Advanced nanomaterial inks for screen-printed chemical sensors

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ABSTRACT

Screen-printing technology is an efficient integrated preparation method for the manufacture of chemical sensors in biological detection due to its low cost, large scale capacity and facile operation. Especially with the fast development of the nanomaterial science, more and more nanomaterials have been introduced in the fabrication of screen-printed chemical sensor devices. Among them, most research just focuses on the modification of nanomaterials on the already screen-printed electrode. However, if the nanomaterial can be directly prepared as the screen-printing ink, the efficiency will be greatly improved due to the process simplification and cost reduction. In this review, the recent progress in the nanomaterial based inks for screen-printed chemical sensors will be summarized, especially emphasizing the nanostructure synthesis and protection methods for the ink preparations. The performance of different nanomaterial inks printed chemical sensors are concluded with the different applications, the theoretical work mechanisms of different nanomaterials are also discussed for comparison.

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1. Introduction

Clark and Lyon [1] developed the first generation of enzymatic biosensor for blood sugar detection, and this research field has attracted increasing interest due to its close relation with human health [2–4]. Although various chemical sensors for biological analysis are emerging with the progress of technology and theory in biology, chemistry, materials, and other areas, few devices have

been transferred to commercial products for real applications [5–7]. There are many reasons that hinder chemical sensor technology transfer from the laboratory to industrial products. One is unsatisfactory performance of the prepared sensors, and another is limitations of the fabrication method for large scale manufacture at low cost.

In early research, chemical sensor performance was considered to be determined mainly by the innate properties of electrode materials. Therefore, research mainly focused on selection of suitable material for sensor fabrication [8–11], and synthesis of new or composite sensing materials became a key research focus. However, with the recent development of nanoscience, above con-
cept are changing. More and more researches have demonstrated that, besides of electrode material properties, the nanostructure of electrode materials can also strongly affect the sensing performance, such as sensitivity, selectivity, and stability [12–15]. Regular nanostructure with uniform distribution can remarkably improve detection performance compared with disordered structures. This is mainly attributed to its high crystallinity and large contact area which possesses more catalytic sites and low electron transfer resistance [16–18]. Thus, innate properties and the nanostructure of the sensing material are now both considered critical for final device performance.

However, most nanomaterial synthesis methods can hardly realize the large-scale preparation of nanomaterials on electrode due to their limits. Therefore, many research outcomes are not suitable for bulk product manufacture. What is strongly needed is a facile method to realize large scale preparation of chemical sensors using nanomaterials.

Screen-printing is a stencil printing method [19–21] that was not popularized until the silk screen was developed [22], which greatly improved printing quality and control. Fig. 1 shows the general principle for screen printing. A screen is the core component to produce the designed pattern. A substrate is placed under the screen, and ink is dropped on a blank area of the board away from the pattern. A scraper pushes the ink to cover the whole pattern region. The ink transfers through the screen openings, and adheres on the substrate. After drying, the pattern is printed on the substrate. However, many parameters can affect the printing process, such as ink composition, screen count, scratching force, ink viscosity, etc. [23]. In mature industrial productions, these parameters have already been studied and addressed for normal printing. However, research has become focused on the development of biosensing materials for screen printing. The simplest biological sensing material is enzyme. Due to the unsatisfactory viscosity of enzyme solution, carbon ink is normally mixed as the ink for printing working electrode. This preparation method was developed in the early research of screen-printed chemical sensors. Till now, various enzymes have been applied to prepare this type of inks, such as horseradish peroxidase and glucose oxidase [24], lactate oxidase [25], CYP450 2B4 [26] and so on. Although this preparation of enzymatic ink is facile, the work electrode which is printed by this kind of enzyme-only ink without other catalytic materials cannot perform superior sensing function due to the low catalytic activity. In recent years, due to advanced function and cost reduction, an increasing number of nanomaterials have been adopted for fabrication of various screen-printed chemical sensors for biological detections [27–29], and the technology has realized accurate control of printed film thickness to several micrometers. Many of these sensors exhibit stable and reliable performance for food inspection [30], clinical diagnosis [31], pollution monitoring [32], etc. However, these applications generally apply nanomaterials on already screen-printed electrodes, rather than modifying the ink preparation [33–37]. Compared with direct application of nanomaterials as the printing ink, this preparation route requires more steps and chemicals, increasing the fabrication cost and time, as well as suffering from relatively poor adhesion between the applied materials and screen-printed electrode.

