

A feature article from the laboratories of Prof. Ching-Ping Wong (Georgia Tech., USA), Prof. Matthew M F Yuen (HKUST, HK China), and Prof. Cheng Yang (Tsinghua Univ., China).

Title: Printed electrically conductive composites: conductive filler designs and surface engineering

A series of technologies has been proposed in recent years using surface engineering methods and the development of novel conductive materials to improve the performances of electrically conductive composites. Recent reports on this subject and related technologies are reviewed in this article.

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Printed electrically conductive composites: conductive filler designs and surface engineering

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Enormous efforts have been made towards the next generation of flexible, low-cost, environmentally benign printed electronics. In this regard, advanced materials for the printed conductive lines and interconnects are of significant importance. To improve efficiency and effectiveness, for several decades, conductive fillers have been filled into dispersants, which lead to the so-called electrically conductive composites (ECCs), which are a key material to the printed electronics varying from substituting the traditional solders to finding new applications in the blooming field of flexible printed electronics. ECCs in various formulations have converged in the current efforts to develop platforms with the desired specifications of electrical and thermal conductance, mechanical strength, and others. This platform is highly versatile and valuable for the emerging novel electronic devices, which emphasize tailoring processing conditions to cater to the key functional materials to optimize outcomes. The properties obtained can facilitate decisions about modifications to treatment. Noble metal fillers, such as silver flakes, have long been studied as active fillers for the ECCs. Owing to the recent progress in nanotechnology and surface modifications, many new avenues have opened for them. By taking advantage of the well-developed surface chemistry of these materials, researchers are enhancing their electrical conductivity, which is essential for broader applications. In recent years, the advances of ECCs have benefited the development of the applications of optoelectronics, e-papers, electromagnetic

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neering, Georgia Institute of Technology (GT) and is the Dean of the Faculty of Engineering School, City University of Hong Kong (CUHK). Professor Wong has been awarded numerous international honors, such as the IEEE CPMT Field Award and David Feldman Outstanding Contributions Award, the IEEE Third Millennium Medal, and the IEEE EAB Education Award. shielding, clinical diagnosis, radio frequency devices, *etc.* Despite the various advantages that they can offer over the traditional technologies, their limitations, *e.g.* low electrical conductivity, poor impact strength, increased contact resistance at elevated temperatures and humidity aging, have been considered as the major obstacles. In this feature article, we introduce the surface engineering techniques of the conductive filler materials that we and others have developed, with an emphasis on how these techniques influence the performance of the ECCs, especially for the improvement of the filler-to-filler electron transfer in the resin dispersants, some of which have potentially been approaching the theoretical upper limit of what they can reach in electrical conductivity. We and others have developed a set of chemical and engineering methods to modify the conductive fillers, enabling tailor-made surface functionalities and charges. These features, in turn, can be harnessed to adjust the electrical property and reliability of the ECCs, and further, to cater to various novel printed electronics, based on *e.g.* low temperature processing conditions.

1 Introduction

For a long time, materials scientists and engineers have been seeking ideal materials as the interconnecting parts to substitute traditional tin/lead (Sn/Pb) solders and electroplated copper lines in microelectronics, because the high processing temperature for solder-reflow, the limitations of alignment resolution, and the limited choice of substrate materials hinder the development in electronic manufacturing.^{1,2} On the other hand, with the fast growth of nanotechnology, flexible electronics which possess superior performances, such as robustness, small size, low cost, user friendliness, and that do not increase the burden on the environment are being developed.3,4 Many materials scientists and engineers have been searching for novel materials for applications in thin-film transistors (TFTs), ultra high frequency (UHF) antennas, membrane keyboards, solar cells and batteries to achieve integrated functionalities which display both flexibility and stretchability.5-9 In the meantime, some other researchers focus on the substrate materials which can cater to the "chip-on-flex" technologies, which are in a position of more imperative need in the current industry and consumer market such as portable and wearable devices for soldiers, patients, children, etc.4,10-12 Moreover, spannable,⁹ foldable,¹³ biocompatible,¹⁴ and 3-D circuits¹⁵ have started to show great promise in various applications in the very near future. However, for achieving all these novel



Prof. Matthew M. F. Yuen received his BS degree from the University of Hong Kong and PhD degree from Bristol University, UK. He was the founding director of a series of facilities in the Hong Kong University of Science and Technology (HKUST) including the Electronic Packaging Lab, Technical Transfer Center, R & D Corporation, and Design and Manufacturing Service Facility. He is now the professor and Head of the Department of Mechanical Engineering, HKUST. functionalities on ubiquitous substrate materials, *e.g.* papers and PET (polyethylene terephthalate) films, printed conductive materials are required to bear a series of novel characters which traditional technologies cannot provide. These characters include lower cost, lower processing temperature, higher electrical conductivity, feasibility in mass manufacturing, and longterm reliability.¹⁶ It is imperative for the current technical trend to develop advanced electrically interconnecting materials with superior performances, especially for their electrical property.

Traditional techniques for the fabrication of conductive lines and interconnecting pitches, such as electroplating, vacuum deposition combined with lithography, and eutectic Sn/Pb solders, have been extensively investigated for the fabrication of electronic devices. However, these techniques often involve complex steps, high temperature (>200 °C) and toxic materials, which make them expensive and time consuming for production. Moreover, since 2003, the European Union has launched the Restriction of Hazardous Substances Directive (RoHS), which is closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE).17,18 The two directives strictly restrict the use of a series of hazardous substances including lead, mercury, cadmium, chromium(vi), polybrominated biphenyls, etc. Alternative materials (e.g. the lead-free solders) to substitute the traditional ones often involve higher processing temperatures, more complicated steps and even higher materials cost. Therefore, recent research has more intensively focused on the development of novel printable conductive materials, which are suitable for the conventional low-cost-printing process (e.g. rollto-roll printing, stencil printing, gravure printing, etc.); more specifically, it focuses on providing maximum conductivity and reliability in various current applications and some others which are under development. Moreover, these printable materials must be cheap, reliable, safe to human health, and processable at even lower temperatures. To all these ends, the electrically conductive composites (ECCs) become one of the best choices in future. With the blooming of nanotechnology, this group of materials is on the road of lower processing temperatures, improved mechanical robustness, flexibility, recyclability, lower cost, and most importantly improved electrical conductivity as compared to solders (Table 1).

In order to facilitate investigation and elucidation, in this feature article, we may tentatively divide ECCs into three categories: electrically conductive adhesives (ECAs), electrically

Table 1	A brief summary o	f different types o	of electrically	conductive composites
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	ECAs	ECIs	SECCs
Electrical resistivity (Ω cm)	10^{-6} to 10^{-3}	$3 imes 10^{-6}$ to $5 imes 10^{-5}$	10^{-5} to 10^{-1}
Curing/solidifying temperature (°C)	150-250	Room temperature and above ^{12,86}	Room temperature and above ¹¹⁹
Metal content (wt%)	Normally 50–80	>95	0-50
Major fillers	Micro-flakes, ⁵⁴ micro-flakes + nanoparticles, ³⁴ micro-flakes + nanowires ⁴³	Nanoparticles, nanoplates ^{5,9}	Nanoparticles, nanowires, carbon nanotube
Other constituents	Polymer resin, polymer resin + organic solvent ¹²⁴	Organic solvent ¹⁵ surfactant ⁸⁶	Carbonaceous matter, polymer, ionic liquid, organic solvent
Methods to achieve	Direct mechanical contact, ¹²⁵	Agglomerations of polymer	Electrolytic contact
percolation	thermal sintering, laser	surfactants, ⁸⁶ decomposition of	·
-	sintering, ¹²⁶ evolution of metal	precursors, ^{10,64} elimination	
	surfaces, ⁵⁴ decomposition of capping agents ³³	of solvents, ¹⁵ plasma, light, microwave sintering ^{70,72,74,77,104,127}	
Viscosity (cP)	1000-50 000	~1	1000-50 000
Printing method	Screen print, stencil print, contact print, direct write	Ink jet print, spray	Screen print, direct write
Reliability	High	Low to medium	Low
Minimum line width (µm)	~50	~ 5	${\sim}50$
Thickness (µm)	${\sim}10$	10-100	${\sim}10$
Major applications	Interconnects, printed 2-D and 3-D circuits	Printed circuits	Stretchable circuits

conductive inks (ECIs), and stretchable electrically conductive composites (SECCs). Fig. 1 shows the schematics and photographic images of the three categories of ECCs. ECAs, especially those based on thermosetting resins, can provide maximum mechanical interconnecting ability and excellent reliability; ECIs are nanometals which are dispersed in an organic solvent or water, and thus they have the lowest viscosity and can be printed with a high resolution through nozzles. After drying the solvent, the nanometals sinter with each other to form a selfsupported continuous film, containing both the metallic part and the residues of some surfactants or lubricants, and thus they are able to provide excellent electrical conductivity but the mechanical property and reliability are not as strong as ECAs. SECCs are a group of novel materials which are a collection or agglomeration of conductive materials with different nature, such as the "bucky" gel,19-21 which can provide excellent elasticity and anti-shocking property, which benefit from the soft matter based dispersants and the conductive fillers with highly anisotropic morphology.

