$(CH_3CH_2OCS)_2Cu$], silver nitrate ($AgNO_3$, 99%), and Methylene Blue (MB, 99%) were purchased from Sigma-Aldrich. Toluene, acetone and ethanol (absolute) were purchased from Merck Ltd (Singapore). Dipropylene glycol monomethyl ether (DPM, 4.5 wt%, Disperbyk 180), polyvinyl alcohol (PVA, Sigma-Aldrich). All the reagents were used as received without further purification.

2 Synthesis of GO-COOH nanosheets, CuS nanoflakes， and Ag nanoparticles

GO was synthesized in accordance to the modified Hummers' method[16]. The final GO product was then used to synthesize the carboxylic acid functionalised graphene oxide (GO-COOH) using pervious reported method[11]. Hexagonal CuS nanosflakes were synthesized in a solution phase via simple wet chemical method via hydrothermal reaction[17]. In a typical process, 306 mg (1mmol) of copper ethyl xanthate [$(CH_3CH_2OCS)_2Cu$] was added to 20 mL of oleylamine and the mixture was heated to 250℃ in an oil bath and incubated at this temperature for 2 hours with nitrogen supplied at headspace, and finally cooled down to ambient conditions. 96 mg of CuS nanoflakes (1 mmol) was then obtained. The product was centrifuged and washed twice with ethanol. The precipitate was then re-dissolved and kept in toluene for further usage. The synthesis method of Ag nanoparticles was similar to that of CuS[17]. Oleylamine-capped Ag nanoparticles were synthesized by reducing silver nitrate in toluene, as previously mentioned[17]. Briefly, 170 mg (1mmol) of silver nitrate was added to 4 mL of oleylamine and 50 mL of toluene, and the mixture was heated to 200℃ under a constant flow of nitrogen gas at headspace. The mixture was maintained at this temperature for 6 hours and cooled down to ambient conditions. 108 mg of Ag nanoparticles (1 mmol) was then produced. The post treatment and storage methods were the same as CuS.

3. Synthesis of GO-COOH-CuS-Ag nanocomposite

The synthesis started with sonication of GO-COOH for 30 minutes. After adding Ag nanoparticles and CuS nanoflakes, the mixture was stirred for 24 hours and then centrifuged and washed twice with acetone and subsequently with ethanol. Finally, the product was kept at 4°C for 2 hours, and freeze-dried. In this synthesis, the amounts of GO-COOH and Ag were fixed at 30 mg and 20 mg, respectively. While the amounts of the main active photocatalyst, CuS were varied at 0, 15 and 30 mg in order to obtain an optimal ratio according to the materials' photodegradation performance. The composites of GO-COOH-CuS-Ag with different CuS contents were named GO-COOH-CuS-Ag-0, GO-COOH-CuS-Ag-15 and GO-COOH-CuS-Ag-30, respectively.

4. The nanocomposite GO-COOH-CuS-Ag glass coatings

According to the preliminary photodegradation results, GO-COOH-CuS-Ag-15 had the best photodegradation performance (refer to the results section). Three final glass coating products were therefore fabricated and coated with varying mass (50mg, 70mg and 100mg) of GO-COOH-CuS-Ag-15, namely 50 GCCA-15, 70 GCCA-15 and 100 GCCA-15 respectively. The powdered composites were first added into mixtures of 95% Dipropylene Glycol Monomethyl Ether (DPM) with different amounts of 4.5% wt. BYK as shown in Table 1. The mixtures were sonicated for 6*h* and then for another 2*h* after the addition of alumina-silica gel [18, 19].

Table 1. Summary of Dip-coating compositions

Material/Condition	**GO-COOH-CuS-Ag (mg)**	**BYK (µL)**	**DPM (mL)**	**Alumina Silica Gel (mL)**
Final glass coating product	50	5	0.5	0.5
	70	7		
	100	10		

The resulting sol-gel mixture was then coated onto glass slides using dip coating method[20]. Finally, the coated glass slides were air-dried naturally for 2 days before annealing in the furnace at 110 ºC for 6 hours with annealing rate of 3.67 ºC/min. Triplicates were prepared for water contact angle (WCA) tests, characterization and photo-degradation experiment.