Another common strategy is the preparation of enzyme containing inks for screen-printing, so that biological material is simultaneously deposited with the printed sensing material. Glucose oxidase [38], acetylcholinesterase [39], lactate dehydrogenase [40], tyrosinase [41], and many other enzymes [42] have been mixed with sensing inks for screen-printing. This method can shorten the preparation procedure, but generally the sensing nanomaterial cannot retain its regular shape and uniform distribution due to strong aggregation of the enzyme molecules. Recently results have confirmed the possibility of direct preparation of the nanomaterial ink for screen-printing. However, there has been no review to summarize the available nanomaterials as screen-printing ink for chemical sensor fabrication, although they have shown promise for the transfer from laboratory to industry.

Therefore, this review discusses the newly developed nanomaterials as printing inks for screen-printed chemical sensors. The materials are classified by their chemical compositions, and in contrast to reviews of screen-printed chemical sensors, we give emphasis to ink synthesis methods for nanostructured materials, as well as nanoscale morphologies, and address the key issue of protecting the material nanostructures during ink preparation. Finally, we compare the performance of screen-printed sensors fabricated using nanomaterial inks. Thus, we provide an overview of nanomaterials and related progress for fabrication of screen-printed chemical sensors, providing suggestions for material selection for ink preparation. This summary of the state of the art also highlights current and potential research areas for further development of nanomaterial based chemical sensors using screen-printing technology.

2. Nanomaterial based screen-printing inks

Although many nanomaterials have been developed for preparation of chemical sensors, few can be directly applied as screen-printing inks. To obtain suitable nanomaterial inks, ex-situ nanostructure synthesis is required. Solution dispersed nanomaterial is preferred due to facile adjustment of viscosity by drying. Otherwise, additives are required for solid state materials to ensure dissolution. However, during drying or dissolution, the nanostructured particles tend to have strong agglomeration, leading to significantly decreased performance and uneven printing. Therefore, designing appropriate nanostructure synthesis methods incorporating the different material properties is the key problem to ink preparation.

2.1. Noble metal nanoparticles

Because of their high catalysis and conductivity, noble metals were employed from very early in the development of chemical sensor preparation [43–45]. However, their nanostructures are mostly provided by in-situ synthesis methods [such as electrodeposition [46], chemical vapor deposition [47], and hydrothermal synthesis [48]] on the substrate, which makes them in appropriate for screen-printed electrode fabrication. The difficulty of ex-situ approaches is prevention of over-aggregation of noble metal nanoparticles in the solution. Fig. 2 shows a potential approach to solve this problem for ink preparation by introducing extra substances to disperse nanoparticles with physical or chemical interaction.

Tangkuaram et al. [49] applied a chitosan solution to disperse synthesized Au nanoparticles. Homogeneous 16.8 nm Au particles were first prepared by Na-citrate reduction of HAuCl4 solution. Then this suspension solution was mixed with the chitosan solution.
as the deposition ink to effectively avoid nanoparticle aggregation. UV–vis spectra confirmed that the small Au nanoparticles produced less aggregation after bonding to the biomolecule. For application, horseradish peroxidase was further modified on the carbon work electrode for \( \text{H}_2\text{O}_2 \) detection. The resulting \( \text{H}_2\text{O}_2 \) sensor showed remarkable storage stability, maintaining 95\% current response up to 30 days.

