

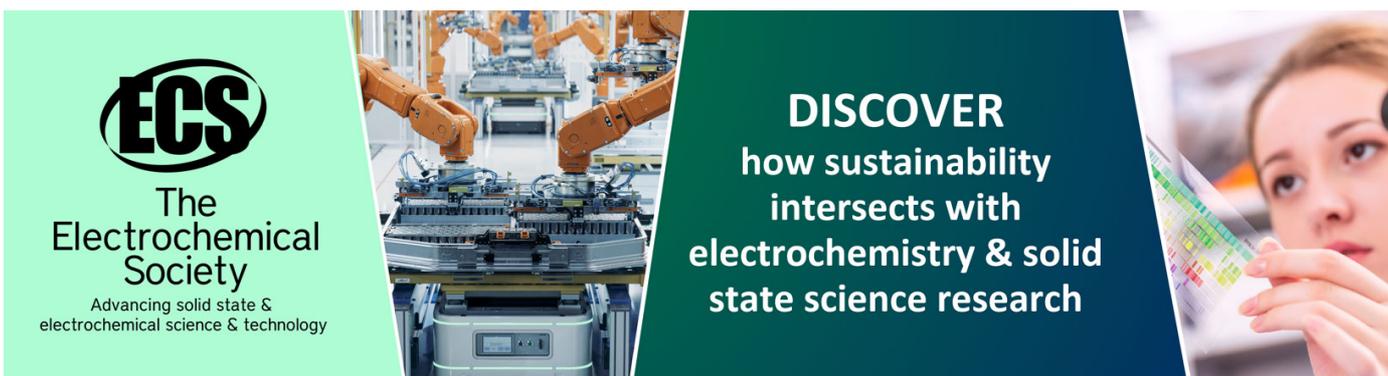
Graphene-stabilized copper nanoparticles as an air-stable substitute for silver and gold in low-cost ink-jet printable electronics

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Graphene-stabilized copper nanoparticles as an air-stable substitute for silver and gold in low-cost ink-jet printable electronics

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Abstract

Metallic copper nanoparticles were synthesized by a bottom-up approach, and *in situ* coated with protective shells of graphene in order to get a metal nanopowder of high air stability and chemical inertness. Using an amphiphilic surfactant, a water-based copper nanocolloid could be prepared and successfully printed onto a polymer substrate by conventional ink-jet printing using household printers. The dried printed patterns exhibited strong metallic gloss and an electrical conductivity of $>1 \text{ S cm}^{-1}$ without the need for a sintering or densification step. This conductivity currently limits use in electronics to low current application or shielding and decorative effects. The high stability of graphene-coated copper nanoparticles makes them economically a most attractive alternative to silver or gold nanocolloids, and will strongly facilitate the industrial use of metal nanocolloids in consumer goods.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Metal nanocolloids have received tremendous attention for a wide range of applications [1–3]. Metal oxidation, however, has traditionally restricted the range of useful nanometals to silver, platinum, palladium and gold [1, 4–10]. Technical low-cost applications such as ink-jet printing of flexible conductors and radio frequency identification (RFID) tags [11, 12], however, require manufacturing costs of typically less than one cent per tag [13–15]. The most evident candidate to substitute silver or gold would be copper, but nanocopper rapidly oxidizes under ambient conditions [16, 17]. We demonstrate how deposition of graphene bi- or tri-layers on copper can be realized on a technical scale and enables full protection of the copper metal core up to 200 °C under humid air. The protected copper can then be used in domestic ink-jet printers for the preparation of conductive patterns under ambient conditions.