5. Characterizations

The morphology of the as-synthesized samples was evaluated by field emission scanning electron microscopy (FESEM, JEOL 7600F). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out by using a JEOL 2010-H TEM microscope. The UV–vis absorption spectra of the 0.1 mg mL^{-1} dispersion solution were measured by using an Evolution 300 spectrophotometer under room temperature. Total organic carbon (TOC) was measured using a TOC analyzer (TOC-L CPH/CPN; Shimadzu, Kyoto, Japan).

6. Photocatalytic degradation of MB under solar irradiation

In order to find the optimal ratio of CuS among the three nanocomposite GCCA-0, GCCA-15 and GCCA-30. MB photodegradation as a pre-screening method was conducted under a solar simulator. Before commencement of irradiation, the reaction suspension containing organic pollutants 100 mg L^{-1} MB and 1g L^{-1}photocatalysts were stirred in the dark for 30min to achieve adsorption equilibrium.

Selected GCCA was used to carry out photo-degradation of 100 mg L^{-1} Methylene Blue (MB) dye under simulated solar light from a 300W Xenon lamp. The coated glass slides were arranged and placed inside of the solar simulator. During the allocated time intervals, the concentration of MB was measured with a UV–Vis spectrometer to determine the degradation efficiency.

Results and discussion

Structural and morphological analysis

FESEM and TEM were employed to characterize the microstructure and morphology of the GO-COOH-CuS-Ag nanocomposite. Both FESEM and TEM images proved that GO-COOH sheets, CuS nanoflakes, Ag nanoparticles, as well as GO-COOH-CuS-Ag nanocomposites were successfully fabricated (Figure 1). High-resolution TEM (HRTEM) images were also obtained to examine the structure and degree of crystallinity of the nano-materials. Fig 1a clearly shows the single layer structure of GO-COOH sheets and its typical size observed was more than 2 μm. The large specific surface area of GO-COOH sheets provided sufficient base for CuS nanoflakes and Ag nanoparticles to attach on. Both CuS and Ag were evenly dispersed on the GO-COOH sheets without any obvious aggregation as evidenced in Figure 1b. This may be attributed to the carboxylic acid functionalised groups on GO sheets, which not only improved its stability in aqueous solution but also increased its ability to adsorb CuS and Ag nanomaterials. The well dispersed and homogeneously distributed CuS and Ag on the GO-COOH sheets can offer a proximate electron interaction between each component, thereby increasing the transfer rate of the photo-excited electrons from the conduction band of CuS to GO-COOH and Ag.

Fig 1d displayed the HRTEM image of a hexagonal CuS nanoflake. The edge length of the CuS nanoflake on the GO-COOH sheets was approximately 15-20 nm. Ag nanoparticles were well separated with similar sizes around 10 nm (Fig 1e). Well-defined lattice fringes of hexagonal CuS nanoflakes and Ag nanoparticles can be seen in Fig. 1d and 1e as well. The lattice spacing of 0.31 nm could be corresponded to the (102) crystal planes of hexagonal CuS, whereas 0.24 nm lattice spacing corresponded to the (111) crystal planes of Ag [21, 22].