Another nanostructured Ag suspension ink was developed for screen-printing by Cho et al. [50]. A 20 nm Ag nanoparticle suspension was prepared by reduction between \( \text{AgNO}_3 \) and formaldehyde solutions, and polyvinyl pyrrolidone (PVP) was applied as a stabilizer to avoid aggregation. However, the suspension viscosity was unsuitable for printing, and the solution purity was inferior. Acetone was used to remove PVP, and diethylene glycol was added and dried to adjust the suspension viscosity. Inks with different silver concentrations were prepared for comparison of printing effects. Lower silver concentrations (<60\%) were unable to produce continuous patterns, which was attributed to unsatisfactory viscosity. The screen count was also investigated, and confirmed that higher screen hole counts produced more exact printed patterns.

Thus, noble metal nanoparticles in solution or colloid can provide sufficient structural stability, and the introduction of stabilizer or reactant with metals before ink preparation has become the main method to protect nanoparticle shape and size. However, due to their high cost and unstable storage, nanostructured noble metal inks are not widely applied in either research or industrial production.

2.2. Carbon based nanomaterials

Carbon materials, including graphite, graphene, carbon nanotubes (CNTs), and their derived materials, have been widely employed as biosensing materials due to their superior conductivity [51–53]. Resin mixed graphite powder is often used as carbon ink for fabrication of screen-printed electrode [54], and work and counter electrodes of commercial screen-printed chips are often prepared using carbon ink. However, these chips are mainly adopted as substrates for further modification of biosensing materials on the work electrode due to the weak catalytic activity of graphite and resin, and are rarely used for direct application of carbon ink for sensing. On the contrary, although the composition element is same, CNTs and graphene have quite different structures and are commonly employed as biosensing materials [55].

Multi-wall carbon nanotube (MWCNT) has been used as screen-printing ink for construction of glucose biosensors [56]. The purified MWCNT powder was ground to fine particles, and then mixed with isophorone solution containing polyvinyl chloride, dimethyl succinate, and dimethyl glutarate to form a homogeneous ink. Alumina ceramic plates were used as screen-printing substrates. The ink exhibited good tolerance to mechanical abrasion as well as excellent adhesion on the ceramic substrate. More importantly, MWCNT ink prepared electrodes showed very low resistance. Fabregas et al. [57] also employed MWCNT as the main component for screen-printing ink, using polysulfone (PS) as the solvent. They produced multi-layered screen-printed electrodes with, from the bottom to top, polycarbonate substrate, silver, carbon, and MWCNT/PS layers. The authors did not explain the reason for the complex layer structure, but the introduction of silver and carbon layers can definitely improve electrode conductivity. They used their nanomaterial ink to prepare an enzymatic biosensor and immunosensor, and the single-walled CNT ink can currently be purchased commercially.

Since the 2004 Noble Prize was awarded, preparation and application of various graphene materials have been applied in many scientific areas [58], and its excellent conductivity and biocompatibility [59] are greatly attractive for chemical sensor. Accordingly, graphene based screen-printing inks have been studied for fabrication of biosensing chips. Ying et al. [60] synthesized graphite oxide from graphite powder, and then obtained reduced graphene oxide (rGO) by ultrasonication and hydrazine reduction reaction by turns. To adjust the viscosity, they added cellulose acetate, cyclohexanone, and acetone as the solvent. After sufficient ultrasonic treatment, a homogeneous viscous ink with ca. 200 nm rGO sheets was harvested (Fig. 3a). Without the assistance of other catalytic materials, rGO-only printed electrodes exhibited low transfer resistance and excellent oxidation activity for simultaneous detection of ascorbic acid, dopamine, and uric acid from the different potentials (Fig. 3b). Karuwan et al. [61] developed a graphene-carbon paste ink by a home-made method. After synthesis of graphene powder from graphite, they simply added the powder to commercial carbon paste ink to prepare the screen-printing ink. They investigated the effects of graphene content on the electrochemical performance, and showed that 10 wt\% was the optimum condition. However, microscopic characterization confirmed the heterogeneous distribution of graphene and graphite particles using this method.