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Nanoparticles and colloids have received unprecedented attention in the scientific community. Whilst oxide nanoparticles are now used in literally thousands of laboratories, the majority of metal nanoparticle related research had focused on noble metals because of their ease of handling under ambient conditions. The obvious cost constraints of silver, gold and platinum has restricted application-oriented research to low-volume, high-technology applications and diagnostics. Considering the traditional use of metals, however, shows that most technical applications have been solved on the basis of non-noble metal alloys. Ultra-lightweight aluminum- or magnesium-based alloys and stainless steel are protected against immediate corrosion by air and water through a thin oxide layer. This protection concept can partially be transferred to non-noble metal nanoparticles, but the typical oxide protection layer thickness of 5–50 nm prohibits the preparation of air-stable nanoparticles with high metal content ($>99\%$) as required for most applications [18]. As a consequence, pure non-noble metal nanopowders generally show astonishing

high reactivity under oxidizing conditions with a tendency to spontaneous ignition (pyrophoricity), reflecting the very high specific surface area of such nanoparticles.

Printing metals is of an undisputed high technical attractiveness, and it requires the preparation of a metal ink, or, in terms of materials engineering, it requires matching the properties of small metal particles with an ink-jet base fluid. While printing can be made under protection gas conditions, large-scale applications demand rugged inks and stability against air and humidity. Capping of reactive surfaces has enabled elegant control on reactivity, particularly in the case of quantum dots [19]. This strategy has been successfully applied by Park *et al* [20], who reported on the use of chemically synthesized, surfactant-capped copper nanoparticles for ink-jet printing. Electrical conductivity, however, was only obtained after vacuum-sintering at temperatures as high as 225 °C. Since classical printing inks are based on carbon black (aerosol-derived carbon nanoparticles), we decided to investigate the potential use of most recently developed graphene bi- and tri-layer coated metal nanoparticles [21, 22] as a potential substitute for the presently used noble metal nanocolloids. Within our work, we realized that graphene bi- and tri-layers on metal particles could serve as a more generally applicable strategy for the broader use of non-noble metal nanoparticles. In the case of graphene-coated cobalt, this has most recently enabled the preparation of low-temperature moldable magnets consisting of 90 wt% graphene-protected, 20–50 nm size cobalt metal nanoparticles [23].

2. Experimental details

2.1. Copper nanoparticle synthesis

Air-stable, graphene-passivated copper nanoparticles were prepared by reducing flame synthesis [21, 24] at a production rate of 15 g h⁻¹. Copper (II) 2-ethyl-hexanoate was prepared from copper acetate (Aldrich, puriss) and 2-ethyl hexanoic acid (Fluka, purum) by heating the corresponding mixtures to 140 °C for 3 h. Acetylene (2.6) and nitrogen (5.0) was purchased from PanGas. Cu-2-ethyl-hexanoate was diluted 2:1 (weight/weight) with tetrahydrofuran and filtered prior to use (Satorius, fluted filter type 288). The precursor then was fed (6 ml min⁻¹, HNP Mikrosysteme, micro annular gear pump m2r-2900) to a spray nozzle and ignited by a premixed methane–oxygen flame (CH₄: 1.2 l min⁻¹, O₂: 2.2 l min⁻¹, PanGas tech.). The spray nozzle was encased in a glove-box fed with nitrogen which was recirculated by a vacuum pump (Busch, Seco SV1040CV) at about 20 m³ h⁻¹. CO₂ and H₂O were continuously removed from the recycle stream using two adsorption columns, packed with zeolite 4A and 13X (Zeochem), respectively. To avoid the accumulation of CO, NO and other impurities in the glove-box atmosphere a purge gas stream continuously passed through the box. A sinter metal tube (GKN Sintermetalle, inner diameter 25 mm) surrounding the flame allowed radial inflow of CO₂ (PanGas, 99.995%) at a flow rate of 25 l min⁻¹. Addition of acetylene (5 l min⁻¹) through the side walls of the porous tube allowed the controlled coating of the nanoparticles by depositing graphene layers [22].

2.2. Nanoparticle analysis

The carbon content of the obtained C/Cu nanopowder was quantitatively measured by microanalysis (LECO, CHN-900). Thermogravimetric (TG) analysis was conducted at a heating rate of 10 °C min⁻¹ (Mettler Toledo SDTA851e). X-ray diffraction (XRD) of the C/Cu powder was done on a Siemens powder x-ray diffractometer with Ni-filtered Cu K α radiation and a step size 0.3°.

