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Published in:
Nano Futures

DOI:
10.1088/2399-1984/ab9a28

Published: 23/07/2020

Document Version
Final published version

Document License
Unknown

Chemical and biological sensing with nanocomposites prepared from nanostructured copper sulfides

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Abstract

Nanostructured copper sulfides have been known as the functional materials in a wide range of disciplines including physics, chemistry, chemical engineering, biomedicine. Combination and/or functionalization of nanostructured copper sulfides with other active materials, in the form of nanocomposites, helps to achieve synergies that allows to utilize them in advanced applications. This review focuses particularly on the potential utilization of copper-sulfide based nanocomposites in chemical and biological sensing. While most of the sensors qualified to be used in physiological and environmental monitoring, several challenges remain and will be discuss in this review.

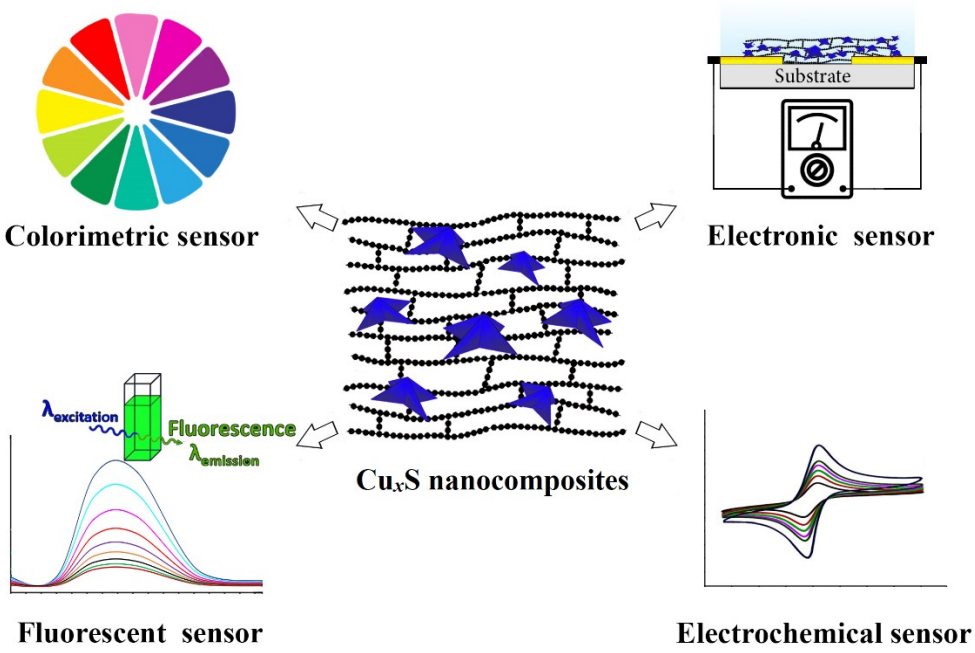
Keywords: copper sulfide, polymer, reduced graphene oxide, carbon nanotube, electrochemical, colorimetric, fluorescence

1. Introduction

Copper sulfides have known to be in the mineral ore as well as a product from the precipitation process which aims to dispose copper ions in wastewater.[1-3] They appear in different phases including the nonstoichiometric $Cu_{1.8}S$ (digenite) and $Cu_{1.96}S$ (djurleite), and stoichiometric CuS (covellite), and Cu_2S (chalcocite);[4-6] and therefore, will be term as Cu_xS with the stoichiometry x increased from $x = 1$ to $x = 2$ throughout this review. Cu_xS possesses a band gap of 1.2–1.5 eV, resulting variation in the electrical conductivity of Cu_xS phases. Cu_xS behave as p-type semiconductors and their electrical conductivity is proportional to the density of acceptor (or x values), i.e. $Cu_{1.8}S$ (2400 Ω^{-1} cm^{-1}) is much more conductive than Cu_2S (<52 Ω^{-1} cm^{-1}).[4] This feature is temperature dependent as Cu_xS undergo phase transitions. Generally, Cu_xS manifests interesting electrical, photocatalytic, optical, thermoelectric and plasmonic properties,[7-12] allowing them to be used in a wide range of applications including energy, drug delivery, and theranostics.[13-17] However, there are still some disadvantages related to the Cu_xS nanoparticles such as unwanted binding to organ, lower photothermal conversion efficiency than other nanoparticles that make Cu_xS has not yet reached the clinic.[18]

This review aims to bring in the readers through a new topic, i.e. the application of the nanostructured Cu_xS in chemo- and biosensing.[13, 19] While the sensing applications of the pristine Cu_xS has been covered by the review of Goel et al.[13] and Shamraiz et al.[19], this review would extend further the progress in using particularly Cu_xS nanocomposites. The nanocomposites herein are consisted of nano-sized Cu_xS of various morphologies and other materials including polymers, carbon-based materials, inorganic dyes, etc. It is therefore important to discuss on several pathways of synthesizing Cu_xS and its nanocomposites prior to the sensing applications of

these nanocomposites (Scheme 1). Last but not least, the author is addressing the major challenges and future directions for these promising Cu_xS based nanocomposites.