Although carbon nanomaterial inks can be produced by mixture with commercial carbon ink or polymers, low catalytic ability is always an obstacle for preparation of high performance screen-printed chemical sensor. The relatively high cost may be another factor hindering large scale production for screen-printing. Its further application should be considered for promoting conductivity for synthesis of other material based inks.
2.3. Other inorganic materials

Aside from noble metal and carbon materials, many inorganic materials have been prepared as screen-printing inks, such as coordination complexes and metal oxides. We provide an introduction of some typical nanomaterials in these categories.

Prussian blue (PB, Fe₄[Fe(CN)₆]₃) is a classic inorganic coordination complex [62], with only three elements, iron, nitrogen and carbon, comprising its cell structure (Fig. 4a), where neighboring iron atoms have different valences (+3 and +2). It shows outstanding electrochemical redox behavior for catalysis of H₂O₂, and hence can be applied for preparation of various chemical sensors after immobilization of different oxidases [63] (Fig. 4b). The common sensing mechanism can be explained as follows:

\[
A \rightarrow_{\text{oxidase}(A)} A_{\text{ox}} + H_2O_2 \quad (1)
\]

\[
P B + e \rightarrow PW \quad (2)
\]

\[
H_2O_2 + PW \rightarrow PB + 2OH^- \quad (3)
\]

where A represents the bio-target, oxidase (A) means the matching oxidase of A, PB is the Prussian blue molecule, and PW represents the reduced PB state.

PB has a large family of analogues, with the different Fe atoms replaced by other metal elements, such as Co, Ni, Mn, Cr, etc. [64]. The analogues retain the face-centered cubic structure, and their formation reactions are also similar using the metal cation and metal cyanide anion. Different analogues provide different biosensing functions. However, PB and its analogues cannot be well controlled for nanostructure formation because of their fast crystallization rate. Accordingly, development of a nanostructure control method for PB ink could provide a versatile strategy for fabrication of PB (and analogues) based sensor devices.

Our group has concentrated much effort on nanostructure control of PB film and its biosensor applications, with many facile approaches developed, such as electrostatic self-assembly [65], aerosol deposition [66,67], electric field induced self-assemble [68], template assisted self-assemble [69], etc. Recently, to realize device production of PB biosensors, we designed an original route for large scale synthesis of PB nanostructured ink [70].

As discussed above, the difficult structural control is attributed to the fast formation rate of PB crystals. To reduce crystallization and aggregation rates, a low speed chemical synthesis approach was developed. Two reaction solutions were simultaneously injected into a high volume water container by a low speed motor, with average injection rate 0.5 ml/min. The resultant PB suspension was composed of numerous very uniform and regular nanocubic crystals (Fig. 4c). After drying and adding carbon ink, a viscous dark blue ink was obtained. The resulting printed biosensor chips (Fig. 4d and e) exhibited high sensitivities in detection of glucose, lactate, and glutamate by the respective immobilizations of glucose, lactate, and glutamate oxidases. Its detection of blood glucose was also demonstrated to be very close with the real content. Without specificity, this method is promising for preparation of PB analogue based screen-printed biosensors.

ZnO is a popular semi-conductor, and widely applied in the fabrication of optical, magnetic and electrochemical sensors [71]. Its band gap between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) is approximately 3.24 eV at 300 K [72]. Therefore, it normally requires high energy for excitation of conduction band electrons. However, due to incorporating existence oxygen, it possesses the detection advantage of oxidizing the bio-target. The biosensing behavior of ZnO is typical of most of metal oxides, and ZnO based chemical sensors can provide analysis of glucose, uric acid, cholesterol, etc. [73,74]. Its abundant nanostructures also provide research opportunities for material science. Nanorod, nanowire, nanoflower, and nanocomb ZnO films have been synthesized by hydrothermal, electrodeposition, and ultrasonication methods [69]. For screen-printing applications, Qi et al. [75] prepared a flower-like ZnO nanorod based ink. The flower-like ZnO nanorod powder was synthesized using a chemical baths method. Zn(OH)₂ was used as the precursor and the dissolution–precipitation reaction produced ZnO nanorods. This powder was further ground and diluted with water to a paste for direct printing.