2.3. Copper ink

A water-based ink of the obtained C/Cu nanopowder was prepared from deionized water (Millipore, electrical resistivity >18 M Ω cm), and it contained 7.2 wt% C/Cu nanoparticles [25]. The addition of a high molecular, block-co-polymeric dispersing additive with acidic, pigment-affinic groups (7.7 wt% relative to C/Cu, Disperbyk 190, BYK Chemie) and an amphiphilic silicon tenside (10.5 wt% relative to C/Cu, BYK 348, a poly-ether-modified poly-dimethylsiloxane) resulted in a stable black ink after high-power ultrasonication (5 min in an ice-bath; Dr. Hielscher, UP400S, 0.4 cycle, 80% intensity). Prior to application, the as-prepared dispersion was centrifuged at 2000 rpm for 2 min (800g, MSE Mistral 3000E) in order to spin down large undispersed aggregates or contaminants, as detailed by Limbach *et al* [26]. The copper content of the dispersion was controlled gravimetrically as Cu(II) oxide after pyrolysis and revealed that most copper was stably dispersed. The hydrodynamic particle size distribution of the Cu ink (diluted to 0.5 wt% Cu with deionized water) was measured using an x-ray disc centrifuge particle size analyzer (Brookhaven Instruments, measuring time 2 h, disc speed 3000 rpm) following the procedure by Limbach *et al* [26].

2.4. Ink analysis

The shear viscosity of the ink was determined at different shear rates from 200–1600 s⁻¹ using a strain-controlled rheometer (ARES, TA Instruments, USA). The density was measured at 25 °C using a 5 ml pycnometer.

2.5. Ink-jet printing and pattern analysis

The ink was printed using a Hewlett–Packard Deskjet 2360 ink-jet printer on the uncoated side of overhead projector transparencies (laser/copier transparencies, Type C, Xerox) and afterward dried in air at 120 °C for 2 h. Conductivity measurements were conducted by determination of the resistance of printed lines with known geometry and film thickness. Scanning electron microscopy (SEM) was performed on a Leo 1530 Gemini at an accelerating voltage of 5 kV.

3. Results and discussion

3.1. Graphene-coated copper nanoparticles

The use of graphene as a technical metal protection coating is related to this material's exceptional stability and extraordinary