As a material extensively used in industry, ECAs have been intensively studied since their invention in 1956;²² yet their electrical resistivity is in the range of about 10^{-3} to $10^{-4} \Omega$ cm, which is about an order higher than that of eutectic solders (about $2 \times 10^{-5} \Omega$ cm).² Since higher electrical resistivity results in higher loss, improving the electrical conductivity of the ICAs has become a major objective for general application. In ECAs, the conductive paths are formed through metallic filler contact in the resin matrix. These fillers must transport (both Ohmic and tunneling) electrons with each other intimately and form a conductive chain.^{1,23} Therefore, silver micro-powders have been

selected as a major filler type for ECAs. As a noble metal, silver has the lowest electrical resistivity (about 1.6 \times 10⁻⁶ Ω cm) among all metals and is rather stable to resist oxidation. It has the melting point of 962 °C, which is much higher than the decomposition temperature of resins (about 500 °C) and other necessary components. However, it has been difficult to render the micro-sized silver fillers build up metallic connections through a simple thermal treatment step. Above a critical filler concentration (percolation threshold), a connected chain network forms in the resin composite, which renders ECAs isotropically conductive (i.e. isotropically conductive adhesives, ICAs). Below that threshold, ECAs are only conductive in the zdirection when they are vertically sandwiched between two mating pads, and thus they are called anisotropically conductive adhesives (ACAs). Both ICAs and ACAs are now extensively applied in many interconnection applications such as liquid crystal displays (LCDs) and solar cell panels. Due to the printable character and excellent electrical conductivity, they are being studied in multiple electronic regimes.

2 Sintering among the micro- and nanofillers in an ICA

The explosion of nanotechnology allows us to obtain welldefined metallic nanostructures in a scalable way, which facilitates the development of novel printable conductive materials. These nanomaterials can provide better electrical conductivity at a much lower processing temperature, which benefit from the melting point depression effect.^{24–26} This effect is intrinsically related to the cohesive energy of the nanomaterials. Since atoms



Fig. 1 Schematics of various forms of ECCs: (A) ECAs; (B) ECIs; (C) SECCs containing 0-D (sphere), 1-D (wire), and 2-D fillers (flake). The corresponding photographic images of each kind of material are shown beneath each schematic. ECA is a gel-like paste with gray luster which can be cured to form a rigid solid (left); ECI is a dark liquid with metallic nanoparticles (dark color) in a solvent (middle); SECC is a gel-like viscous liquid which shows dark color when it contains carbon materials (e.g. CNT). When the solvent is eliminated, it becomes an elastomeric solid.²¹

near the surface have fewer bonds with each other, less energy is needed for them to leave the surface. Thus a size-dependent melting point of a material can be calculated through classical thermodynamic analysis. Gibbs–Thomson equation (eqn (1)) suggests such a relationship (formulation 1):

$$T_{\rm M}(d) = T_{\rm MB} \left(1 - \frac{4\sigma_{\rm sl}}{H_{\rm f}\rho_{\rm s}d} \right) \tag{1}$$

where $T_{\rm MB}$ = bulk melting temperature; $\sigma_{\rm sl}$ = solid-liquid interface energy; $H_{\rm f}$ = bulk heat of fusion; $\rho_{\rm s}$ = density of solid; and d = particle diameter.

Based on this relationship, as shown in Fig. 2, there is a chart showing the melting point depression with the decrease of the particle size of gold.²⁷ The melting point of gold nanoparticles (NPs) decreases to below 200 °C when the size is around 5 nm.²⁸ This suggests that smaller size of the NPs causes an exponential reduction of the melting point.²⁹ By adjusting the morphology of the nanomaterials, it is possible to form a conductive network with an even lower percolation threshold.

As compared with the conventional ICAs with pure micronsized fillers, nowadays, a few research groups have started working on partially introducing nano-sized fillers so as to improve the electrical conductance, taking advantage of the depressed melting point of the metal nanofillers. The addition of NPs effectively promotes sintering among the fillers at relatively low temperatures (*e.g.* 200 °C), which results in the microfillers building up metallic interconnections. However, simply mixing nano-sized fillers into the ICA formulations is not sufficient to effectively reduce electrical resistivity. Instead, it may dramatically increase the bulk resistivity of the composites,^{30,31} which is related to the increased number of contact points and the reduced contact areas amount the conductive fillers.³² A few recent studies have suggested thermal treatment to debond or decompose the surface species, *e.g.* the lubricant (organic small molecules) and silver oxide being prerequisites for sintering Ag NPs. Residues on the fillers may increase the electrical resistivity of the composite significantly even though the Ag NP fillers are in same size and distribution. Zhang *et al.*



Fig. 2 Melting point vs. particle diameter of gold nanoparticles (reproduced with permission from copyright AIP).²⁷ A schematic showing the melting point decreasing trend along with the particle size declining.

studied the case of using Ag NPs prepared through the combustion chemical vapor condensation (CCVC) method. Using this method, there is no organic molecule adhering to the surface of the Ag NPs. Their results showed that when the ICAs (4 : 6 molar ratio of Ag NPs to Ag flakes, totally 80 wt% in a bisphenol A type of epoxy resin) were cured at 180 °C, the electrical resistivity was as low as $4.8 \times 10^{-5} \Omega$ cm, which was three orders of magnitude lower than those cured at 150 °C.³³ When compared, ICAs containing Ag NPs with carbonaceous residues coated on them showed a slightly higher electrical resistivity when cured at 180 °C, since carbonaceous matters are only partially decomposed at this temperature, and their presence hindered the sintering of Ag NPs.

In order to trigger the sintering of silver in an ECA at even lower temperatures, Jiang et al. studied a way of surface modifying the Ag fillers using organic molecules.³⁴ In their work, through modifying the surface of the fillers by diacids, a dramatic improvement in electrical conductivity was observed (see Fig. 2, a schematic of the function of NPs in building up metallic connections in ICAs). The low-temperature sintering property of the NPs facilitates the development of a percolation network in the ICA after curing at 150 °C. As shown in Fig. 3 (scanning electron microscopy, SEM images), after annealing the silver nanopowders at 150 °C, sintering was observed; while further decreasing the annealing temperature to 100 °C did not promote the sintering of the NPs, which suggests a temperaturedependent relationship. The interesting part is that both the surface modification of the NPs and thermal energy play a key role in initiating the detachment of the surfactant, and thus the nanopowders are able to sinter with each other. Otherwise the electrical resistivity of the ICA samples was recorded to be as high as $2 \times 10^6 \,\Omega$ cm, which was 12 orders higher. Moreover, it was suggested that the debonded diacid may act as a flux to inhibit the formation of the silver oxide layer on the silver NP surfaces. This fluxing process aids the sintering process of silver NPs, which decreases the number of contact points among the particles and results in lower electrical resistivity.32

In 2010, Zhang et al. studied the thermal decomposition effect of a carboxylic acid based lubricant towards the electrical conductivity of the ICAs. They suggested that the fatty acid based lubricants may interact with the silver surface and lead to the breakage of the O-H bond in the fatty acid and subsequent formation of carboxylate species, i.e. -COOAg35 (Fig. 4). It was found that the lubricant monolayer can significantly influence the sintering process of the mixture of silver microflakes and NPs (6:4 by weight). Thermal decomposition of silver carboxylate at the silver flake surfaces produced Ag NPs, and the process is related to temperature, decomposition atmosphere, and heating rate. When the ICAs were cured in the air, the final products were metallic silver and gases (CO₂ and H₂O). This phenomenon was also confirmed by Liu et al., who revealed that at 230 °C the thermal decomposition product of silver behenate was CO₂, and at 260 °C hydrogen and water were obtained.³⁶

Generally, as compared to the conventional micro-filler based ICA formulations, adopting the multi-model filler systems is rather effective in improving the electrical conductivity, which benefits from the depressed melting point of the



Fig. 3 Comparison of the morphologies of surface functionalized silver nanoparticle powders before and after annealing at 100 and 150 °C for 30 min: (A) non-annealed diacid surface functionalized Ag NPs; (B) diacid surface functionalized Ag NPs annealed at 150 °C for 30 min; (C) untreated Ag NPs annealed at 100 °C for 30 min; and (D) surface functionalized Ag NPs annealed at 100 °C for 30 min (reproduced with permission from copyright ACS).³⁴ The yellow arrows show the morphological changes due to thermal sintering of the diacid modified Ag NPs.