Another synthesis strategy was developed using ZnO nanowires [76]. ZnO nanowires were prepared from zinc nitrate hexahydrate solution. A hexamethyleneetetramine solution was then added and heated to 90 °C for 3 h. ZnO was extracted and dried to form a powder and subsequently mixed with commercial carbon paste to produce screen-printing ink. Thus, to synthesize nanostructured ZnO ink, one must first synthesize the powder, and then mix this with water or solvent to adjust the viscosity. This is probably due to the very weak solubility of metal oxides. Although the synthesis reaction begins in solution, the formed crystal is easily precipitated out of the suspension. Directly using the reacted product will result in non-uniform distribution of nanocrystals. Therefore, fine powder is produced by drying and grinding.

Similar to ZnO, many other metal oxide nanocrystals have been used for as screen-printing inks, such as bismuth oxide, tin-doped indium oxide, β-manganese oxide, etc. [77–79]. The nanostructured metal oxides normally possess high catalysis, particularly for oxidation, but the high band gap and weak conductivity may be an issue for sensing performance.
2.4. Nanostructured conductive polymers

Compared with polymers, inorganic materials normally possess much higher catalysis and conductivity. However, polymer malleability and plasticity is superior. Polymer was long believed to be unable to conduct due to strong resistance caused by the long organic chain. However, this concept was changed with synthesis of conductive polypyrrole (PPy) in 1978 by IBM. Subsequently, a series of conductive heterocyclic and benzene polymers have been developed and applied for chemical sensor fabrications, including polyaniline (PANI) and polythiophene [80].

The molecular weight and viscosity of these materials can be controlled to satisfy the requirements of screen-printing ink, and importantly, the printed electrode can exhibit excellent bending ability and light weight, which is a significant difference from inorganic materials. In recent decades, nanosize control technologies have been introduced in fabrication of nanostructured polymers, and some have produced nanostructured polymer inks for printing.

PPy has been widely used in the fields of battery, sensor and capacitor due to its good conductivity which arises from its π-conjugated backbone structure [81]. PPy is normally obtained by polymerization of pyrrole (Py) monomer. Yawale et al. [82] continuously added Py monomer into FeCl3/methanol solution to realize polymerization by the increasing oxidation potential, attributed to methanol evaporation. After purification, 60 wt% PPy was mixed with butyl carbitol and ethyl cellulose to prepare the paste ink. SEM characterization showed that the printed electrode surface had a nanosized honeycomb-like structure, and this structure also can be adjusted by controlling the Py/FeCl3 ratio.

Subsequently, PPy ink has been developed for preparation of wholly printed biosensors [83]. Although this ink was used in injecting printing, its application is promising to extend to screen-printing. PPy was also obtained by polymerization from Py, but the composition of the reaction solution included polyvinyl alcohol and gemini surfactant with oxidants of p-toluenesulfonate hexahydrate and FeCl3. This polymerization route required quite long (24 h) reaction times and more than 64 h for purification. For the construction of biosensors, enzymes, including horseradish peroxidase and glucose oxidase, were mixed into PPy to prepare PPy/enzyme inks for printing. SEM images showed the prepared inks had very small nanoparticles covered by enzymes. The printed electrode provided fast response and stability in detection of H2O2 and glucose. The substrate was flexible polylethylene terephthalate, with good blending and folding capacity.