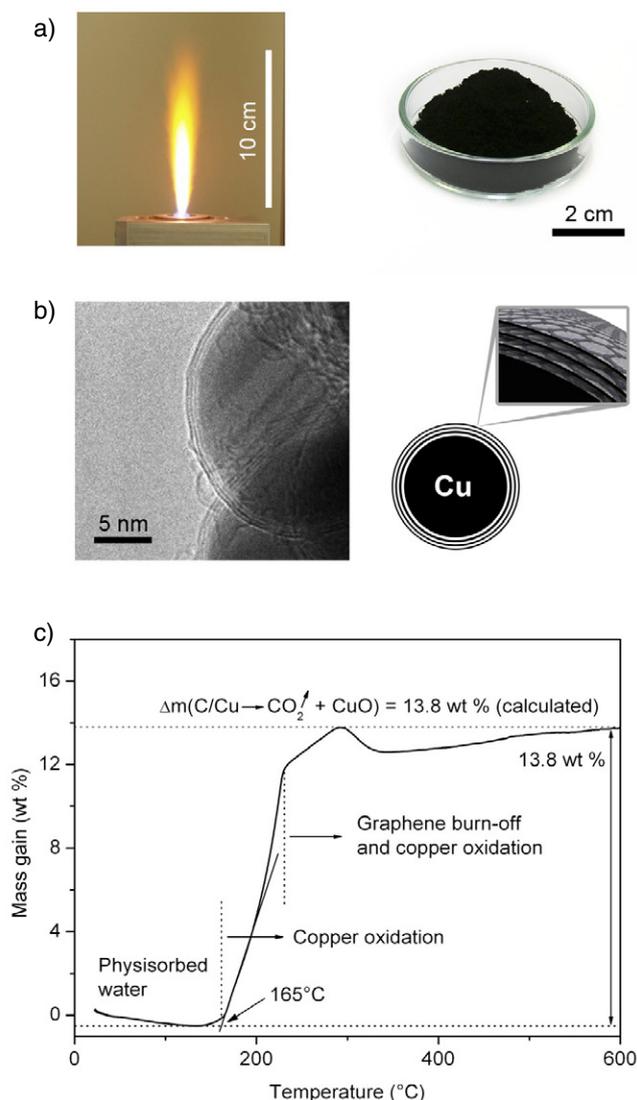


Figure 1. Graphene wrappings for increased thermal stability. (a) Photograph of a spray flame under reducing conditions (left) and as-prepared air-stable C/Cu nanopowder (~30 g sample, 9.1 wt% carbon). (b) Transmission electron micrograph of a single copper nanoparticle with a thick graphene wrapping of 3 nm and a corresponding schematic illustration. (c) Thermogravimetric analysis of C/Cu confirms the exceptional thermal stability of these non-noble metal nanoparticles up to 165 °C.

electronic material properties [27, 28]. Its use as a raw material was introduced by Stankovich *et al* [29] through the successful incorporation of graphene sheets into a polymer with final conductivity of 0.01 S cm^{-1} . Since the handling of single graphene sheets is difficult, we used a bottom-up approach to synthesize graphene wrappings directly onto individual copper nanoparticles in a single process step [21, 22]. Combustion of copper carboxylates under reducing conditions [22, 24] in a spray flame reactor results in copper aerosols. Additional feeding of acetylene to the hot copper aerosol promotes carbon deposition on the metal nanoparticle's surface through catalytic decomposition of acetylene (C_2H_2) or/and the

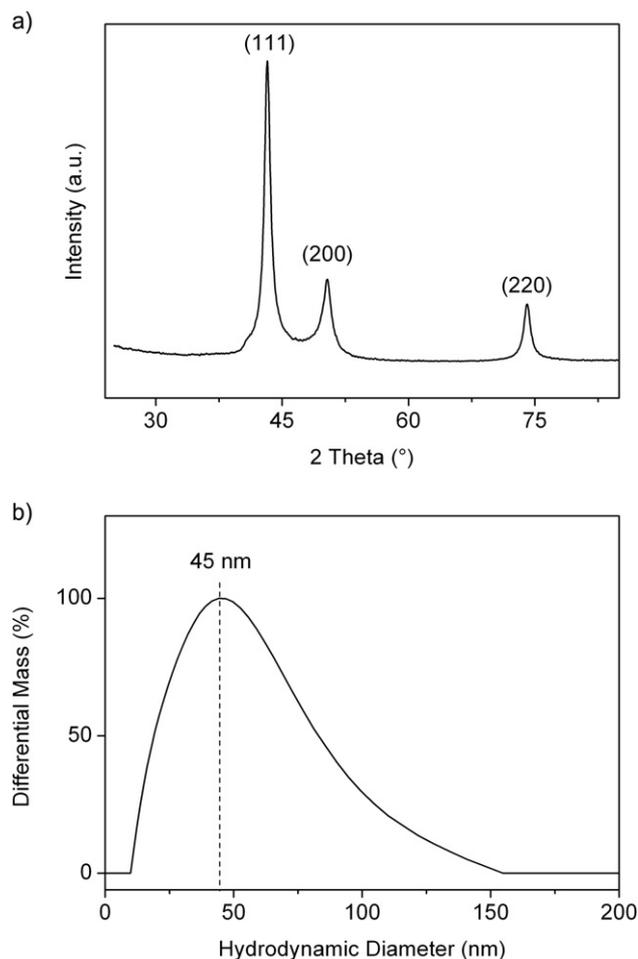
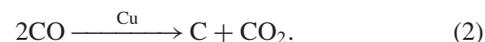