NPs. However, this method has some limitations in application. For example, the increased viscosity due to the decreased average size of the fillers inevitably causes incompatibility with the printing process parameters, thus diluents or rheology adjusters become necessary and may cause other problems; on the other hand, since the added nano-fillers are near-spherical, the isotropicity of the composite becomes increased, which causes the rise of percolation threshold, which is adverse for the cost concern. Moreover, the reported thermal sintering temperatures for the dual model ICAs are often above 140 °C, which renders the materials incompatible with many plastic and paper substrates that are possibly used in the devices.^{14,37,38} Therefore, improving the anisotropic property of the nano-sized fillers may help to lower the percolation threshold and partially solve the above existing problems.



Fig. 4 A schematic illustration of the sintering between Ag NPs and Ag flakes within a polymer matrix (reproduced with permission from copyright ACS).³⁵ With the presence of Ag NPs, the Ag flakes are able to sinter each other rapidly and form metallurgical bonds effectively due to the melting point depression effect. The lubricant attached at the Ag flake surface is effectively removed due to the sintering process.

Prof. Younan Xia and his coworkers developed the polyol based method to reduce AgNO₃ into various shapes and sizes of NPs, which shed some light on the recent progress in the controlled synthesis of anisotropic conductive fillers.^{39–41} In this way, silver nanowires are able to be prepared in large quantities using facile methods.⁴² As a 1-D nanomaterial with the aspect ratio over 100, Ag nanowires are able to build up electrical percolation with a much lower threshold than that of silver microflakes. Taking this advantage, Fei Xiao *et al.* demonstrated that a combination of the dicarboxylic acid treated silver nanowires and silver microflakes can develop an excellent percolated network with extremely high electrical conductivity.⁴³ The ICAs filled with 75% of the silver fillers (3 : 2 weight ratio of micro-flakes and nanowires) reached 5.8 × 10⁻⁶ Ω cm when the sample was sintered at 300 °C.

3 Surface engineering of the micro-sized fillers

Rendering the sintering to take place at the contacting points among the fillers is an efficient way to improve the electrical conductivity of an ECA. In other words, making the surface of the micron-sized fillers sinter with each other may be more effective than un-selectively sintering all nano-sized fillers in an ECA. Moreover, using the micron-sized fillers would not increase the viscosity of the paste. Commercial silver microflakes are usually obtained through a mechanical machining process (e.g. ball milling); their size and shape are carefully tuned to cater to the specific applications in the packages. Therefore, they are cheaper and more environmentally benign than preparing NPs through the "bottom up" ones such as the wet methods. However, the current machining process often involves lubricants (e.g. hexadecanol, stearic acid, etc.),44 which interferes with the intimate contact at the metal interface. On the other hand, several factors regarding the fillers are known to affect the magnitude of the percolation threshold, such as shape, size distribution, and the surface-modification method of the filler particles. Through replacing the surface species with novel molecules and modulating the structure and hierarchy of the molecules self-assembled at the metal surfaces, the conductivity of the network built up by the metal fillers can be significantly improved.⁴⁵ To this end, a few surface engineering steps have been attempted. For example, by adding a small amount of short chain dicarboxylic acid to the ICA pastes, the long chain lubricant layer (typically a fatty acid such as stearic acid) can be substituted. Thus the electrical resistivity of the ICA can be reduced significantly due to the easier electronic tunneling/transport among the flake-to-flake interfaces.^{46,47} Additionally, Li *et al.* demonstrated that carboxylic acids were rather effective in promoting the conductivity among the conductive network which is built up by the silver microflakes and NPs (Table 2).⁴⁷

In addition to the carboxylic acid treatment, a suitable reduction process can be helpful to further boost the electrical conductivity of the ICAs. For example, thermal decomposition of silver carboxylate can reduce the electrical resistivity of the filler NPs.35 The direct introduction of reducing agents (e.g. aldehydes, NaBH₄, etc.) can easily improve the electrical conductivity by converting Ag⁺ to Ag⁰ at the filler surfaces.^{46,48} Hot PEG (polyethylene glycol) may also effectively eliminate the lubricants at the surface of the silver flakes and reduce the oxides so as to improve the electrical conductivity of the flexible polyurethane based ICAs.49 Another analogous strategy for the surface treatment of fillers is the addition of oxygen scavengers, such as the treatment of the ICAs by sodium sulfate (Na_2SO_4) , hydrazine (H₂N-NH₂), carbohydrazide (H₂N-NH-CO-NH- NH_2), diethylhydroxylamine ((C_2H_5)₂N-OH), and hydroquinone (HO-C₆H₄-OH).⁵⁰⁻⁵² In addition, thiols, pyridine and so forth have been used to modify the surface of the silver fillers in the ECAs (Table 3).53

Even though it sounds counter-intuitive, modulating the filler surfaces with oxidative molecules, such as iodine, has been demonstrated effective in improving the electrical conductivity of the ICAs as well. The surfaces of the silver micro-flakes were found to be iodinated into a nonstoichiometric structure containing both AgI and excessive silver clusters. Even though AgI is a relatively stable compound (as compared with AgCl and AgBr) with a band gap of about 3 eV, the nonstoichiometric AgI/Ag

			Curing param	eters	Electrical resistivity	γ (Ω cm)
	Filler loading by weight	Chemical treatment	Temperature (°C)	Time (min)	Without chemical treatment	With chemical treatment
Zhang <i>et al.</i> ³⁵	80% of 4 : 6 molar	Thermal decomposition of silver	260	10	$>3 imes 10^{-4}$	$6 imes 10^{-6}$
ra	ratio of Ag NPs	carboxylate and sintering	230	5	$>3 imes 10^{-4}$	$8.1 imes 10^{-5}$
	and Ag Fs		230	3	$>3 imes 10^{-4}$	$9.8 imes 10^{-5}$
Zhang <i>et al.</i> ³³	80% of 4 : 6 molar	Decomposition of silver oxide and	180	60	$4.8 imes 10^{-5}$	_
-	ratio of Ag NPs and Ag Fs	sintering	150	60	2.44×10^{-2}	_
Jiang et al. ³⁴	80% of 4 : 6 molar ratio of Ag NPs and Ag flakes	Carboxylic acid treatment of Ag NPs	150	90	$2 imes 10^6$	$5 imes 10^{-6}$
Zhang <i>et al.</i> ⁴³	75% of 2 : 3 Ag	Dicarboxylic acid modification:	300	30	$5.8 imes10^{-6}$	_
0	NWs and Ag Fs	sintering	250	30	$3.2 imes 10^{-5}$	_
	5	5	200	30	$3.3 imes10^{-5}$	_