Scheme 1. Current applications of Cu_xS nanocomposites in chemical and biological sensing

2. Synthesis of Cu_xS nanostructures and nanocomposites

As the Cu_xS nanostructures promote their use to advanced applications, discussing several main approaches for synthesizing nanostructured Cu_xS is essential. Indeed, the synthetic methods affect properties of Cu_xS-based nanocomposites which navigate appropriate sensing platforms for target analytes (section 3).

2.1 Hydrothermal and solvothermal methods

Hydrothermal and solvothermal synthesis are the methods of synthesis of Cu_xS nanocrystals from the solutions of copper salts (e.g. copper sulfate, copper acetate) or electroless plated copper

precursor in hot water or organic solvents (e.g. ethylene glycol), respectively.[20-23] The conventional hydrothermal method using for preparation of Cu_xS includes heating the aqueous solution containing copper salt and sulfide compounds (e.g. Na_2S, $Na_2S_2O_3$) at the temperature between 70 and 180 °C. Pressure can be applied in the reaction chamber. The products are dark brown or black solid Cu_xS precipitates of various morphologies such as nano-size rods and spheres (Figure 1). Next, the resulting nanocomposites are the Cu_xS impregnated onto the surface of different polymers including textile[23], poly(viny1 alcohol) (PVA) and poly(2-cyano-1,3-phenylene oxide), polyethylene terephthalate[24], commercial Kapton@polyimide[25], poly(aniline-co-m-chloroaniline)[26], cornstarch[27], and amylose[28]. Advantages of the hydro/solvothermal method over others are the high crystallinity and composition unchanged of Cu_xS phases.

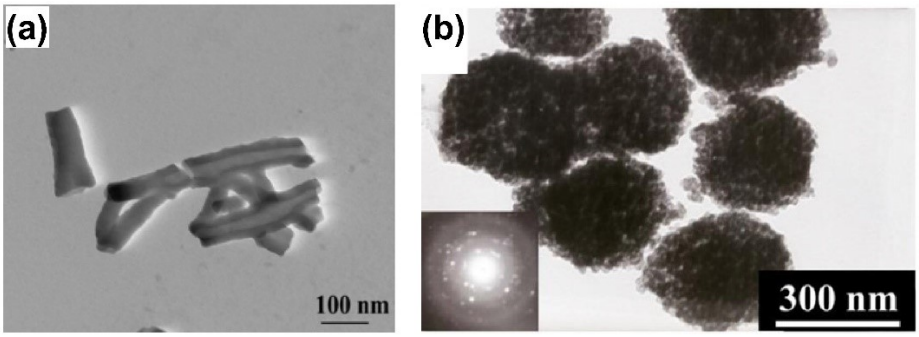


Figure 1. Morphologies of Cu_xS nanostructures; (a) CuS nanorods[26] and (b) CuS/amylose nanospheres[28], synthesized by hydrothermal methods. (Reproduced with permission from [26, 28]).

2.2 Sonochemical method

In sonochemical method, a high-intensity ultrasound in the range of 20 kHz - 10 MHz generates acoustic cavitation of very high temperatures (up to 25000 K) and pressures (more than 1000 atm)[29] that is used for synthesis of various Cu_xS and dichalcogenide nanostructures.[30-34] The significant advantage of the method is cost-effective and a minimum amount of by-products, thus the synthesis is easily scaled up. For instance, Mulla et al.[35] has developed simple way of preparing nanostructured $Cu_{1.8}S$ and CuS by immersing a 99.999% purity copper plate into an iodine solution and using ultrasound as the elemental source directly for the synthesis (Figure 2a). The method is able to produce a large amount of $Cu_{1.8}S$ and CuS (Figure 2b), i.e. up to few grams but the price of extremely pure copper plate needs to be considered.