PANI itself is an insulator, but can become conductive with incorporation of salts or surfactants due to protonation of its imine nitrogens. Conductivity can exceed 100 S/cm with introduction of toluenesulfonamide during polymerization [84]. Some printed PANI inks have included nanostructures. Direct application of synthesized PANI for screen-printing is unsuitable due to strong particle aggregation which can block the screen. Therefore, Gill et al. [85] applied 10 wt% polyvinyl butyral as binder,
10 wt% PS surfactant as blocking agent, to prevent aggregation of PANi nanoparticles, and ethyleneglycolmonobutylether as solvent. The thickness of the resulting PANi film can be controlled within 35 μm, and provides very low electrical resistance. The authors also prepared a PANi film by direct drop deposition for comparison, and found the resistance was at least 10^4 times that of the screen-printed film. Screen-printing compressed the nanoparticles and provided a connected electron path, decreasing the resistance, whereas drop deposition tended to produce cracks and vacancies during drying which blocked electron transfer.

Poly(3,4-ethylenedioxythiophene) (PEDOT), a derivative of polythiophene, is one of the most popular conductive materials in biosensor fabrication, and has been demonstrated to possess superior conductivity to PPy [86]. Its positive charge is also beneficial for enzyme immobilization and electron transfer due to electrostatic interaction. However, PEDOT solubility is very weak, which hinders uniform distribution of nanoparticles in screen-printing ink. To solve this problem, Istamboulie et al. [84] applied poly(styrenesulfonate) (PSS) as electrolyte during the PEDOT formation reaction. Ethylenedioxythiophene (EDOT) and PSS were dissolved together in water with continuous drop-wise addition of ammonium peroxysulphate. The polymerization reaction was processed ultrasonically for one hour, and a dark blue aqueous ink was obtained that could be directly printed as the working electrode. Conductivity of prepared electrode was enhanced with increasing PEDOT ratio, reaching 2420 S/cm for 100% PEDOT. After the immobilization of acetylcholinesterase, the work electrode showed high oxidation ability to the choline at the potential 100 mV vs. Ag/AgCl.

The nanostructure of conductive polymer based ink is difficult to control, and normally produce irregular nanoparticle placement. In contrast to inorganic materials, polymers don’t have a redox center, and consequently their catalysis performance is weak. However, the pliability of their printed products is promising to develop fabrication of portable miniature chemical sensor devices.

3. Applications for biological analysis

3.1. Effects of screen-printing configuration on the performance

Screen-printing is a convenient large scale method for production of chemical sensor chips, and many sensors have been developed, particularly electrochemical sensors. The structure is normally constructed by screen-printing a three electrode system composed of working, counter, and reference electrodes.

However, there is no criterion for the screen pattern when screen-printing the chemical sensor. Therefore, the reported sensor chip configuration performance vary for different designs, which may influence the sensing performance. Tangkuaram et al. [54] examined the performance of chemical sensor chips with different configuration, as shown in Fig. 5a. They used cyclic voltammetry (CV) characterizations to investigate the reversibility and conductivity of six chips prepared using the same electrode materials. Configuration 5 showed possessed the best electrochemical sensitivity and reversibility, attributed to the largest counter electrode, which can promote rapid transfer of large quantities of ions during the sensing process. Configuration 1 chips produced redox peaks, but no obvious signal change with increasing concentration of K₂Fe(CN)₆. Configuration 2 chips had the reference electrode between the work and counter electrodes, and these produced high current errors for repeated experiments. The authors explain that electron transfer between work and counter electrodes was blocked by the reference electrode. The other three chips showed good performance, but inferior to configuration 5 chip due to smaller counter electrodes. Thus, the screen-printed configuration made a significant difference to the sensor chip performance, and optimal results were for larger counter electrode, and locating the reference other than between the working and counter electrodes.

3.2. Applications of different nanomaterial printed chemical sensors

The analysis of physiological index is essential for clinic evaluation of health status. Due to the complex composition of blood or body fluid, different chemical sensors are required to recognize the different targets. Chemical sensors screen-printed from nanomaterial inks have been successful applied in detection of various physiological substances.