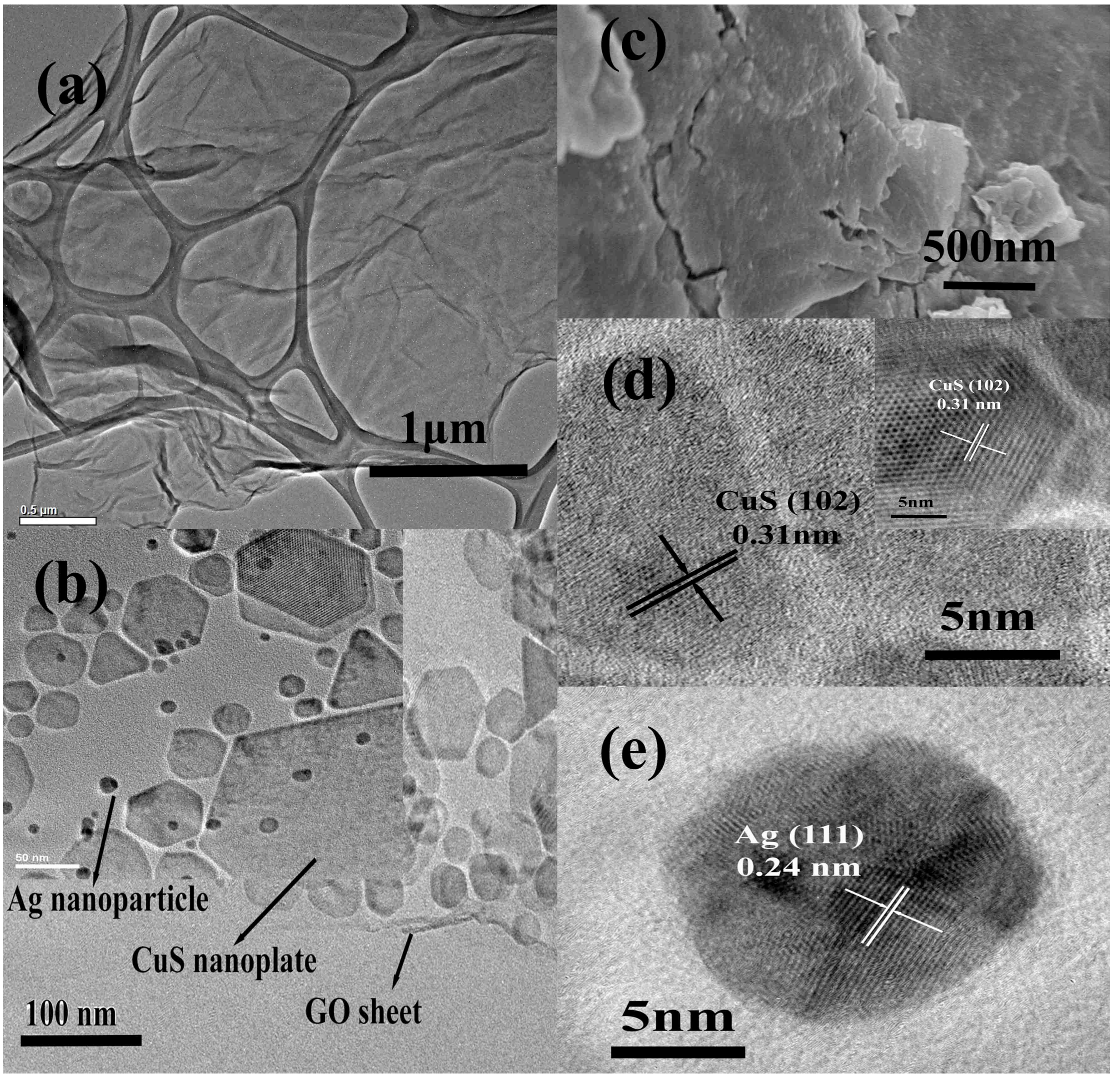

Figure 1. TEM images of (a) GO-COOH sheet, (b) GO-COOH-CuS-Ag nanocomposites, FESEM images of GO-COOH-CuS-Ag nanocomposites at (c) 30,000 magnification, and HRTEM images (d) Single hexagonal plate of CuS, and (e) single Ag nanoparticle.

Optical properties of composites

Based on the UV-Vis DRS spectra shown in Figure 2, GCCA-15 yielded the highest absorption intensity, followed by GCCA-30 and GCA in the UV and visible light regions. The curve of GCCA displayed an absorption edge at around 400 nm， whereas the curves of both GCCA-15 and GCCA-30 nanocomposites showed prominent red shift to 462 nm and 440 nm respectively. This is reasonable due to the bonding effect between GO-COOH and CuS, which enhanced the visible light response. However, for GCCA-30, the reactive sites of GO-COOH were blocked by the excess CuS nanoflakes, which reduced its visible light absorption intensity compared to GCCA-15. Hence, GCCA-15 required the least energy to be photoexcited and was expected to be the most efficient in electron transfer from CuS to GO-COOH sheets and Ag nanoparticles.