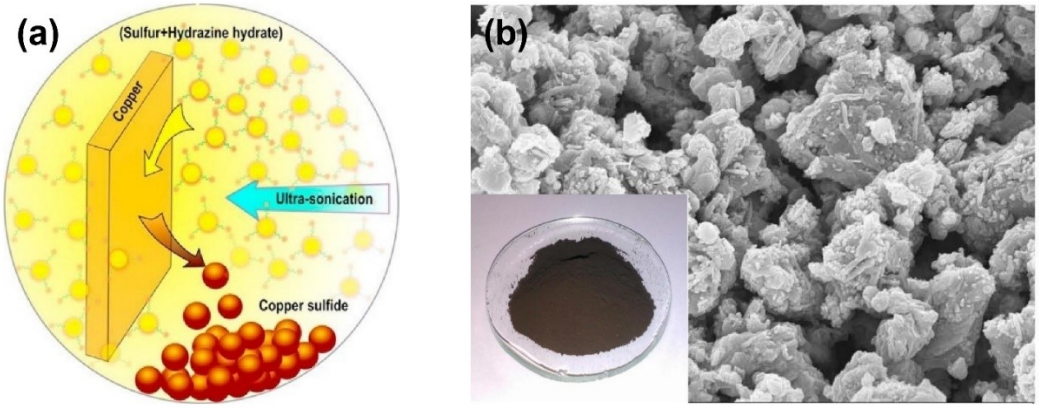


Figure 2. (a) Large-scale sonochemical synthesis of Cu_xS nanostructures from the copper plate that immersed in the solution of sulfur and hydrazine hydrate during sonication; and (b) SEM image of $Cu_{1.8}S$ (inset is the photograph of Cu_xS powders). (Reproduced with permission from [35]).

2.3 Gas-solid reaction

The gas-solid reaction uses hydrogen sulfide (H_2S) atmosphere at room temperature to react with copper (e.g. a copper substrate with rough surface) in order to receive the Cu_xS nanostructures.[21, 36] As a results, isolated and uniform Cu_xS nanorods are well-aligned on the copper substrate, which can be visibly identified in black and fluffy color. For further nanocomposite processing, coating of the polypyrrole (PPy)[21] or amphiphilic polythiophene[37] on the Cu_2S nanorods has been reported. These conducting polymers form as a smooth, robust, and uniform film by chemical electropolymerization at the liquid-liquid or air-liquid interface. As the copper substrate is pretreated to obtain the nanostructures before Cu_xS formation, the method manifests the advantage of well design of nanoarchitectures.

3. Chemical and biological sensing using the Cu_xS nanocomposites

The diversity of Cu_xS phases and morphologies combining with new properties of other electroactive and photoactive materials contribute to improvement of the sensitivity and selectivity for biological and chemical sensors. Table 1 shows the list of sensors based on Cu_xS nanocomposites which have been reported from the literatures. By dividing the section into different types of sensors instead of the practical applications of the Cu_xS nanocomposites, the author therefore emphasizes the features of Cu_xS and its nanocomposites.

Table 1. List of biogical and chemical sensors using Cu_xS nanocomposites. The list is categorized into four groups of (electronic, electrochemical, optical, and other) transducers.

Analyte	Composite	Sensor	LOD	Ref.
Electronic sensor				
Ethanol	CuS-polyolefine	p-n junction	<5000 ppm	[38]

Ethanol	CuS-gelatin	chemiresistor	unreported	[39]
Humidity	CuS-PVA	chemiresistor	unreported	[40]
Humidity	CuS-PSS	chemiresistor	unreported	[41]
Electrochemical sensor				
H_2O_2	Cu_2S-MWCNT	amperometry	50 nM	[42]
H_2O_2	Cu_2S-MWCNT/	amperometry	200 nM	[43]
Glucose (non	DWCNT			
enzymatic)				
Nitrite	Cu_2S-MWCNT	amperometry	330 nM	[44]
Bisphenol A	CuS-CNT	DPV	50 nM	[45]
Glucose	CuS-(S-rGO)	amperometry	32 nM	[46]
Chloramphenicol	CuS-rGO	amperometry		[47]
Dopamine	CuS-rGO	DPV	22 nM	[48]
Caffeic acid	Cu_2S-rGO	amperometry	22 nM	[49]
H_2O_2	CuS-rGO	amperometry	100 nM	[50]
hydrazine			300 nM	
Alkaline phosphatase	CuS-rGO	DPV	20 mU L^{-1}	[51]
H_2O_2	CuS-rGO	amperometry	270 nM	[52]
Gatifloxacin	CuS-rGO	eletrochemiluminescence	3.5 nM	[53]
Amlodipine besylate	CuS-rGO	electrochemical &	6.9 nM	[54]
		eletrochemiluminescence		
Trichloroacetic acid	CuS-rGO	cyclic voltammetry	200 nM	[55]

H_2O_2	CuS-OMCs		1000 nM	[56]
H_2S	Cu_9S_8/PPy/ZIF-67	amperometry	2.1 μM	[57]
Glucose (non-enzymatic)	CuS/PPy/SiO_2	amperometry	1 μM	[58]
Glucose	CuS-MoS_2	amperometry	300 nM	[59]
Optical sensor				
3,3′,5,5′-tetramethylbenzidine	CuS-MMT	colorimetric	30 μM	[60]
cholesterol	CuS-BNNs	colorimetric	2.9 μM	[61]
kanamycin	CuS-ssDNA	fluorescence	0.04 nM	[62]
phenolic	CuS-chitosan	fluorescence	30 μM	[63]
pH	$Cu_{1.8}$S-DMTD	fluorescence	pH 3-10	[64]
Other sensor				
Cr(VI)	silica gel-CuS	FAAS	0.15 μg L^{-1}	[65]