Figure 2. Determination of the metallic copper phase and particle size distribution. (a) Powder x-ray diffractogram of the as-prepared C/Cu nanopowder confirming the formation of metallic copper within the particle's core. (b) Hydrodynamic particle size distribution of the nanocolloid (measured by an x-ray disc centrifuge (XDC)). The mean hydrodynamic diameter of the particles in the ink confirms a high degree of dispersion.

disproportionation of carbon monoxide (CO) on the metal surface:



Both CO and C_2H_2 were abundant in the flame off-gases used here, as confirmed by mass spectrometry [21]. The tendency of copper surfaces to coat with carbon under such conditions fully agrees with long-term experience on copper catalysts used in methanol decomposition [30] or its use in steam reforming of methane [31]. The graphene shells have been characterized by Raman spectroscopy and solid state ^{13}C nuclear magnetic resonance spectroscopy [21, 22]. A more detailed description of the carbon deposition and the shell's physical properties can be found in [21]. The chemical reactivity of such carbon shells is close to that of carbon nanotubes, as most recently shown by Grass *et al* [22]. The metallic copper core was confirmed by x-ray powder diffraction analysis (XRD, figure 2(a)), showing the characteristic peaks for face-centered cubic copper.

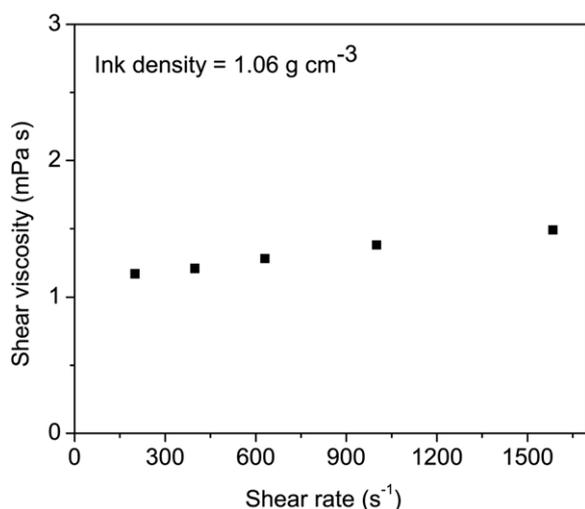


Figure 3. Ink shear viscosity. Over a wide range of shear rates the C/Cu ink (7.2 wt% C/Cu) exhibits a very low viscosity of 1–2 mPa s which is close to that of water. In between the measured range the ink viscosity behaves in a nearly Newtonian manner, exhibiting a slight increase with higher shear rates.

3.2. Air stability of copper nanoparticles

The thermal stability of the nanopowder was measured by thermogravimetric analysis (figure 1(c)), which confirmed the inertness of the copper core up to 165 °C, where CuO starts forming. At around 300 °C, the sample mass decreases, which could be attributed to carbon layer oxidation and burn-off [32]. At this temperature the weight loss by carbon burn-off is superposed by still ongoing copper oxidation (weight gain), resulting in a net mass loss which is lower than the carbon content of 9.1 wt%. Heating the powder to 600 °C resulted in a total mass increase of 13.8 wt%, which remains in agreement with the theoretical mass gain (figure 1(c)) of C/Cu and further confirms the absence of oxide impurities in the as-prepared nanopowder.

3.3. Properties of the copper ink

Ink properties such as viscosity, density and surface tension are important factors during the jetting process in terms of droplet formation [33] and spreading behavior. The wetting additive used herein is a surface-active silicone tenside which is able to dramatically reduce the surface tension of water, making it wet almost every surface. The ink therefore even spreads on low-energy surfaces including polymers like polyethylene. The viscosity of the copper ink (7.2 wt% C/Cu) was determined to be in the range of 1–2 mPa s (figure 3) which is almost as low as the viscosity of water (1 mPa s). Over the measured range of shear rates the behavior of the viscosity is nearly Newtonian, exhibiting a minute increase with higher shear rates.