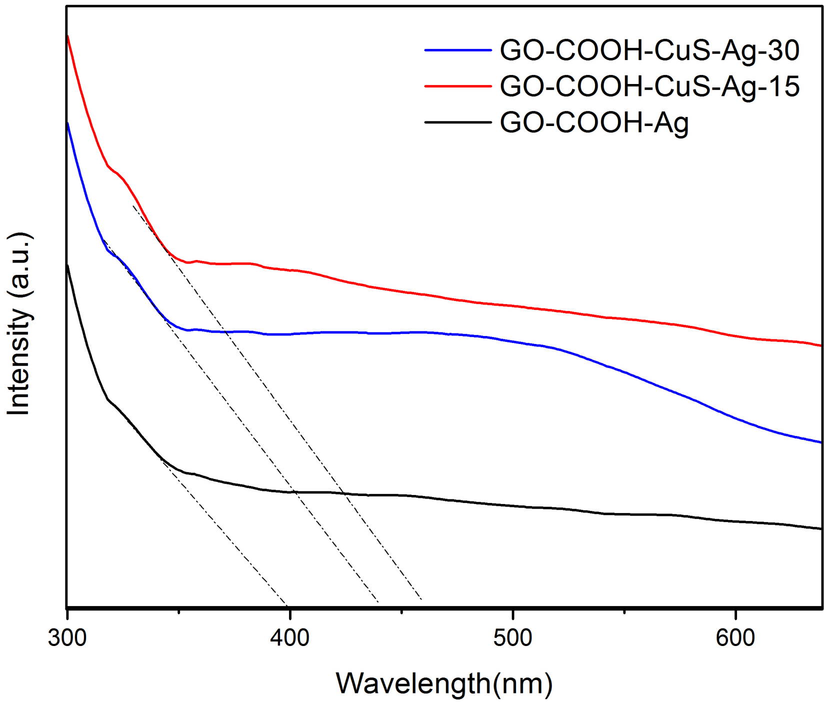

Figure 2: UV-Vis diffuse reflectance spectra of GO-COOH-Ag (GCCA), GO-COOH-CuS-Ag-15 (GCCA-15) and GO-COOH-CuS-Ag-30 (GCCA-30).

Photocatalytic degradation of MB on GCCA nanocomposites

In order to select the nanocomposite with highest photocatalytic activity for the subsequent coating, the photodegradation of MB on the three GCCA nanocomposites were investigated. GCCA-15 showed the best MB photodegradation performance among the three nanocomposites, indicating that the most desirable synergistic interaction with the 30 mg GO-COOH and 20 mg Ag requires the optimal ratio of 15 mg CuS. This ensures the effective charge transfer from the conduction band (CB) of CuS to GO-COOH sheets and/or Ag nanoparticles thus the low recombination rates of photogenerated electron-hole pairs can be achieved. Therefore, GCCA-15 was chosen to fabricate the varied mass glass coatings in the subsequent study.