Table 3	A comparison of the	e recently reported ICAs based	on surface engineering methods
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			Curing parame	ters		
	Fillers in the ICA (wt%)	Chemical treatment	Temperature (°C)	Time (min)	Before treatment (Ω cm)	After treatment (Ω cm)
Zhang et al. ⁴⁴	Silver flakes (80)	Silver carboxylate coated silver flakes and reduction by diglycidyl ether of polypropylene glycol	150	30	2.3×10^{-4}	$2.5 imes10^{-5}$
Zhang <i>et al.</i> ⁶¹	Silver coated copper flakes (80)	Silver coated Cu flakes modified by an amine-based silane coupling agent (SCA)	150	60	$1.3 imes 10^{-3}$	$2.4 imes 10^{-4}$
Yang <i>et al.</i> ⁵⁴	Silver flakes (75)	Surface iodination	150	30	$2 imes 10^{-4}$	$5.9 imes 10^{-6}$
0	Silver flakes (27.5)	Surface iodination	150	30	>1	$4.8 imes10^{-4}$
Yang <i>et al.</i> ⁴⁸	Silver flakes (85)	NaBH ₄ treatment	50	15	$4.5 imes 10^{-4}$	8.0×10^{-5}
U	Silver flakes (75)		50	15	$3.8 imes10^{-3}$	$3.5 imes 10^{-4}$
Li et al. ⁴⁹	Silver flakes (80)	PEG-600 treatment (150 °C, 30 min)	150	60	>10 ⁻⁴	$1.0 imes10^{-5}$
	Silver flakes (40)	PEG-600 treatment (150 °C, 30 min)	150	60	>1	$8.8 imes 10^{-4}$

nanostructure has totally different properties. Due to the large number of interstitial sites which allow the silver cation to migrate, these nanostructures are peculiarly sensitive to the environmental changes, and they exhibit a strong tendency for reconstruction when the silver micro-flake fillers are in close contact with each other.54 Meanwhile, the evolution process is accompanied by the morphological and optical-absorption change.55 Thus the iodination process adopts a fashion of diffusion-controlled inward movement and the silver surface may result in a defect-abundant nonstoichiometric Ag/AgI structure.56 Consequently, Ag⁺ can transport through the defective regimes and reconstruct the surface morphology,^{57,58} producing numerous fresh metallic silver clusters. The process was verified by the UV-vis analysis. As shown in Fig. 5, the surface of silver foil which is freshly iodinated shows two broad absorption bands at \sim 370 nm and \sim 640 nm, and another distinct sharp absorption at \sim 427 nm. The first two peaks grow as time elapses, which are correlated to the surface plasmon resonance (SPR) of the Ag_n^0 clusters;59,60 while the peak at ~427 nm is assigned to the characteristic band of β-AgI (wurtzite). The UV-vis absorption peaks vary along with the time and both SPR bands increase the intensity and red shift, which is induced by the plasmon coupling in a long range or a high-order coupling effect of a multi-Agparticle. Studies by Yang et al. suggested that the evolution process of iodinated silver surface contributes a lot to the formation of a conductive network among the silver microflake fillers.54 Under the optimal conditions, iodinated ECA samples exhibited a dramatic improvement in electrical conductivity. The electrical resistivity of the modified ECAs was $\sim 6 \times 10^{-6} \Omega$ cm with 75% by weight of the filler in bisphenol-A type of epoxy matrix, which suggests that even without adding metallic NPs as powder fillers, excellent electrical percolation can be obtained in a micro-sized filler network.

The decomposition of the surface protecting layers during the thermal curing process may play an analogous role in the enhancement of electrical conductivity. In a recent study by Zhang *et al.* on the Ag-coated Cu flakes for the ICA applications, an amine-based silane coupling agent (SCA) was used to promote the electrical conductivity of the conductive components.⁶¹ Before the SCA treatment, the ICA sample containing 80% by weight of the bi-metallic fillers can only achieve $1.28 \times 10^{-3} \Omega$ cm; while after treatment, the electrical resistivity can be as small as $2.4 \times 10^{-4} \Omega$ cm. Moreover, the contact resistance of the ICAs filled with the modified Ag-coated Cu flakes can be stabilized (less than 10% increase) for more than 1000 hours of aging (85 °C/85% RH) after three reflow cycles with a peak



Fig. 5 UV-vis absorption spectra (reflective mode) of the iodinated silver evaporated wafer surface at different time intervals after the iodination treatment (reproduced with permission from copyright RSC).⁵⁵ The red arrows show the evolution of the SPR peaks (approximately 370 nm and 640 nm) of silver clusters as time passes by (the blue dots are the schematics showing the ripening of silver nanoclusters during the evolution process); the green arrow shows the declining of the absorption band of AgI (approximately 420 nm) due to the decomposition of AgI.

temperature of 255 °C. The main reason for the excellent reliability is possibly related to the coordination of nitrogen on the amine-based SCA to the exposed copper of the Ag-coated Cu flakes, thus protecting copper from oxidation during thermal curing.⁶¹

4 Low-temperature sintered nanocomposites

Nano-metal based printed conductive materials have been intensively studied since the last decade. These materials are in the form of inks, and therefore are often referred to as "electrically conductive inks (ECIs)" (Table 4). They are intrinsically an aggregation composed of the sintered nano-metals and some other organic residues (e.g. surfactants). In order to improve the sintering effect, there is no resin added to the ECIs; instead, only necessary solvent and surfactants or lubricants exist in them. These characters enable the nanometal components to more easily sinter with each other and form a continuous metallic contact at rather low temperatures, leaving the lubricants or surfactants in the interstitial positions (as shown in Fig. 1b) or eliminating them.28 Taking this advantage, the metal based ECIs appear to be superior over the carbon (carbon nanotube, graphene, etc.) based conductive inks, when referring to electrical conductivity. On the other hand, since van der Waals force dominates among the sintered metal NPs and the substrate, ECIs might not offer strong enough adhesion on many substrates for use as an interconnecting material or for mechanical reliability on flexible substrates, thus they are usually printed as planar circuits rather than the interconnecting parts.62,63 Moreover, when combined with the ink-jet printing technique, very fine lines (down to several microns in width and space) can be produced based on the ECIs. In order to prepare the ECIs, certain kinds of reducing agents are needed; the metal cations (e.g. Ag^+ and Cu^{2+}) or precursors dispersed in the solution are reduced. With the presence of surfactants, the nanocrystals grow up and turn into homogeneous NPs which are dispersed in the reaction solution. They are finally purified and re-dispersed in an appropriate solvent and are ready for use. Therefore, the NPs are often prepared through the wet method and are involved with stronger reducing agents. For example, hydrazine, NaBH₄, citric acid, ascorbic acid and formaldehyde are often used in aqueous solutions; alcohols and phenols are often used in organic solutions. As compared, aqueous conductive inks are more preferred than the organic ones due to the environmental concerns. Those aqueous ECIs prepared through a citric acid-NaBH4 solution or in a similar way can lead to a product with the particle size as small as 15 nm.64 The melting point of the Ag NPs prepared in this way is much reduced as compared to that of bulk silver (962 °C). To date, various conductive silver films, patterns, and tracks have been fabricated successfully by sintering,26,33,62,65-68 including some novel ones such as microwave sintering,69,70 laser radiation sintering,71-73 xenon flash light sintering,74 electrical sintering,75 chemical sintering,76 and plasma sintering,77 which show some promise in alleviating the adverse thermal shocking effect towards the substrate materials and other components due to

the thermal sintering process. The low temperature sintering property of the NPs excellently provides a solution in forming conductive lines on those substrates *e.g.* paper and PET (poly-ethylene terephthalate) films, which are susceptible to heat.^{37,42}

It has been considered that the difficulties in low temperature sintering (<200 °C) of the metallic (e.g. Ag) NPs arise from the excellent stability of the polymeric dispersants (such as polyvinylpyrrolidone) or other small molecules with a long alkyl chain which cannot be decomposed or debonded from the metal surfaces at low temperatures.78-80 Thus the removal of organic molecules is a prerequisite for sintering to occur. Recently, some research groups demonstrated that sintering of Ag NPs at room temperature is feasible. Wakuda and co-workers triggered the sintering of Ag NPs at room temperature by dipping the films into a solution of organic stabilizer, which sheds some light on the development of novel low-temperature curable conductive interconnects.11,12,15,81 In their works, Ag NPs were sintered at room temperature by drying the solvent (toluene) in either air or methanol. The paste showed an electrical resistivity of 4.9 \times 10 $^{-4}$ Ω cm when dried in air and 7.3 \times $10^{-5} \Omega$ cm when dried in methanol.^{11,15} Microstructural observations revealed that the Ag NPs formed agglomerations and coarsened during the sintering process at room temperature. Clear connections were observed under SEM analysis.