For a given configuration, the detection target and performance are largely determined by the printed material properties on the working electrode. Many nanomaterials have been synthesized as inks for fabrication of screen-printed chemical sensors, as summarized in Table 1.

Most research on screen-printed chemical sensors used glucose as the detection target for performance evaluation. Glucose oxidase must be immobilized on the prepared working electrode to oxidize glucose for generation of a response signal (current or potential). During this process, the main functions of the printed nanomaterials are signal magnification by electrocatalysis and signal transfer by conductivity. Thus, these material properties are for sensing performance, particularly sensitivity. However, comparing the listed glucose sensors (Table 1), nanomaterial electrocatalysis seems to be the most important factor.

Nanostructured silver and Pb, which have superior catalytic activity, are beneficial to promote sensitivity. Pb is called artificial peroxidase due to its remarkable catalysis for H₂O₂. Therefore, although silver has higher conductivity than Pb, which is a semiconductor [96], the sensitivity of Pb nanocubes still exceeds that of Ag nanoparticles. Most other materials show much lower performance. Aside from PbO₂ and cobalt phthalocyanine, screen-printed chemical sensors can be operated under negative potential to provide good selectivity.

PB can be applied for detection of various physiological targets after immobilizations of different oxidases. As shown in Table 1, Pb nanocube ink printed chemical sensors also exhibit high performance for analysis of lactate and glutamate at low concentrations. This nanomaterial ink and preparation route can be extended to preparation of other chemical sensors for analysis of more substances.

Following glucose detection, many other applications have been also realized by chemical sensors with various nanomaterial inks, such as detections of dopamine, hCG Hormone and pesticide. These reported results show these sensors have good detection performance. We believe this trend will only accelerate and many more nanomaterials will be adopted for ink preparation for sensing of physiological substances.

4. Conclusions and future perspectives

We have summarized typical nanomaterials that have been used as inks for direct fabrication of screen-printed chemical sensors, as well as the strategies for their nanostructure synthesis and ink preparation. The resulting sensors exhibit very high performance due to strong catalysis or conductivity attributed to the nanostructured materials. Their applications have extended to clinical diagnosis, food safety, and pollution monitoring. Some chemical sensor devices have also been fabricated to provide real-time detection. Only a very small subset of nanomaterials has been studied for potential screen-printing chemical sensors, exhibiting advanced performance and potential industrial production. These achieve-
ments will encourage development of more nanomaterials for high performance screen-printing inks for sensor fabrication.

However, some problems remain, and require further research. The main challenge is protection of the nanomaterials without aggregation during ink preparation. The present method is addition of stabilizer agents before viscosity adjustment by mixture of polymers or commercial carbon paste. However, most current stabilizers have weak conductivity or catalysis, which reduces the final nanomaterial performance. Development of suitable stabilizers with nanomaterial protection but strong catalysis and/or conductivity will accelerate the transfer from nanomaterial research to commercial manufacture of chemical sensor device.

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References


Table 1

Chemical sensors screen-printed by the nanomaterials based inks.