3.1 Electronic sensors

In gas and humidity sensing, the Cu_xS nanocomposites plays a role of the sensing layer in electronic device, e.g. in the p-n junction and chemiresistor. In this layer, Cu_xS of high conductivity is a conductor while the polymer matrix is a gas receiver. The change in electrical conductivity of the composite is hypothesized either by swelling of the polymer or by the change in permittivity of nanocomposite affecting the hopping conductivity between CuS nanoparticles upon exposure of gas molecules.[40] In both cases, percolation threshold of the nanocomposites is important as it is responsible for not only the chemiresistivity of the sensing layer but also its sensitivity when the

filler concentration is close to threshold. The gas sensitivity of the Cu_xS nanocomposite based electronic sensors also depends on the rate of matrix filling and the chemical data of the testing gas.

Monitoring volatile ethanol is extremely important for safety control of traffic as well as industrial production of ethanol. Two nanocomposites derived from Cu_xS, i.e. CuS-polyolefine and Cu_2S-gelatin have been used to detect ethanol (Table 1).[38, 39] The CuS-polyolefine is one of the first CuS-based composite that was developed 30 years ago. Copper was electroless plated into porous polyolefine (Hipore as the commercial name) film, and followed with sulfurizing the copper to achieve CuS (Figure 3a).[38] The method is, however, out-of-date nowadays as many toxic or unfriendly-environment chemicals such as $SnCl_2$, concentrated HCl, and formaldehyde have been used. The composite is only conductive when the amount of CuS is >35 *wt*% and then found the p-type semiconductor. Better percolation-threshold nanocomposite of 16 *wt*% CuS in gelatin has achieved by Muradov et al.[39] and then demonstrated to sense ethanol. The gelatin in the composite containing polar amino acids on the polypeptide chain that forms hydrogen bonds with ethanol molecules.

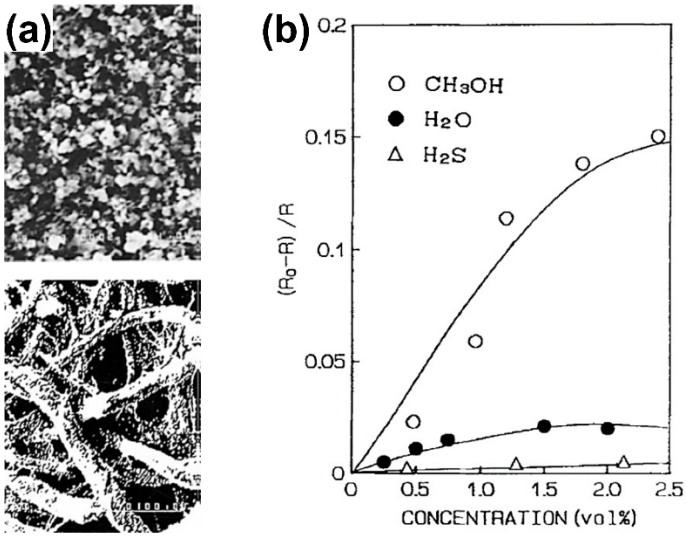


Figure 3. (a) CuS (35 *wt*%)-Hipore 2000 (×l000 magnification) and (b) CuS (40 *wt*% magnification)-cellulose (×400 magnification), (c) relative resistance response of the sensor to different (*vol*%) concentrations of ethanol, water and H_2S using CuS(35%)-Hipore 2000. (Reproduced with permission from [38])

Using the hydrophilic polymer such as polyphenylene sulfide (PPS) and polyvinylalcohol (PVA) in the nanocomposites with the CuS nanoparticles (Table 1), extends the applications of Cu_xS to humidity sensing.[40, 41] Like ethanol monitoring, the humidity sensors are important in industrial processing (semiconductor manufacturing, home and automobile appliances) and environmental control (agriculture, food and storage).[66] Response of both nanocomposites upon exposure of water vapors caused by decrease in electrical conductivity of the sensors which is attributed to the change of permittivity of the nanocomposite.[40] The percolation threshold of the nanocomposites are observed in the concentration range from 16 to 22 *wt*%, accompanied by a conductivity change from 10^{-9} to 10^{-2} (Ω cm^{-1}). Different from PVA, PPS is the sulfide source *per se* reacting with copper acetate to form Cu_2S at the melting temperature (285 °C) of PPS.[41] The Cu_2S nanocrystals have polydispersity of 5 – 60 nm that is only obtained with equimolar ratio of PPS and copper acetate.