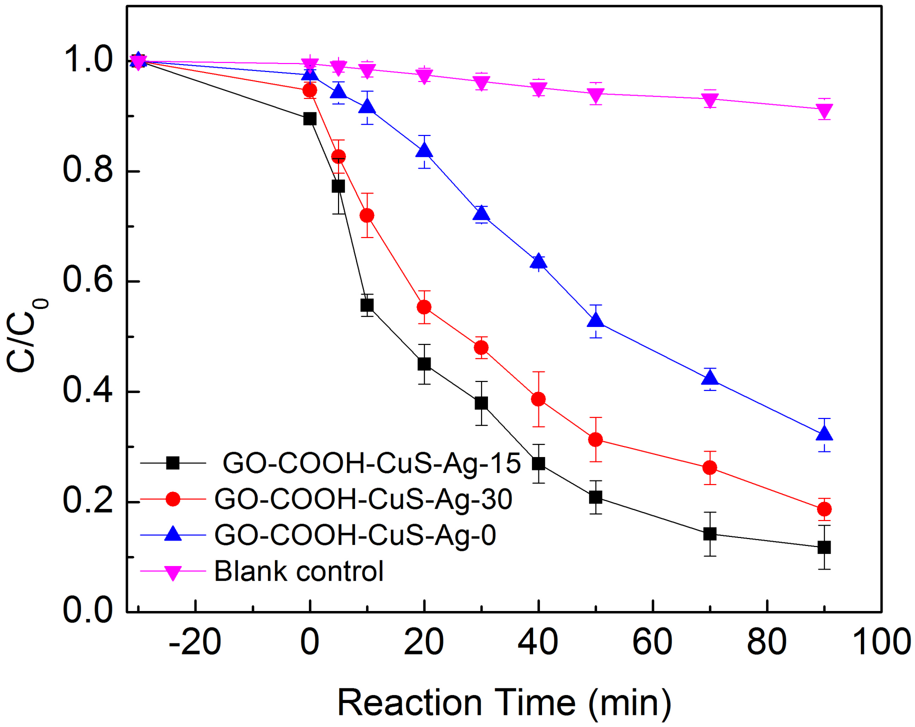

Figure.3. Degradation of MB by different ratios of GO-COOH-CuS-Ag nanocomposites under solar light

Morphology of GCCA-15 coated glasses

As can be seen from the Fig. 4 which shows GCCA-15 coated glass slides, the color was even, which proved that the nanocomposite was evenly coated on the glass by the aid of alumina-silica gel, BYK and DPM. The Water Contact Angel (WCA) was illustrated in S1. The general trend holds that with increasing amounts of GCCA-15 employed in coating, the WCA increases, implying an increase in hydrophilicity.

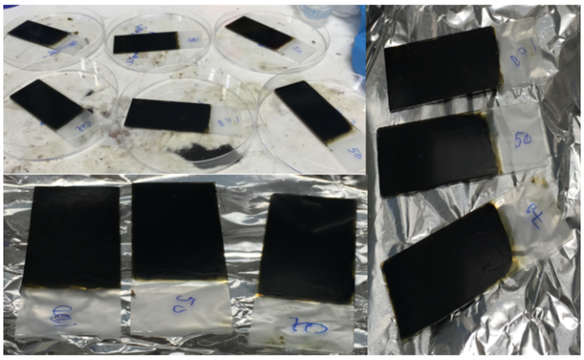

Figure 4. Coating pictures for GO-COOH-CuS-Ag-15 coated glasses (sol-gel)

According to SEM images, the thickness of the cross section of glass coatings was 16.4 μm, 22.9 μm and 40.1 μm respectively for 50 mg, 70 mg and 100 mg of GCCA-15 loaded. The regular height was increasing as the coated nanocomposite increased.

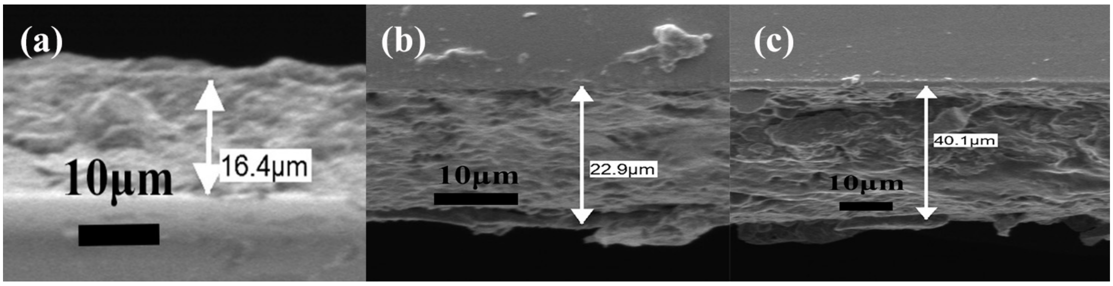

Figure. 5. SEM image of the cross section of glass coating (a) 50 mg (b) 70 mg (c) 100 mg

Photodegradation of MB and disinfection performance of GCCA nanocomposite glass coating

As shown in Figure 6, glass coating prepared with 70 or 100 mg GCCA-15 shows the nearly the same best MB photodegradation performance, in which 75.5% MB removal achieved within 90 mins under solar light irradiation. The results suggest that the photodegradation performance may not increase with the further increase of coated mass once the effective surface is saturated with sufficient material loads, as only the top layer(s) can be irradiated by solar light. Among the three loads tested, for the consideration of economic-friendly performance, the optimal mass was 70 mg nanocomposites on the 5 cm^2 glass.