Besides the near-spherical NPs, the nanoplate-based conductive inks5,9 recently showed some promise as conductive ink particles. Silver nanoplates are obtained through a wetchemical method,⁸² which utilize silver nitrate as the precursor and NaBH4 as the reducing agent in aqueous solutions. Sodium citrate as a capping agent is critical in controlling the shape and size of the silver nanoplates, which has been discussed by Yin et al.83 The silver nanoplates obtained in this way have the size ranging from several to hundreds of nanometers, and the thickness is less than 10 nm. The size of the nanoplates is much smaller than the machine-made microflakes while the shapes are similar to each other. Due to the anisotropic morphology, these silver nanoplates may find applications in the conductive inks as well as ECAs. The shrinkage of the size makes them advantageous in the interconnect applications which require ultrahigh resolution and miniaturization. Lee et al. suggested that the inkjet-printed conductors based on these nanoplates showed an electrical resistivity of about 2.63 \times 10⁻⁵ Ω cm after curing at 100 °C, which is lower than that of the control sample using spherical NPs ($4.3 \times 10^{-1} \Omega$ cm).⁵ Tai and Yang demonstrated that sintering the silver nanoplate-based conductive lines at 200 °C for 20 minutes can effectively reduce the electrical resistivity down to $9.4 \times 10^{-6} \Omega$ cm.⁸⁴ Other silver nanostructures have also been investigated. For example, silver nanowires have been demonstrated as excellent foldable printed conductors which are able to form a reticular conductive network on ordinary paper substrates.42 Without any thermal sintering step, after drying the aqueous solution under ambient conditions, the Ag nanowire-based conductors exhibited an electrical conductivity (about 5 imes 10 6 S m⁻¹) close to that of the eutectic solders. Additionally, the electrical resistivity of the printed area can be even lowered 10-20% by hot laminating (125 °C) the samples.42

Table 4 A table of the recently reported printed conductive ink materials which were sintered at room temperature

	Preparatio	on method					
	Solution type	Reducing agent	Surfactant	Particle size (nm)	Sintering temperature	Chemical agent	Electrical resistivity (Ω cm)
Wakuda <i>et al.</i> ¹¹	Toluene	Thermal reduction	Dodecylamine	15.9	Room temperature	Drying in the air	$4.9 imes10^{-4}$
Wakuda <i>et al.</i> ¹⁵	Toluene	Thermal reduction	Dodecylamine	7	Room temperature	Methanol dipping	$7.3 imes10^{-5}$
Magdassi <i>et al.</i> ⁷⁶	Water	Ascorbic acid	PAA	10	Room temperature	PDAC solution dipping	$6.8 imes10^{-6}$
Layani <i>et al.</i> 7	Water	Ascorbic acid	PAA	14	Room temperature	HCl vapor	${\sim}10^{-5}$
Lee et al. ⁵	Water	NaBH ₄	Sodium citrate	~ 100 (nanoplates)	100 °C in the air	_	2.63×10^{-5}
Tai and Yang ⁸⁴	Water	Hydrated hydrazine	Sodium citrate	<65 (nanoplates)	200 $^\circ \rm C$ in the air	_	$9.4 imes10^{-6}$
Yang et al. ⁴²	Glycerol	Glycerol	PVP	$80 \times 10\ 000$ (nanowires)	_	_	2.6×10^{-5}

Magdassi and co-workers demonstrated that Ag NPs (5-80 nm in diameter, average diameter = 11.1 nm, 0.013 wt%metal content) stabilized by poly(acrylic acid) sodium salt (PAA) can coalesce at room temperature when they contact the poly(diallyldimethylammonium chloride) (PDAC) solution.85 The addition of PDAC, a positively charged polymer, causes aggregation in the above dispersion. Highly conductive silver films were obtained by using this method.^{76,85} Moreover, it was found that, spontaneous sintering of all the Ag NPs occurred without any heating treatment. They further developed a series of approaches to achieve coalescence and sintering of metallic NPs at room temperature, through the spontaneous coalescence of Ag NPs. The sintering mechanism is based on the chemical removal of the NP stabilizing ligands, which results in in situ coalescence. This agglomeration effect brings about a significant difference in the Ag NP patterns, thus resulting in a drastic decrease of electrical resistivity, which is able to achieve about 5 times of that of bulk silver.76,86 Based on a similar mechanism, they further demonstrated that direct exposure of the printed patterns (based on Ag NPs) on plastic substrates to HCl vapor can result in the room-temperature sintering effect as well, which is due to the removal of PAA, the polymeric stabilizer, from the particles' surface by the chloride ions, thus enabling a close contact between the particles.⁷

Long and co-workers developed a rapid sintering method of Ag NPs in an electrolyte solution (CaCl₂, MgSO₄, NaCl, *etc.*) at room temperature, and used polydopamine as the guiding adhesive layer.⁸⁷ Polydopamine acts as both an anchoring agent to the substrate and a reducing agent. Moreover, catechol was used as the reducing agent and benzoquinone (the oxidation product of catechol in the silver-plating reaction) forms a blockage that interferes with electron transport between the adjacent Ag NPs. The addition of the metallic cations (concentration varied from 1×10^{-5} to 0.1 M) induces the coalescence of the Ag NPs at room temperature, which is possibly due to the formation of ion pairs between Ca²⁺ and the benzoquinone radical anion. The silver atoms become unstable and tend to coalesce with each other. The square resistance of the Ag NP thin films decreased from tens of kilo-Ohms to lower than

1 Ohm after a treatment time of about 10 seconds in the metallic cation solutions.

In 2011, Kao *et al.* demonstrated that a dual-nozzle ink-jet system can produce conductive lines *via* mixing of $Ag(NH_4)^{2+}$ and a formaldehyde solution, which is a modified Tollens' process (Table 5).⁸⁸ The silver ammonia solution and formaldehyde are simultaneously inkjet-printed onto glass slides under ambient conditions, and then the silver lines were sintered at different temperatures for an hour. This method involves silver ammonia solution as the ink instead of the Ag NPs, and the printing process essentially involves the following chemical reaction (formulation 2):

The sintered silver lines consist of clusters of Ag NPs with a mean diameter of ~80 nm with the sintering temperature of 100 °C. After sintering at 150 °C, the particles fused into aggregates of about 150 nm in diameter and the grain boundary significantly decreased. Before sintering, the electrical resistivity of the printed silver line is about $2.7 \times 10^{-5} \Omega$ cm, after sintering at 150 °C, the electrical resistivity dropped down to $1.2 \times 10^{-5} \Omega$ cm. Because the printed materials are in the solution form, the nozzle of the inkjet printer can be much smaller (*e.g.* 100 nm in diameter) than the conventional ones. Moreover, the viscosity is lower than those nanoparticle based inks, and the maximum silver content is limited by the solubility of the diamminesilver(1) cation in water, since the ink does not contain Ag NPs; the tiny nozzles have less problems of being blocked by the solid through them.

In 2012, Walker and Lewis synthesized a reactive silver ink which showed enormously high electrical conductivity and prototyped its applications on paper substrates.^{64,89} Analogous to Kao *et al.*'s method,⁸⁸ they utilized silver ammonia aqueous solution as the precursor too, while formic acid was selected as the reducing agent instead of formaldehyde. The reactive silver inks were printed through a unique highly flexible and

 Table 5
 A comparison of the recently reported ink-jet printed in situ reacted silver conductive lines

	Before treatment (Ω cm)	After treatment (Ω cm)	Curing temperature (°C)	Viscosity (cP)
Kao <i>et al.⁸⁸</i> Walker and Lewsi ⁶⁴	2.7×10^{-5}	$\begin{array}{c} \textbf{1.2}\times \textbf{10}^{-5}\\ \textbf{1.6}\times \textbf{10}^{-6} \end{array}$	150 90	0.92 2

ultrafine nozzle. This method suits the printing conditions using very tiny nozzles (*e.g.* 100 nm). The maximum silver content was only limited by the solubility of the precursor (diamminesilver(i) cation in water). Upon annealing at 90 °C, the printed electrodes exhibited an electrical conductivity equivalent to that of bulk silver. Based on the X-ray diffraction (XRD) analysis, the residue acetate groups were removed upon heating to 90 °C for 15 min. Before heating, the dried film contained approximately 57 wt% of silver and 43 wt% of silver acetate. The development of the *in situ* reaction based inkjet printing method as well as the aqueous based ECIs may be beneficial to the development of the environmentally benign electronic manufacturing technology.