3.2 Electrochemical sensors

Electrochemical sensing using Cu_xS nanocomposites presented herein is indeed the most important and successful applications of the materials. This is due to the suitable band gap of Cu_xS, providing substantial electrocatalytic as well as photoelectrocatalytic activity. While the carbon-based materials such as carbon nanotube (CNT) and reduced graphene oxide (rGO) has intensively used

to enhance the electrocatalytic activity of Cu_xS, one can also find other Cu_xS nanocomposites with ordered mesoporous carbons (OMCs), metal organic framework (MOF) ZIF-67, SiO_2 nanospheres, and molybdenum disulfide (MoS_2) (Table 1).

Among mentioned materials, CNTs possess unique properties including high electron conductivity, well-developed routes of functionalization, and low percolation threshold of CNT-based nanocomposites.[67] In most works, the multiwalled CNTs (MWCNTs) are used to hybridize with Cu_xS.[42-45] For example, the Cu_2S-MWCNT modified glassy carbon electrode (GCE) exhibits significant response to H_2O_2 of nM-level concentration (Table 1) which is important for glucose sensing as H_2O_2 is a product of glucose oxidation.[42] GCE is the first-choice electrode for Cu_xS-nanocomposite based electrochemical sensors, particularly, amperometric sensors of which the anodic current (e.g. of H_2O_2 electrooxidation) is measured. Not only used in H_2O_2 detection, Myung et al.[43] developed amperometric sensors based on Cu_2S-MWCNT, for glucose sensing under non-enzymatic way[68] (Figure 4). The synergetic combination of Cu_2S and CNT leading to the electrocatalytic activity of the nanocomposites is attributed to the matching between the (002) planes of Cu_2S and the (002) planes of the MWCNTs (Figure 4b and 4c) during the in-situ solvothermal growth of β-Cu_2S nanocrystals on the MWCNTs.

