Supporting Information

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Manufacturing Graphene-Encapsulated Copper Particles by Chemical Vapor Deposition in a Cold Wall Reactor

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Supporting Information

Figure S1. RTEM images of GCPs synthesized under low (a) and high(b) H$_2$/CH$_4$ ratio

From Figure S1a, the graphene deposited by higher H$_2$/CH$_4$ ratio resulted in irregular stacking and disturbing layers. On the other hand, the graphene synthesized by lower H$_2$/CH$_4$ ratio led to the formation of more ordered layer stacking.

Figure S2. XPS spectra of C1s for pristine Cu particles and GCPs
As shown in Figure S2, a small hump located at 288 eV represented C=O bonds may explain by the presence of sodium citrate in pristine Cu particles. However, they rarely existed in GCPs after graphene growth process. It was inferred that sodium citrate was decomposed and converted into carbon layers during annealing. Moreover, the two strong fingerprint narrow bands situated at around 284 eV stands for typical C-C/C=C bonds, and clear indicated the significant sp2 hybridization of graphene structure within GCPs.\(^{[1]}\)

**Figure S3.** EDS images of pristine Cu particles (a, b, c, d, e) and GCPs (f, g, h, i).

Figure S3b, S3c, S3d, S3g and S3h represent the elemental distributions of Cu(green), C(red) and O (light blue) within pristine Cu particles and GCPs, respectively. Figure S3e and S3i are the EDS data of pristine Cu particles and GCPs. For pristine Cu EDS data, the exhibition of O element illustrated the present of sodium citrate reflected as white spots attached on the surface, and
the vanished of oxygen in GCPs EDS data indicated the decomposition of sodium citrate that had been transformed into pure carbon constituted white gibbosity as shown in Figure S3f.

![Figure S3f](image)

**Figure S4.** XRD patterns of both pristine Cu particles and GCPs exposed in air more than 60 days.

After aging test for both pristine Cu particles and GCPs exposed in air for more than 60 days at room temperature, an oxidative Cu$_2$O phase was clearly observed for Cu particles. However, the antioxidant performance of GCPs is significantly improved by treating Cu particles with encapsulation of graphene shell, interpreted by negative detection of oxidative phase in X-ray diffraction pattern.

**Materials and fabrication of TCA**

The typical polymer matrix of TCA is composed of a resin ($N,N$-Diglycidyl-4-glycidyloxyaniline, from Sigma-Aldrich), a silicon coupling agent (3-Glycidoxypropyltrimethoxysilane, from Sigma-Aldrich), a curing agent (1-(2-
Cyanoethyl)-2-ethyl-4-methylimidazole, from TCI), and a diluent agent (Ethylene glycol diglycidyl ether, from TCI). Here, in this study, the polymer matrix contains 74.05 wt% resin, 20 wt% diluent agent, 1 wt% silicon coupling agent and 4.95 wt% curing agent. Functional metal fillers such as 10 um flake Ag (from Sigma-Aldrich), nano-Ag with diameter ranging from 20 nm to 40 nm (from Alfa Aesar), Cu particles, and GCPs were used as fillers in TCA.

The detailed fabrication process of TCA is as follow: stoichiometric amounts of resin, diluent agent and coupling agent were mixed and initially processed by shear mixing for 10 mins. Metal fillers and curing agent were thereafter added and kept for additional 20 mins under shear mixing, in order to obtain a homogenous viscous phase. Finally, 5 mins ultrasonic treatment was carried out for uniform distribution of spherical metal fillers. The primary mixture of TCA was transferred into a teflon mould and cured at 150°C in an oven for 1h. After this, sample was taken out from the mould and polished by sandpaper, the finished TCA has a diameter of 12.7 mm and thickness of 2 mm, as shown in Figure S5.

Figure S5. Samples of TCA for thermal conductivity measurement
Thermal conductivity measurements

The thermal conductivity is decided by following equation:

\[ \lambda(T) = \alpha(T) \cdot \rho(T) \cdot C_p(T) \]

herein, \( \alpha(T) \) is the thermal diffusivity, \( \rho(T) \) is the density and \( C_p(T) \) is the specific heat capacity. \( T \) is the environment temperature. Density \( \rho \) is measured by Archimedes method. Thermal diffusivity \( \alpha \) and specific heat capacity \( C_p \) were measured by NETZSCH LAF447 NanoFlash instrument.