In order to investigate the long-term stability of glass coatings, the photocatalytic degradation of MB by 70 GCCA-15 was repeatedly performed over five cycles. As shown in Fig. 6 b, no evident change was observed for the photo- catalytic activity through the 5 cycles of experiments for MB degradation, indicating good photocatalytic stability of the glass coatings. In addition, TOC analysis was monitored as a function of the mineralization rate of MB and its related intermediates. As shown in Fig. 6c, the TOC decreased over time, and the 70 and 100 mg GCCA-15 glass coatings displayed the highest TOC removal efficiency.

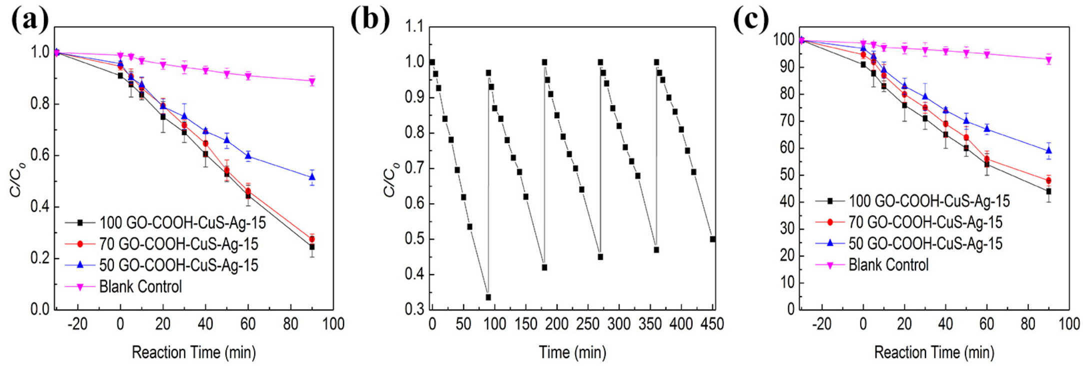

Figure. 6. (a) Photocatalytic performance for MB by different amount (50 mg, 70 mg and 100 mg) of GCCA-15 nanocomposite glass coating under solar light, (b) five consecutive cycling curves of MB photodegradation by 70 mg GCCA-15, and (c) TOC concentrations versus time.

Conclusions

The application of GO-COOH-CuS-Ag glass coatings in organic removal in aqueous environment and bacteria disinfection was explored in this study. The results clearly demonstrate its potential in high performance of photodegradation and photo-disinfection properties with the edge of simplifying the recovery and reuse process in contrast to powdered form, reducing problems including the agglomeration of powdered particles that may cause blockages. Consequently, the multifunctional GO-COOH-CuS-Ag nanocomposite coated glass may also offer a solution in organic matter removal in gas phase such as volatile organic compounds (VOCs) removal and indoor air pollution control.

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References:

1. Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W., ENVIRONMENTAL APPLICATIONS OF SEMICONDUCTOR PHOTOCATALYSIS. *Chemical reviews* **1995,** *95*, (1), 69-96.
2. <environmental applicaiton of photocatalysis.pdf>.
3. Jiang, Y.; Raliya, R.; Fortner, J. D.; Biswas, P., Graphene Oxides in Water: Correlating Morphology and Surface Chemistry with Aggregation Behavior. *Environ Sci Technol* **2016**.
4. Modesto-López, L. B.; Miettinen, M.; Torvela, T.; Lähde, A.; Jokiniemi, J., Direct deposition of graphene nanomaterial films on polymer-coated glass by ultrasonic spraying. *Thin Solid Films* **2015,** *578*, 45-52.
5. <Graphene based material and their composites as coatings.pdf>.
6. Yao Tong, S. B. a. M. S., <Graphene based material and their composites as coatings.pdf>. *Austin Journal of Nanomedicine and Nanotechnology* **2013,** *1*, (1).
7. Prasai, D.; Tuberquia, J. C.; Harl, R. R.; Jennings, G. K.; Bolotin, K. I., Graphene: Corrosion-Inhibiting Coating. *Acs Nano* **2012,** *6*, (2), 1102-1108.
8. Wang, W.; Yu, J.; Xiang, Q.; Cheng, B., Enhanced photocatalytic activity of hierarchical macro/mesoporous TiO2–graphene composites for photodegradation of acetone in air. *Applied Catalysis B: Environmental* **2012,** *119-120*, 109-116.
9. <graphene coating wastewater degradation.pdf>.
10. Basu, M.; Sinha, A. K.; Pradhan, M.; Sarkar, S.; Negishi, Y.; Govind; Pal, T., Evolution of Hierarchical Hexagonal Stacked Plates of CuS from Liquid-Liquid Interface and its Photocatalytic Application for Oxidative Degradation of Different Dyes under Indoor Lighting. *Environmental Science & Technology* **2010,** *44*, (16), 6313-6318.
11. Yu, S.; Liu, J.; Zhu, W.; Hu, Z. T.; Lim, T. T.; Yan, X., Facile room-temperature synthesis of carboxylated graphene oxide-copper sulfide nanocomposite with high photodegradation and disinfection activities under solar light irradiation. *Scientific reports* **2015,** *5*, 16369.
12. Zhou, Y.; Yang, J.; He, T.; Shi, H.; Cheng, X.; Lu, Y., Highly stable and dispersive silver nanoparticle-graphene composites by a simple and low-energy-consuming approach and their antimicrobial activity. *Small* **2013,** *9*, (20), 3445-54.
13. Zeng, B.; Chen, X.; Chen, C.; Ning, X.; Deng, W., Reduced graphene oxides loaded-ZnS/CuS heteronanostructures as high-activity visible-light-driven photocatalysts. *Journal of Alloys and Compounds* **2014,** *582*, 774-779.
14. Liu, L.; Liu, J.; Wang, Y.; Yan, X.; Sun, D. D., Facile synthesis of monodispersed silver nanoparticles on graphene oxide sheets with enhanced antibacterial activity. *New Journal of Chemistry* **2011,** *35*, (7), 1418.
15. Liu, L.; Bai, H.; Liu, J.; Sun, D. D., Multifunctional graphene oxide-TiO(2)-Ag nanocomposites for high performance water disinfection and decontamination under solar irradiation. *Journal of hazardous materials* **2013,** *261*, 214-23.
16. Hummers, W. S.; Offeman, R. E., PREPARATION OF GRAPHITIC OXIDE. *Journal of the American Chemical Society* **1958,** *80*, (6), 1339-1339.
17. Shen, C.; Hui, C.; Yang, T.; Xiao, C.; Tian, J.; Bao, L.; Chen, S.; Ding, H.; Gao, H., Monodisperse Noble-Metal Nanoparticles and Their Surface Enhanced Raman Scattering Properties. *Chemistry of Materials* **2008,** *20*, (22), 6939-6944.
18. Tiwari, S. K.; Mishra, T.; Gunjan, M. K.; Bhattacharyya, A. S.; Singh, T. B.; Singh, R., Development and characterization of sol–gel silica–alumina composite

coatings on AISI 316L for implant applications. *Surface and Coatings Technology* **2007,** *201*, (16–17), 7582-7588.
19. Nikolic, L.; Radonjic, L., Alumina strengthening by silica sol-gel coating. *Thin Solid Films* **1997,** *295*, (1–2), 101-103.
20. Lu, Y. F.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W. L.; Guo, Y. X.; Soyez, H.; Dunn, B.; Huang, M. H.; Zink, J. I., Continuous formation of supported cubic and hexagonal mesoporous films by sol gel dip-coating. *Nature* **1997,** *389*, (6649), 364-368.
21. Liu, L.; Bai, H.; Liu, J.; Sun, D. D., Multifunctional graphene oxide-TiO2-Ag nanocomposites for high performance water disinfection and decontamination under solar irradiation. *Journal of Hazardous Materials* **2013,** *261*, (0), 214-223.
22. Basu, M.; Sinha, A. K.; Pradhan, M.; Sarkar, S.; Negishi, Y.; Govind; Pal, T., Evolution of Hierarchical Hexagonal Stacked Plates of CuS from Liquid−Liquid Interface and its Photocatalytic Application for Oxidative Degradation of Different Dyes under Indoor Lighting. *Environmental Science & Technology* **2010,** *44*, (16), 6313-6318.