<table>
<thead>
<tr>
<th>Material</th>
<th>Nanostructure</th>
<th>Application</th>
<th>Potential (V)</th>
<th>Sensitivity</th>
<th>Limit of detection</th>
<th>Linear range</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold/CNT/PS</td>
<td>Nanoparticle/ Nanotube</td>
<td>H2O2</td>
<td>–0.4</td>
<td>0.176 μA·M⁻¹·cm⁻²</td>
<td>10 μA</td>
<td>0.01–1.13 μM</td>
<td>[49]</td>
</tr>
<tr>
<td>CNT/PS</td>
<td>Nanoparticle</td>
<td>H2O2</td>
<td>–0.2</td>
<td>0.12 μA·M⁻¹·cm⁻²</td>
<td>25 μA</td>
<td>0.01–0.5 μM</td>
<td>[57]</td>
</tr>
<tr>
<td>PPy</td>
<td>Nanoparticle</td>
<td>H2O2</td>
<td>–0.2</td>
<td>1.42 μA·M⁻¹·cm⁻²</td>
<td>10 μA</td>
<td>0.01–10 μM</td>
<td>[80]</td>
</tr>
<tr>
<td>Silver</td>
<td>Nanoparticle</td>
<td>Glucose</td>
<td>–0.05</td>
<td>20.09 μA·M⁻¹·cm⁻²</td>
<td>–</td>
<td>0.2–6 mM</td>
<td>[88]</td>
</tr>
<tr>
<td>Lead oxide</td>
<td>Nanoparticle</td>
<td>Glucose</td>
<td>0.7</td>
<td>0.183 μA·M⁻¹·cm⁻²</td>
<td>–</td>
<td>0–10 mM</td>
<td>[89]</td>
</tr>
<tr>
<td>PB</td>
<td>Nanocube</td>
<td>Glucose</td>
<td>0.05</td>
<td>83.404 μA·M⁻¹·cm⁻²</td>
<td>10 μA</td>
<td>0.01–1.3 μM</td>
<td>[70]</td>
</tr>
<tr>
<td>Cobalt phthalocyanine</td>
<td>Nanoparticle</td>
<td>Glucose</td>
<td>0.5</td>
<td>1.12 μA·M⁻¹·cm⁻²</td>
<td>200 μA</td>
<td>0.2–5 μM</td>
<td>[90]</td>
</tr>
<tr>
<td>CNT</td>
<td>Nanoparticle</td>
<td>Glucose</td>
<td>–0.2</td>
<td>0.21 μA·M⁻¹·cm⁻²</td>
<td>–</td>
<td>1–5 μM</td>
<td>[85]</td>
</tr>
<tr>
<td>Au-TiO2</td>
<td>Nanoparticle</td>
<td>Glucose</td>
<td>–0.2</td>
<td>30 μA·M⁻¹·cm⁻²</td>
<td>–</td>
<td>0–1 μM</td>
<td>[56]</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>Nanosheet</td>
<td>Glucose</td>
<td>0.1</td>
<td>63.799 μA·M⁻¹·cm⁻²</td>
<td>10 μA</td>
<td>0.01–0.5 μM</td>
<td>[70]</td>
</tr>
<tr>
<td>Graphene</td>
<td>Nanosheet</td>
<td>Glucose</td>
<td>–0.05</td>
<td>31.642 μA·M⁻¹·cm⁻²</td>
<td>10 μA</td>
<td>0.01–1 μM</td>
<td>[70]</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>Nanosheet</td>
<td>Phthalocyanine</td>
<td>–0.4</td>
<td>4 μA·M⁻¹·cm⁻²</td>
<td>16 μA·M⁻¹·cm⁻²</td>
<td>0–600 μA·m⁻²·cm⁻²</td>
<td>[11]</td>
</tr>
<tr>
<td>Au-TiO2</td>
<td>Nanoparticle</td>
<td>Organophosphate</td>
<td>–0.2</td>
<td>11.88 μA·M⁻¹·cm⁻²</td>
<td>0.01 μM</td>
<td>0.01–100 μM</td>
<td>[94]</td>
</tr>
<tr>
<td>CNTs/Cu(B)</td>
<td>Doped CP-DDS</td>
<td>Sodium alkylsulfate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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Biographies

Wanqin Jin is Professor of chemical engineering at Nanjing Tech University and his current research focuses on the development of membrane and biosensing materials, electrochemical analysis and the production transfer of biosensors by screen-printing technique. He was an Alexander von Humboldt Research Fellow (2001), and a visiting Professor at Arizona State University (2007) and Hiroshima University (2011, JSPS invitation fellowship). He has published over 250 internationally refereed journal papers and edited a book on materials-oriented chemical engineering. He serves as associate editor and an editorial board member for several journals and is a council member of the Aseanian Membrane Society.

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