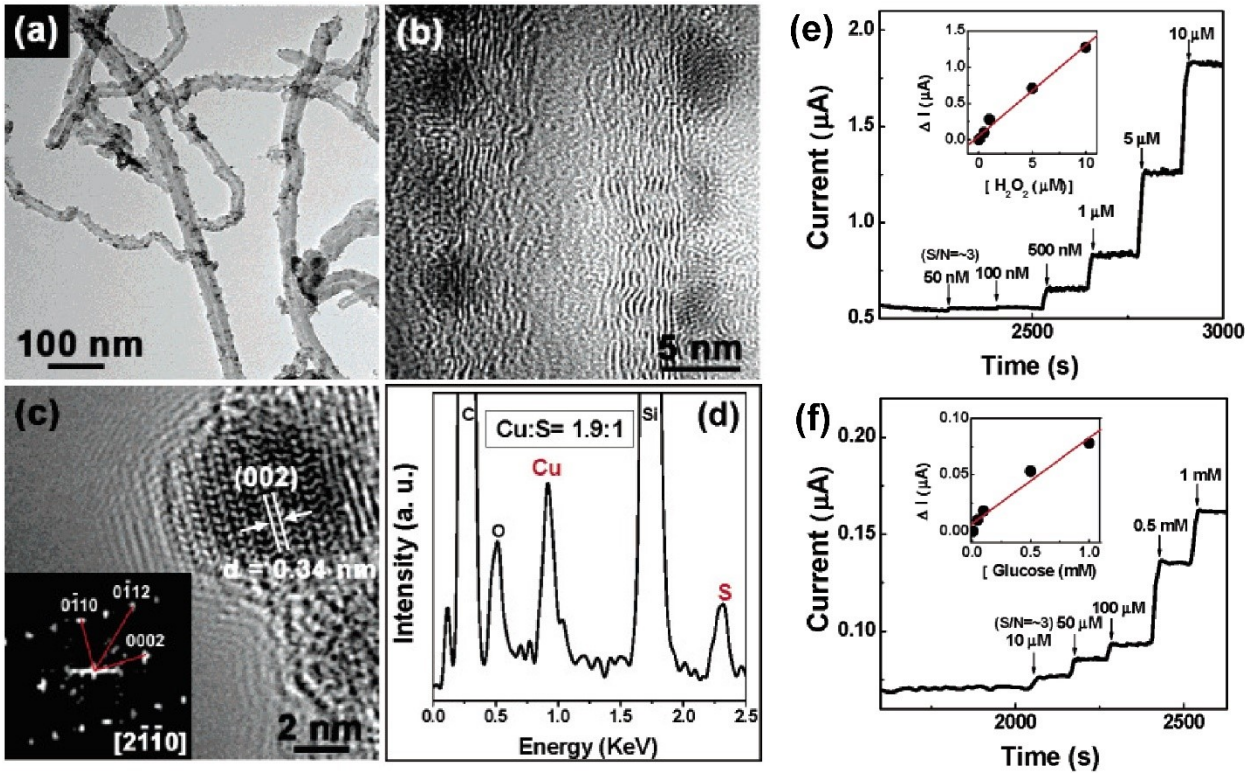


Figure 4. (a and b) Cu_2S-decorated MWCNTs (the size of the spherical Cu_2S nanocrystal of ~4 nm can be measured from Figure 4b), (c) the Cu_2S nanocrystal binds tightly to the wall of the MWCNT, with the (002) planes parallel to the wall (inset is the corresponding FFT ED pattern), (d) Energy-dispersive X-ray spectroscopy (EDX) confirmation of the Cu/S ratio = 2:1, the (e) chronoamperometric response of Cu_2S-MWCNT/Nafion-modified GC electrodes at 0.55 V upon subsequent addition of H_2O_2 solution (the inset is a calibration curve for corresponding H_2O_2 concentrations), (f) chronoamperometric response of Cu_2S-MWCNT/(glucose oxidase)/Nafion electrodes upon the addition of glucose solution (the inset is a calibration curve for glucose concentrations). (Reproduced with permission from [42])

The Cu_xS-MWCNT nanocomposites are also reported for sensing nitrite[44] and bisphenol A[45] at the nanomolar level (Table 2); the analytes which is ubiquitous within environmental,

food, industrial and physiological systems, and thus required to be tested and controlled.[69-72] For instance, the flower-like CuS-MWCNTs were successfully synthesized in accompanied by poly(vinyl pyrrolidone) (PVP)[45] which amplify anodic current of bisphenol A measured at GCE by differential pulse voltammetry (DPV). Notably, the amplification of the CuS-MWCNT/GCE is ten times compared to that measured by unmodified GCE.

Graphene oxide (GO) is the single-layer form of graphitic oxide. While the graphitic oxide is prepared from graphite,[73] the hydrophilic GO can be exfoliated in water. The GO becomes conductive once the conjugation system is restored through the reduction of GO; this results reduced GO (rGO).[74-76] As exfoliation play as an important step in preparation of rGO, the sonochemical method as exfoliation assistance[77] is often used in preparing the nanocomposite of the Cu_xS and rGO.[46-49] During the preparation, the Cu_xS can experience phase transition, e.g. the surface of covellite CuS transforms to the digenite $Cu_{1.8}S$ phase when the sulfur-doped rGO (S-rGO), a mild oxidant is used.[46] This modification results excellent electrocatalytic activity over glucose under non-enzymatic way (Table 2) when compare to the bulk CuS and S-rGO alone. Additionally, the sensor demonstrates high accuracy (>95%) when validated in real biological samples such as human blood serum, urine and saliva. High electrocatalytic activity of the Cu_2S-rGO nanocomposite is also observed from a screen-printed electrode[47], which then apply for reduction of chloramphenicol - an antibiotic drug,[78] used in many infectious bacterial diseases (tuberculosis) and typhoid in animals and human. Other examples of using the Cu_xS-rGO nanocomposites includes the electrochemical sensors for dopamine neurotransmitter in bovine serum albumin[48] and caffeic acid[49] (Table 1). Interestingly, the limit of detection (LOD) of caffeic acid achieved by nanocomposite-modified electrode surpassed the LODs of many existing methods. The chemical sensor is able to quantify the amount of caffeic acid spiked in carbonated

soft drinks and red wine without sample pretreatments. The hydrothermal and solvothermal methods has also been used in preparation of nanocomposites of Cu_xS with rGO. The synthetic approach is relatively similar to that of Cu_xS (see Section 2.1); the dispersed rGO is either pre-synthesized[50, 51] or in-situ reduced from GO by using a reducing agent such as PVP[52]. Both nanocomposites are electrocatalytic and the latter one, in particular, applied to detect both H_2O_2 levels in human serum and urine and H_2O_2 released from human cervical cancer cells using amperometry (Table 1). However, the LOD of 270 nM of H_2O_2 is not as low as that achieved by the CuS-CNT nanocomposites (mentioned above).