3.4. Electrical properties of ink-jet printed copper patterns

The air-stable C/Cu nanopowder (figure 1(a)) can be processed into a stable, water-based ink with 7.2 wt% C/Cu using commercial dispersing agents and wetting additives as used

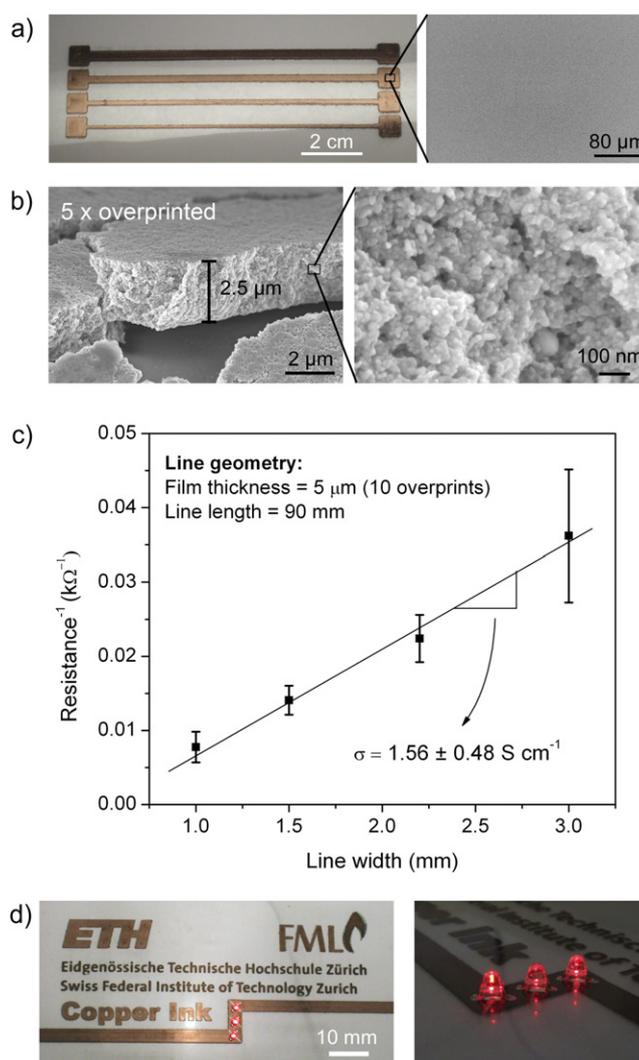


Figure 4. Printed copper patterns. (a) Line patterns for electrical conductivity measurements. The inset shows a homogeneous and crack-free print surface. (b) Manually cracked pattern for investigation of the film thickness after five overprints, revealing a print thickness of 500 nm per print cycle. The magnification inset of the fracture surface shows the inner structure of the composite film. (c) Graph showing the decrease of resistance with larger line width of the pattern (error bars obtained from five samples at each line width). The mean electrical conductivity was $1.56 \pm 0.48 \text{ S cm}^{-1}$. (d) Light-emitting diodes directly glued onto printed copper lines.

in carbon based ink dispersions (see section 2.3 for details). The copper metal dispersions were deep black, stable for several weeks and have a viscosity similar to classical ink-jet formulations. They can be directly filled into a commercial ink-jet printer's cartridge and processed using a standard low-cost ink-jet printer (e.g. Hewlett-Packard Deskjet 2360). The printed patterns show a copper-like metallic luster (see figures 4(a), (d)). The current non-optimized patterns have a relatively low, but sufficiently high, electrical conductivity to operate light-emitting diodes (figure 4(d)) that were directly put onto the copper lines printed on a flexible polymer foil substrate (uncoated side of the laser/copier transparencies). The magnification inset in figure 4(a) confirms the preparation of homogeneous and