5 Improving the anti-corrosion property of the cheap-metal-based conductive composites

Considering the high materials cost of the silver based ECAs, research on the Cu based ones has attracted much attention in recent years because of its huge potential to replace silver. Copper has the second highest electrical conductivity (only 6% less than that of Ag), while the price is currently about 100 times cheaper than silver and it is 1000 times more abundant. However, the major problem of the copper based ECAs in real application is related to the inherent tendency to oxidize under ambient conditions. Recently, there have been a few reports presenting various approaches which help solve this problem. Usually an inert coating layer for the copper microfillers is needed. This layer may be of polymers, self-assembled alkene chains, amorphous carbon, graphene or inorganic materials such as silica, or even an inert metal layer. These surface modification approaches are promising in solving the existing problems of the cheap metal based conductive composites (e.g. copper based ICAs), so as to open new possibilities in printed electronics which have high demands for low materials cost, e.g. printed solar cells, radio frequency identification (RFID) tags, electroluminescence devices, etc. Conventionally, self-assembled monolayer formulations including dodecanethiol (DT), mercaptobenzothiazole (MBT), benzotriazole (BTA), imidazole (IMD), hexadecanthiol (HDT) and benzothiazole (BT) can be bonded on the surface of copper films as a corrosion inhibition layer. However, the low thermal stability of the coating layers is a drawback to the reliability for the copper based ECAs, especially when undergoing the 150 °C resin curing process. In 2007, Yim et al.

developed a method of using silane coupling agents to enhance the oxidation prevention property of copper fillers for conventional ICAs.⁹⁰ After reflowing at 260 °C for 3 times and at 80 °C/80% RH for 24 hours, the electrical resistivity increased 134%.⁹⁰ Moreover, for a bimodal copper filler system (80 wt% Cu micro-flakes and Cu NPs 94 : 6), the electrical resistivity of the silane coupling agent modified ICA sample remained 7.5 × 10⁻⁴ Ω cm. As compared to those samples without any surface modification, the electrical conductivity, thermal stability and oxidation prevention ability were all significantly improved.

In the field of copper based ECIs, a few reducing agents can be used to produce Cu NPs, e.g. NaBH4,91-94 hydrazine,95-97 acid,98,99 sodium phosphinate,100 ascorbic 1,2-hexadecanediol,¹⁰¹ and sodium formaldehyde sulfoxylate.¹⁰² The size of the Cu NPs can be fine-tuned in a large range between 3 nm and 200 nm, which is controlled by the use of surfactants. However, after purification, the Cu NPs must be stored in a reductive or inert environment to prevent oxidation. This oxidation problem increases the difficulty in sintering and reduces the electrical conductivity. Yan et al. demonstrated that the PVP coated Cu NPs can be sintered through a low-temperature process under higher pressure.13 Copper cation is reduced to NPs by sodium hypophosphite monohydrate (NaH₂PO₂ \cdot H₂O) in the presence of PVP. Those NPs sintered at 200 °C under 5 MPa for 30 minutes were able to effectively prevent the oxidation of the NPs when heated in the air. Moreover, the bonding provided by the NPs can effectively interconnect copper wire to copper pads. The interconnects prepared by Cu NPs have a low resistivity of $1.1 \times 10^{-3} \Omega$ cm. Sintering at 300 °C resulted in a resistivity of 8.6 \times 10⁻⁵ Ω cm.

Luechinger *et al.* demonstrated that through depositing the bi- or tri-layer graphene on copper NPs with the size of ~50 nm by using the reducing flame technique, the copper metal core can be well-protected by the graphene sheets in humid air.¹⁰³ Moreover, the graphene sheet can offer a certain level of electrical conductance at the surface of copper, thus the printed line can maintain $6.4 \times 10^{-2} \Omega$ cm. Even though the electrical conductivity is still too high for any real application and needs further improvement, the facile preparation method and the well-improved reliability offer a new route to the future solution of the copper based electrically conductive composites (Table 6).

In 2007, Park *et al.* adopted a high baking temperature (325 °C) in vacuum for the direct-written copper conductive patterns through the ink-jet printing method, and copper(II) sulfate pentahydrate was used as the precursor of the copper lines. The electrical resistivity of the printed lines was measured to be $1.72 \times 10^{-5} \Omega$ cm.¹⁰⁴ Jeong *et al.* demonstrated that through adjusting the molecular weight of the PVP capping agent, the copper oxide layer on Cu NPs synthesized in ambient atmosphere can be minimized. After annealing in vacuum (10^{-3} Torr) for 60 min between 200 °C and 325 °C, interparticular connections for developing electrical conductivity were achieved.¹⁰⁵ Electrical resistivity measured here is on the order of $10^{-5} \Omega$ cm when the temperature is higher than 250 °C. Woo *et al.* demonstrated that carboxylic acid exerts a positive effect on the sintering of the inkjet-printed Cu NP

Table 6 A comparison of the recently reported Cu nanoparticle based printed conductors

	Chemical treatment	Content	Curing temperature (°C)	Additional condition	Electrical resistivity (Ω cm)
Yim et al. ⁹⁰	Silane coupling agent	80 wt% Cu flakes (30-40 μm) and	130	_	$1.28 imes 10^{-3}$
		20 wt% epoxy 80 wt% Cu flakes (30–40 μm) and Cu Ps (1–5 μm) (94 : 6) and 20 wt% epoxy		_	7.5×10^{-4}
Yan <i>et al.</i> ¹³	_	Pure Cu NPs (40.4 nm)	240	5 MPa pressure	$9.5 imes10^{-3}$
			260	-	$8.0 imes10^{-3}$
			300		$8.6 imes10^{-5}$
			350		$2.9 imes10^{-4}$
Woo <i>et al.</i> ³²	_	Pure Cu NPs (65 nm)	200	In the presence of formic acid	$3.1 imes10^{-6}$
			250	In the presence of formic acid	$2.3 imes10^{-6}$
Park <i>et al.</i> ¹⁰⁴	_	Cu NPs (40–50 nm)	325	Vacuum(10 ⁻³ Torr)	$1.72 imes10^{-5}$
Jeong et al. ¹⁰⁵	_	Cu NPs (35–60 nm)	275	Vacuum (10^{-3} Torr)	$9.2 imes10^{-5}$
			325	()	$3.4 imes10^{-5}$
Yabuki and Arriffin ¹⁰⁷	_	Cu NPs (20 nm)	200	In hydrogen gas	$2 imes 10^{-5}$
Yabuki <i>et al.</i> ¹⁰⁸	Decomposition of Cu(II) formate and <i>n</i> -octyl amine complexes	Cu NPs (100–300 nm)	140	In nitrogen gas	$2 imes 10^{-5}$

films.³² For example, with the presence of formic acid vapor, the electrical resistivity reached $3.1 \times 10^{-6} \Omega$ cm and $2.3 \times 10^{-6} \Omega$ cm when annealed at 200 and 250 °C, respectively. It appears that in the case of saturated monocarboxylic acids (*e. g.* formic, acetic, propionic, butyric), the acids with shorter hydrocarbon chains perform better in reducing the surface copper oxides when copper is printed into conductive lines. Moreover, using oxalic acid can more effectively reduce copper oxide than formic acid and the annealing time can be shortened for obtaining highly conductive printed copper films. This reductive annealing process allows fabrication of copper patterns with a low resistivity ($3.82 \times 10^{-6} \Omega$ cm) which annealed at 250 °C (using oxalic acid), which is comparable to the resistivity of bulk copper.

Besides the in situ reduction combined sintering method, it is noted that vaporized self-assembled multilayers on the Cu nanopowders can form a passivation layer against oxidation.¹⁰⁶ On the other hand, Yabuki and Arriffin demonstrated that some other reductive protective gases (e.g. H₂) can promote the electrical conductivity during the sintering process.¹⁰⁷ The resulting copper lines showed a resistivity of less than $2 \times 10^{-5} \,\Omega$ cm after annealing at 200 °C with the presence of H₂. They further demonstrated that copper(II) formate and n-octyl amine in nitrogen atmosphere were able to decompose and result in a film with a resistivity of 2 \times 10 $^{-5}$ Ω cm by calcination at 140 $^\circ C.^{108}$ According to the above examples, it appears that it is still challenging to totally solve the oxidation problem effectively in an economic and convenient way. Nevertheless, current Cu based ECCs may possibly find some niche markets which require relatively low device reliability and short lifecycle, such as those disposable railway tickets with the printed inlay RFID antennas.