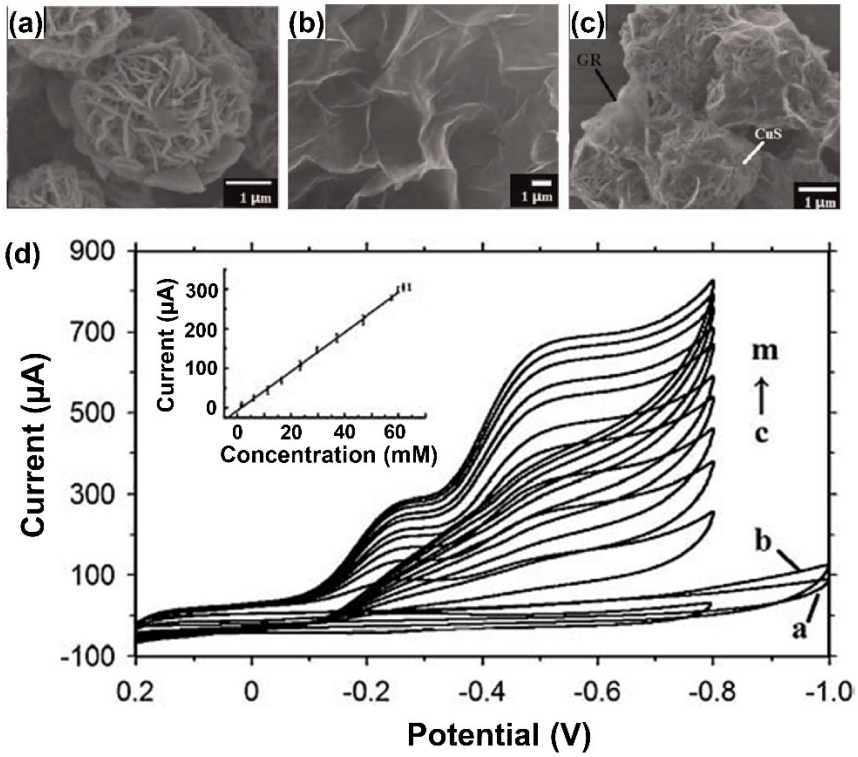


Figure 5. SEM images of (a) CuS sphere, (b) rGO, and (c) CuS-rGO composite; (d) the cyclic voltammograms recorded at carbon/(ionic liquid) electrode which coated with (curves a & b) chitosan/CuS-rGO and (curves c-m) chitosan/hemoglobin/CuS-rGO recorded for 0, 1, 7, 12, 16, 25, 30, 38, 48, 56, 64 mM trichloroacetic acid in 0.1 M PBS buffer (pH 3.0). The scan rate is 100

mV s^{-1}. Inset is the calibration curve for the corresponding concentrations of trichloroacetic acid. (Reproduced with permission from [55])

Not only is CuS-rGO used as electrocatalytic materials, CuS-rGO is also served as a mediator to accelerate the electron transfer, i.e. between the electrode and the electroactive centers of graphite-like carbon nitride (g-C_3N_4) nanosheets[53], $Ru(bpy)_3^{2+}$[54], the hemoglobin (Figure 5)[55]. The process, for example, reduces Fe(III) to Fe(II) at the center of hemoglobin which later catalyzes the trichloroacetic acid – the chemical used as herbicide from 1950s[79] and as chemical peels[80] with LOD of 200 nM (Table 1). As of the same mechanism, g-C3N4 nanosheets and $Ru(bpy)_3^{2+}$ are applied for enhancing sensitivity to gatifloxacin in mouse plasma[53] and amlodipine besylate[54], respectively (Table 2). These electrochemical sensors exhibit the advantages such as high sensitivity, good reproducibility and long-term stability.

Other form of carbon-based materials are also used in preparation of the nanocomposites such as ordered mesoporous carbons (OMCs).[56] Compared with the pristine OMCs, the Cu_2S-OMCs modified electrode displays high electrocatalytic activity towards H_2O_2 (Table 1).[56] This is helped with well incorporation of the Cu_2S nanoparticles inside the pores of the OMCs.

Non-carbon based materials such as PPy/ZIF-67[57], PPy/SiO_2[58], and MoS_2[59] has also been employed in Cu_xS-based nanocomposites. Additionally, the first two studies have incorporated with PPy in order to increase the conductivity of the final hybrid materials. Indeed, the sensitivity of Cu_xS-based chemical sensors using PPy possess 2-fold higher than those without PPy. Last but not least, the MoS_2, like other materials mentioned earlier, demonstrates enhancement to the electrocatalytic activity of the nanocomposite.[59] Besides, it is even more

interesting that the chemical sensors prepared from CuS-MoS_2 is capable to detect glucose under non-enzymatic condition of nearly neutral pH.

3.3 Optical sensor

Section 3.2 has brief mentioned the photoelectrochemical sensor prepared from the Cu_xS-based nanocomposites that have been used in detection of H_2S. In this section, more applications of the Cu_xS-based nanocomposites in the field of optical sensing are provided. They are divided in two groups based on the detection methods, i.e. the colorimetric and fluorescent sensing.[81-83]

Compared to fluorescence sensing, advantages of the colorimetry are simplicity, low cost, no requirement of instrument. For instances, the Cu_xS nanocomposites with Ca^{2+}-montmorillonite (Ca-MMT)[60] and boron nitride nanosheet (BNN)[61] were designed to establish convenient sensing by evaluating the color change of, e.g. the solutions inside a Eppendorf tube (Figure 6a). This is due to both materials owing the intrinsic peroxidase-like catalytic activity towards typical peroxidase substrates such as 3,3′,5,5′-tetramethylbenzidine (TMB) (Figure 6) and cholesterol. Figure 6a illustrates color of CuS-BNNs changes from light to dark cyan when concentration of TMB increases which can be seen by UV-vis spectroscopy (Figure 6b). However, LOD of the sensors in both studies range up to μM level (Table 1) which is the main limitation of this method.