crack-free surfaces within the printed pattern. Using a polymer substrate with five consecutive overprints, a total film thickness of 2.5 μm could be measured by SEM after manually cracking the print pattern (figure 4(b)), and this indicates a deposition layer of about 500 nm per print cycle. The different printing steps could not be distinguished since no individual layers appear in the cross section (figure 4(b)), confirming a good layer to layer adherence. The fracture surface of the cracked pattern revealed some natural porosity (magnification inset in figure 4(b)) as expected from the use of a particulate ink. While such ink is of considerable stability in the present form, later developments may target additional processing steps to compact the present films. Feature and shape coherence was demonstrated using well-defined line patterns with known geometry (figure 4(a)) and further used for electrical conductivity measurements. The correlation between the inverse resistances and the corresponding line widths (figure 4(c)) allowed determination of the material homogeneity and print scalability. Since the conductivity scales with the width and layer thickness, the pattern must be of uniform structure even when applying several print cycles on a single location. The conductivity measurements yielded a mean specific electrical conductivity of $1.56 \pm 0.48 \text{ S cm}^{-1}$. At present, this value is still very low if compared to the conductivity of bulk copper ($5.9 \times 10^5 \text{ S cm}^{-1}$) [34]. It can be attributed to the high volume content of non-conducting matter (dispersant, wetting agent) in between the C/Cu nanoparticles and the individual nanoparticle's considerable electrical resistance [21]. This inherent resistivity may be attributed to the low conductivity perpendicular to the graphene layers. At present, these untreated, as-printed copper patterns can be applied to temperature-sensitive substrates and applications where a low electrical conductivity is sufficient (radiation shielding, high-frequency RFID). In order to become competitive to presently used gold or silver inks, however, an after-treatment such as a densification step (e.g. sintering and removal of the carbon protection layers) would be required, or modification of the graphene structure by doping [35]. Both approaches offer a broad variety of potential improvements since graphene coatings are amenable to detailed chemical design, as suggested by Grass *et al*, who initiated covalent organic chemistry on cobalt nanomagnets [22].

The fascinating electronic properties of graphene have revealed carbon's most astonishing potential well beyond classical applications in chemistry and material sciences. The present work illustrates graphene's potential as a protective shell material, enabling control and design of the chemical reactivity of non-noble metals. This ultimately enables a large material class (upper transition metals) to profit from processing as nanoparticles under ambient conditions. The air stability of graphene bi- and tri-layer covered copper demonstrated here further evidences the exceptional chemical robustness of shells merely 1 nm thick. With an electrochemical potential difference of 0.37 V between copper ($E_{\text{red}}[\text{Cu}^{2+} + 2e \leftrightarrow \text{Cu}] = 0.34 \text{ V}$; against standard H-electrode) [34] and ambient air ($E_{\text{red}}[0.2 \text{ bar O}_2, \text{O}_2 + 2e \leftrightarrow \text{O}_2^{2-}] = 0.715 \text{ V}$, by the Nernst equation), the graphene shell sustains a chemical gradient of over 1 GV m^{-1} [23].

4. Conclusion

We have demonstrated that copper as a low-cost non-noble metal can resist oxidation under ambient conditions if coated by graphene bi- or tri-layers. Carbon coatings offer an economically attractive route to the broader use of metal nanoparticles for ambient conditions. Our present example using copper as a substitute for silver or gold ink-jet printing demonstrates a first step in the development of commodity metal nanoparticle applications. Though currently inferior to the conductivity of printed gold or silver, the direct one-step synthesis of C/Cu and the use of well-established ink chemistry allowed use of the metal ink in off-the-shelf ink-jet printers and makes metal printing available to virtually any laboratory without the need for special equipment. Controlling the oxidation and corrosion of the technically most important non-noble metals through the controlled deposition of graphene coatings will enable a much broader use of common transition group metals in the form of nanomaterials.

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