6 Printed stretchable conductive nanocomposites with anisotropic fillers

Most conventional circuits contain brittle materials that will break if stretched by more than a few tenths of one percent. They are placed on rigid resin based substrates which have excellent impact resistance and can provide adequate protection. Thus conventional ECAs are composed of common engineering resins e.g. epoxies, polyesters, polyimides, polyurethanes, and polyacrylates, which have a similar nature to the substrate materials.^{1,49,109} Yet scientists and laypeople are more interested in the systems that are built on polymer-based flexible PCBs, which offer a bendable and even stretchable property. This makes the systems insensitive to fatigue strain and would greatly expand the application space of electronics in e.g. medical devices,14 energy devices,110 robotics,111 military,112 and lighting applications.¹¹³ Recent technical advances often rely on circuit configurations that contain waves, meanders, spanning structures, and even encapsulated conductive fluids.114-118 When compared, ECCs which are able to be printed onto highly flexible or stretchable substrates appear to be advantageous over the other techniques. The ideal printed ECCs should possess high conductivity, flexibility, cyclability, oxidation resistance, low curing temperature, and good adhesion.119 Among them, a low Young's modulus (e.g. 1-100 MPa for rubber) and elastomeric property are the most important characters which distinguish them from conventional ICAs. Traditional conductive elastomers (conductive rubbers) have been applied successfully in the EMI (Electromagnetic Interference) applications and pressure and moisture seals for decades, yet they are often extruded or molded into various shapes and layouts to cater to different application scenarios. Moreover, their electrical resistivity is often higher than $10^{-3} \Omega$ cm, which is related to the high contact resistance among the fillers. Therefore, developing novel stretchable and highly conductive ECCs with excellent processability (such as printing with high resolutions) would be of great promise (Table 7).

Since 2003, Aida and Lee have conducted research on a group of soft materials which are named "bucky gels", which are composed of carbon nanotubes and imidazolium ionic liquids.¹⁹ As a gel-like mixture, they can undergo elastic and plastic deformations on elastomeric substrates. Even though the dispersion mechanism for CNTs in ILs is still unclear, the possible reasons may be related to the cation- π interaction between the surface of CNTs and the imidazolium IL, the weak van der Waals interactions or electrostatic interactions.¹²⁰ In 2008, Sekitani et al. demonstrated that the bucky gels dispersed in a crosslinked fluorinated copolymer can be used as a stretchable conductor which has a maximum stretchability of 134% and a conductivity of 0.017 Ω cm. Similar to the conventional conductive rubbers, the new materials can be screenprinted and their electrical resistivity is much lower. This stretchable conductor is composed of super-growth single wall CNTs (SWCNTs), an ionic liquid (e.g. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI)), and a fluorinated copolymer (e.g. polyvinylidene fluoride-hexafluoropropylene copolymer). These conductive inks can be strained over 100% without mechanical damage or delamination from the PDMS matrix. The devices based on this stretchable soft conductive composite can be stretched by 30-50% and spread over a hemisphere without any mechanical or electrical damage.113

Conductive composites with a soft and stretchable nature can render the fabrication of the material into novel geometries and show great promise in developing novel medical and energy devices. This group of materials often contains the conductive components with at least one dimension in micron size, such as carbon nanotubes, so as to maintain electrical conductivity

along the stretching direction under strain. However, carbon nanotubes are not enough to maintain a high electrical conductivity. Decoration of the carbon nanotubes with conductive components so as to develop an effective non-axial electrical conductive path has been demonstrated to be feasible to meet this requirement.¹²¹ In 2010, Chun and Baik et al. demonstrated a new way of fabricating a stretchable conductor with enhanced electrical conductivity.121 In their work, the surface of multiwall CNTs (MWCNTs) was decorated with Ag NPs and the MWCNT-silver composite was dispersed in a hybrid paste containing IL, silver flakes, and polyvinylidene fluoride,¹²¹ which exhibited $1.75 \times 10^{-4} \Omega$ cm in its resistivity. In 2012, the same group further demonstrated that the silver micro-flakes and Ag-decorated MWCNTs can be mixed in a nitrile butadiene rubber (NBR) matrix and achieved a stretchable conductive composite with the electrical resistivity as low as 2.67 \times 10⁻⁵ Ω cm. This conductive composite can be stretched to a strain of over 600% when it is rolled into a helical ribbon form on a PET film without noticeable change in electrical conductivity.¹¹⁹ Since the Ag NPs decorated on CNT surfaces have better wettability with the silver flakes as compared to the unmodified CNT surfaces, the silver parts inside the elastomeric NBR matrix are able to sinter with each other at elevated temperatures (i.e. 150 -170 °C), due to the large surface area and high mobility of Ag atoms in the NPs. They further proved that the electrical resistivity of the stretchable conductive composite was as low as $1.75 \times 10^{-4} \Omega$ cm and can be strained to 140%. Finally, the printable character allows these materials to be able to be applied in scalable manufacturing processes and used in future novel electronics with larger dimensions and novel functions.

7 Current applications and processing issues of the printed ECCs

Currently the most extensively applied ECCs in industry are the ECAs. They were originally designed for substituting the

Table 7	A comparison	of the recently	reported printed	stretchable	conductors	(SECCS)
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			Electrical resisti	Electrical resistivity (Ω cm)		
	Conductive fillers	Maximum strain (%)	0% strain	Maximum strain		
Conductive rubber ²⁰	Carbon particles	>180	5	5		
Sekitani <i>et al.</i> ²⁰	20 wt% SWCNT; 20 wt% IL (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide)	134	0.017	0.16		
Sekitani <i>et al.</i> ¹¹³	15.8 wt% SWCNT; 30.6 wt% IL (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide)	29	0.0098	~ 0.01		
	0.4 wt%; 2.8 wt% IL (1-butyl-3- methylimidazolium bis(trifluoromethanesulfonyl)imide)	118	0.103	~ 0.10		
Chun <i>et al.</i> ¹²¹	29.5 wt% <i>n</i> Ag-MWCNT (30 : 70 by weight); 59.0% IL (1-butyl-4- methylpyridinium tetrafluoroborate); 8.6 wt% silver flakes	140	1.75×10^{-4}	0.05		



Fig. 6 Photographic images of the current processing examples for the ECAs in industry. (A) A worker is screen-printing the ECA based radio frequency identification (RFID) tag antenna in his work line. (B) Several RFID tag-incorporated garment labels ready for the heat-transfer printing process. (C) Garment pieces with the labels in (B) which were heat-transferred onto them. (Upper: before washes; bottom: after washing for forty cycles.) The RFID read range performance remained the same after the heat-transfer process and the subsequent washing cycles. (D) A microscopic photograph of the ECAs filled in the through-hole vias in a printed circuit board for the purpose of vertical interconnections. (E) A photographic image showing a commercial KNS-istack dispensing machine which is dispensing ECAs on a printed circuit board.

eutectic solder pastes, thus the two materials have similar viscosities (in the range from about 1000 cP to 50 000 cP), which are often handled *via* the screen printing method or on a dispensing machine (Fig. 6). The screen printing method has a long history, dating back to some 2000 years ago in ancient



Fig. 7 Electrical resistivity of some recently reported ECAs (silver based), ECIs (silver based) and room temperature processed SECCs. (Data are collected from the tables in this manuscript.) The colored partition areas indicate the distribution of the characteristic electric property and the processing condition of the three different materials.