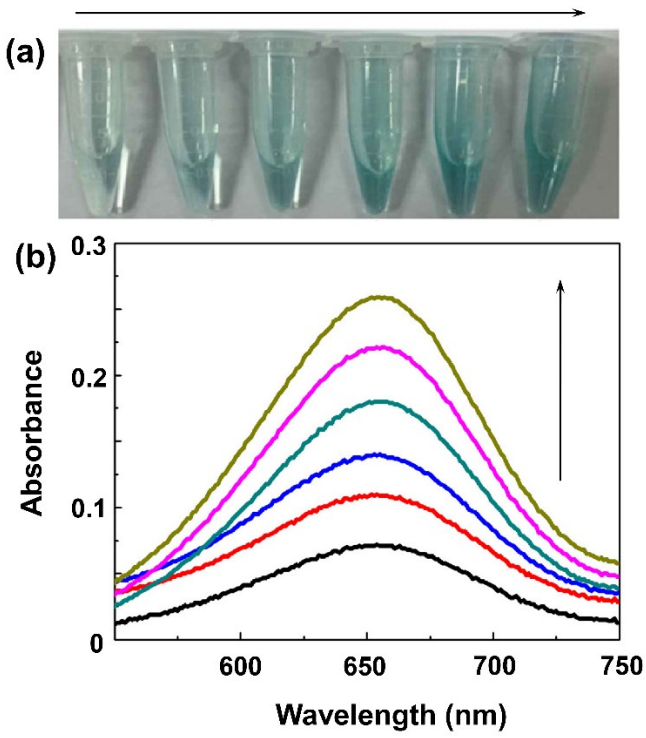


Figure 6. The (a) photograph and (b) UV-vis spectra of the mixed solutions of TMB and CuS-BNNs in 0.2 M Britton–Robinson buffer (pH 3.0) at 35 °C. The arrow shows the increase of TMB concentrations from 0.01 to 0.1 mM. (Reproduced with permission from [61])

Compared to the colorimetric sensors, fluorescent sensors theoretically accommodate much lower LOD. Indeed, fluorescence assay for detection of sub-nM kanamycin, an aminoglycoside bactericidal antibiotic, has been developed.[62] Kanamycin used to treat a wide variety of infections but serious side effects include ringing in the ears or loss of hearing, toxicity to kidneys, and allergic reactions to the drug.[84] The concentration of kanamycin is monitored by increase in fluorescence intensity once two single-strand DNA (ssDNA), which one labeled with CuS nanoparticles and another with fluorescent streptavidin paramagnetic particles, complexed. In contrast, a fluorescent sensor based on the CuS-chitosan nanocomposite films is less sensitive to resorcinol, an antifungal drug.[63] The LOD calculated for smallest change in the fluorescence

intensity is 30 μM. Last but not least, fluorescence of the Cu_xS nanocomposite has found pH-dependent and therefore a pH sensor has been prepared from the digenite $Cu_{1.8}S$ nanoclusters functionalized with 2-mercapto-5-amine-1,3,4-thiadiazole (DMTD).[64] The materials provided high sensitivity to a broad range of pH (Table 1).

4. Perspective

One can find the Cu_xS and its nanocomposites have been expanded in wide range of scientific disciplines as mentioned in the Introduction. The specific works on chemical and biological sensing, however, is still modest, i.e. less than 30 publications (Table 1) have been reported directly on the use of Cu_xS nanocomposites in chemo- and biosensors in the last 30 years. Nevertheless, the recent years obverse dramatic increase in the number of publications indicating the potential of Cu_xS nanocomposites. This is probably due to benefits of Cu_xS which are highlighted by the following features: low cost, abundancy of the resources, ease of production, the manipulatable band gap and electrical conductivity, and low-toxicity.

As Cu_xS *per se* possesses high electrocatalytic activity like other enzymes such as glucose oxidase, chemical sensors using Cu_xS nanocomposites seems to dominate those used in biosensors (Table 1). The reduction ability of Cu_xS is inevitable which has been exploited in most of the electrochemical sensors listed in Table 1. In addition, CuS has been used to reduce the Cr(VI) from food and water samples to Cr(III),[65] and then detected by use of flame atomic absorption spectrometry (Table 1). Yet, high electrical conductivity and synergy effect to photoactive materials make Cu_xS benefit electronic and optical sensors.

The summary provides unambiguous evidence on the perspective of the future works on sensing applications, related to the Cu_xS nanocomposites. Harnessing the non-toxicity of Cu_xS

would allow to build up, for example, the wearable or tattoo-like sensors – the technology of today.[85, 86] However, the attention also needs to be in the recovery of Cu_xS and its nanocomposites in order to achieve eco-friendly sensors.

Acknowledgement

T.-P.H acknowledges financial support from the starting fund from AAU's Research Profiling (Grant No. 301843), the Magnus Ehrnrooth Foundation, and the Academy of Finland (Grant No. 323240).

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