Thermal diffusivity is calculated by following equation:

\[ \alpha(T) = 0.1388 \cdot d^2/t_{50} \]

Herein, \( d \) is the thickness of the sample and \( t_{50} \) is half of the diffusion time, which is the total time for temperature increase from environment temperature to the maximum temperature on sample surface after receiving irradiation of optical pulse. For specific heat capacity measurement, graphite powders were sprayed on the surface of sample and standard sample whose specific heat capacity was known. Specific heat capacity of test sample was obtained according to the inversely proportional relationship between the height of temperature rising signal and specific heat capacity.

Temperature-time curves were obtained after laser flash test.

**Thermal conductivity of TCAs**

**Table S1** Summary of thermal conductivity of TCAs

| Fillers  | The Percentage of Fillers | Thermal Conductivity (W m\(^{-1}\) K\(^{-1}\)) | Thickness (mm) | Measurement Method | Reference |
|----------|---------------------------|-----------------------------------------------|----------------|--------------------|----------|
| Cu powders | 68.25 wt% | 0.74 | 8 | Hot Disk TPS-2500 | [2] |
| Material                        | Graphene Sheet | Graphite Nano-flake | Graphene Encapsulated on PMMA | Near Spherical Ag | Ag Surface Modified by Iodine | Flake Ag | 40 wt% MicronAg + 45 wt% Flake Ag | 5 wt% BN + 75 wt% Flake Ag | 5 wt% NanoSiC + 75 wt% Flake Ag | Flake Ag | Flake Ag | 5 wt% GCPs + 75 wt% Flake Ag | 40 wt% GCPs + 45 wt% Flake Ag |
|--------------------------------|----------------|--------------------|-------------------------------|-------------------|-------------------------------|----------|--------------------------------|--------------------------------|--------------------------------|----------|----------|----------------------------|-------------------------------|
| Dry weight loading            | 10.1%          | 10.1%              | 1.4 wt% graphene              | 85 wt%            | 85 wt%                        | 85 wt%   | 85 wt%                          | 80 wt%                          | 80 wt%                          | 76 wt%   | 85 wt%   | 80 wt%                     | 85 wt%                         |
| Steady-state heat conduction method | 4.01           | 1.84               | 1.4                           | 1.7               | 13.5                          | ~2.5     | ~5                             | ~1.5                           | ~3                             | 1.9      | ~4       | 1.75                      | 4.13                         |
| Laser flash                   |                |                    |                               |                   |                               |          | a FLASH-LINE-5000 and a laser flash method |                  |                               |          |          |                            |                               |
| Method                        |                |                    |                               |                   |                               |          |                               |                  |                               |          |          |                            |                               |
| This work                     |                |                    |                               |                   |                               |          |                               |                  |                               |          |          |                            |                               |
Figure S6. Synthetic process carried out in an Aixtron nanoinstruments-black magic

References

[1] D. R. Chowdhury, C. Singh, A. Paul, Rsc Adv 2014, 4, 15138.

[2] Y. X. Fu, Z. X. He, D. C. Mo, S. S. Lu, Appl Therm Eng 2014, 66, 493.

[3] Y. X. Fu, Z. X. He, D. C. Mo, S. S. Lu, Int J Therm Sci 2014, 86, 276.

[4] O. Eksik, S. F. Bartolucci, T. Gupta, H. Fard, T. Borca-Tasciuc, N. Koratkar, Carbon 2016, 101, 239.

[5] H. Y. Wu, S. W. Chiang, W. Han, Y. H. Tang, F. Y. Kang, C. Yang, Compos Sci Technol 2014, 99, 109.

[6] H. W. Cui, Q. Fan, D. S. Li, X. Tang, J Adhesion 2013, 89, 19.

[7] H. Lai, X. Lu, S. Chen, C. Fu, J. Liu, International Symposium on Advanced Packaging Materials: Microtech 2010.

[8] Z. Zhang, L. L. Ye, A. Kukovecz, Z. Konya, J. Bielecki, J. Liu, Ecs Transactions 2012, 85, 1011.
[9] M. Inoue, J. Liu, presented at *Estc 2008*, 2008.