China. It is a convenient and inexpensive method to obtain fine patterns (smaller than 100 micron) on planar and columnar surfaces in large areas, yet the rheological property of the paste is one of the critical factors in determining the quality of the printed zone. As discussed in the above context, the addition of nano-sized fillers to the ECA paste formulation inevitably increases the viscosity of the paste, which may cause problems in dispensing and printing processes. Therefore, the selection of resin dispersant is critical to determine the adhesion strength, reliability and printing resolution of the ECAs. Besides, a prolonged stability of the paste under ambient conditions ensures a longer working life of the paste on the production line, which is a prerequisite for industrial applications. ECAs, including ICAs (isotropically conductive adhesives), ACAs (anisotropically conductive adhesives), and even NCAs (non-conductive adhesives), are now widely applied in electronic packages to replace solders; they are applied in surface mount technology (SMT), flip chip, chip scale package (CSP), and ball grid away (BGA) applications. ACAs have been widely used in flat panel display modules in film forms (anisotropically conductive films, ACFs), ICAs have been printed onto the solar cell panels as the forefront electrode, and ACAs have been used to interconnect the surface mounted RFID chips to the interposer or the antenna. With the development of the low temperature sintering technology and the optimization of the formulations, the processing conditions could be further simplified to suit the applications in the low cost printed electronics (as shown in Fig. 6, the inlay RFID antennas based on

Journal of Materials Chemistry C



Fig. 8 Various available methods to develop metallic coalescence at the nano- and micron scale. (A) Sintering of silver nanostructures due to surface species agglomerations; (B) *in situ* formation of conductive areas due to reduction of Ag cation; and (C) surface evolution induced silver sintering.

ECAs are directly incorporated into the heat transfer process for producing garment labels).

As compared with ECAs, ECIs are primarily composed of metallic NPs and solvents. The metallic NPs are stabilized by surfactants; thus the inks maintain a very low viscosity of about 1 cP, which is similar to water. This character makes them very suitable for the application of inkjet printing technique, which requires a low viscosity of the ink to ensure it can get through the tiny nozzles. As a consumer-oriented printing technique, inkjet printing is a computer printing technique which creates a digital image by propelling droplets of ink onto a substrate. Inkjet printers are very popular for the personal users and in offices ranging from small inexpensive consumer models to very large professional machines. Because the inkjet printing method adopts drop-by-drop printing steps, the processing efficiency is much lower than other printing methods e.g. screen printing, while the drop-on-demand character of inkjet printing enables this method to be able to realize the desirable functions by dropping inks with different nature (e.g. conductive and dielectric ones). Thus in a single printing cycle, an electrical device with full function can be realized. On this platform, small devices can be prototyped or produced easily and cheaply.122

The SECCs are the conductive fillers dispersed in a polymer matrix which exhibit stretchable character. They have similar viscosities to the ECAs and thus can adopt the processing methods such as screen printing and direct writing.¹¹³ The advantages of the SECCs not only include the unique stretchable property but the character of low temperature processing conditions. These characters make them suitable for some applications on elastomeric or highly strained surfaces. It has been envisaged that these new materials can be applied in the stretchable electronic skins for medical applications, and in the combat uniforms and helmets containing flexible and lightweight impact sensors, *etc.*^{113,121,123} Moreover, the electrical devices based on them could be scrolled, folded, and even worn like clothing or jewelry rather than being carried, so as to realize more functions. However, considering the fact that the SECCs

have relatively weak cohesion in themselves and are often involved with small polar molecules (*e.g.* ionic liquids), it is still necessary to develop a suitable packaging method to further improve their reliability in real applications.

There have been emerging printing techniques such as writing the ECCs into more complicated 3-D structures and some others e.g. spraying methods.^{64,115} No matter which processing techniques are chosen, there are several issues that should be addressed. For example, most ECAs are dispersed in thermosetting resins and thus they often involve a curing process which is usually at about 150 °C (even though some water-based ECAs can be processed at about 50 °C);48 yet most recently reported ECIs and SECCs are able to be processed near room temperature. Moreover, ECIs have the lowest resistivity due to the efficient sintering ability at low temperatures, and SECCs still have room for reducing their electrical resistivity, as shown in the partition areas in Fig. 7. Further, ECAs and SECCs are often involved with those fillers with the anisotropic shape, thus after the printing process, the arrangement of the filler position may be affected by the shear alignment effect, which may cause discrepancy of electrical conductance in in-plane and vertical directions. Moreover, the decoration or modification of the filler materials will often increase the viscosity of the paste, which may decrease the printing resolution. Thus the design of the filler materials of the ECCs must be taken into account when referring to the printing or fabricating methods. Nevertheless, the advanced printing techniques render them capable for finding novel applications which may involve the ubiquitous substrate materials, e.g. papers, rubber band and clothes; the materials and environmental costs may be significantly reduced.

8 Concluding remarks and perspectives

In summary, we and others have developed a set of chemical and physical methods to engineer nano- and micro-fillers which possess appropriate surface functions, reactivity and electron transfer property so as to improve the electrical performance of

ECCs. These modifications, in turn, can be harnessed to help those readily developing conductive paths at relatively low temperatures, which can greatly enhance the ability of the ECCs to cater to novel flexible printed electronics applications. In addition to that, they have shown great promise to meet the higher electrical/mechanical/thermal performance, fine pitch capability, low-temperature processing and strong adhesion/ reliability requirements for electronic packaging modules and assemblies. The cross coupling of the surface modifications, low temperature sintering property and the data about the evolving course of the particle diffusion of the agglomerations of the filler powders can facilitate an informed decision about the strategy (Fig. 8). Nano-materials which exhibit excellent lowtemperature sintering properties are currently regarded as the most cost-effective choice, while they inevitably face the relatively high viscosity when combined with polymeric dispersants, thus they are more favorably prepared in dilute suspensions and applied in the inkjet printer inks. On the other hand, those surface modified micron-sized metallic fillers and nano-fillers are often combined with resins and polymer solutions, which exhibit strong mechanical and bonding strength, and are more compatible with some large-scale fabrication methods (e.g. screen, gravure, and stencil printing) and more suitable in the applications requiring high reliability. 1-D nanofillers such as silver nanowires and copper nanowires may have advantages in the development of future ultra-low cost ECAs and transparent printed conductors. The SECCs can enable the production of electrical devices with stretchability as well as the conventional functionalities, which is essential for the development of novel devices in some niche areas. However, the conductive channels built up in the stretchable matrix are not easily constructed through a "sintering" way (Fig. 9). Currently, in most cases ionic liquids dispersed in the stretchable matrix are an indispensable part to promote the electrical conductance among the versatile fillers.

To date, ECCs with the electrical resistivity as low as 10^{-5} and even $10^{-6} \Omega$ cm have been developed, which is near to that of the pure bulk metal (*e.g.* $1.6 \times 10^{-6} \Omega$ cm for silver). Their preparation and fabrication methodologies have been significantly enriched in the last decade. Benefitting from the lowered processing temperature, more ubiquitous substrate materials *e.g.* paper are able to be incorporated to cater to a lower environmental threat and easier recycling. The large variety of available choices of substrate materials ensures the printed electronic circuits have advanced properties *e.g.* stretchability, foldability, light-weight, low cost, *etc.* Moreover, the improved rheological property and long working life ensure them to be compatible with the advanced printing techniques, *e.g.* 3D printing technique to realize the unmet and consumer oriented functionalities.

Currently, ECCs are targeted for their wiring functions more than their original function as interconnects for substituting solders. Yet the reliability of the ECCs is still a challenge to meet the upcoming needs. Moisture diffusion and oxidation issues are critical problems for the ECCs, as there are numerous interfaces in the micro- and nano-scale in these composites. Moreover, when researchers try to lower their Young's modulus, the reliability issues (*e.g.* moisture diffusion) become more serious, considering the polymeric nature of the resins and gel dispersants. Therefore, it is imperative to develop suitable packaging and sealing technologies for protecting the ECC circuits, or the formulation of the resin or gel dispersants for the ECCs shall be further improved; that topic will be discussed elsewhere.

Even though the outlook is clear and exciting, it is fair to admit that we are still on the road of development. In this feature article, we have dealt mostly with nanostructure-related filler formulations; so far this has been on the basis of low temperature sintering platforms that have been previously validated in the ordinary printing methods. While various new modification and fabrication methods may no longer be a challenge, a more critical issue is how to leverage capabilities and to translate them into practice, especially making them compatible with the current industrial infrastructure more rapidly. The related investigations to address questions such as how and to what extent these new formulations can advance low-cost consumable electronics are being undertaken in our laboratories and those of others.



Fig. 9 A flow chart showing various methods and steps to achieve high electrical conductivity and reliability.

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