

Technology Offer

## Graphene Balls and electrochemical cells containing these materials

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We offer a new simple and low cost technology to fabricate graphene-encapsulated metal or metal compound nanoparticles. The resulting hybrid nanoparticles are protected by granted substance claims in US, CN, TW and EP (DE, FR, GB, BE). Currently the patent protected graphene coated nanoparticles are discussed as high performance electrode materials in the lithium ion battery business (for example Samsung's "Graphene Balls").

### Background

The unique electronic, mechanical and thermal properties of graphene make graphene coated inorganic nanoparticles very promising materials for the future. These hybrid nanoparticles can be used in sensors, as fuel cell catalysts, in photovoltaics and optoelectronics, and also as material for high performance battery electrodes.

For example Freddy Kleitz and Claudio Gerbaldi [1] recently described graphene-wrapped mesoporous Cu-Ni oxides that exhibit unprecedented electrochemical behavior, such as high reversible specific capacity, excellent coulombic efficiency and long-term stability at high current density.

In November 2017 a press release of Samsung [2] reported on so called "graphene balls", a breakthrough battery material that enables a 45% increase in capacity, and five times faster charging speeds than standard lithium-ion batteries. The corresponding Nature Communications publication [3] describes the "graphene balls" as silicon oxide nanoparticles with a coating of graphene. In January 2018 Samsung SDI highlighted these "graphene balls" as a new, high performance battery material during the Detroit Motor Show [4].

Thus it is predictable that graphene coated nanoparticles will be used for introducing high performance batteries into the market.

### Technology

Researchers from Max-Planck-Institute for Polymer Research in collaboration with BASF fabricated graphene-encapsulated  $\text{Co}_3\text{O}_4$  nanoparticles by co-assembly between negatively charged graphene oxide and positively charged metal oxide nanoparticles [5].

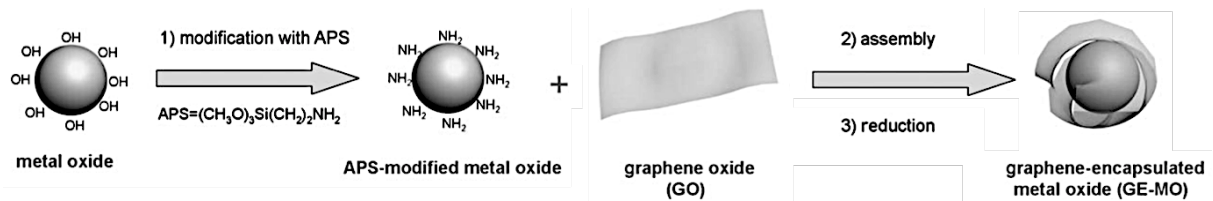


Fig. 1: Fabrication of graphene-encapsulated metal oxide (GE-MO) including 1) modification of the metal oxide by grafting aminopropyltrimethoxysilane (APS) to render the oxide surface positively charged; 2) hybrid assembly between positively charged oxide nanoparticles and negatively charged graphene oxide by electrostatic interactions; and 3) chemical reduction.

When used in battery electrodes, the unique hybrid architecture exhibits different features such as suppression of aggregation of oxide nanoparticles, accommodation of volume change during the cycle process, leading to a rise to a high oxide content in the composite and maintenance of a high electrical conductivity of the overall electrode.

Fig. 2: Galvanostatic discharge-charge profiles of a) GE- $\text{Co}_3\text{O}_4$  and b) bare  $\text{Co}_3\text{O}_4$  electrodes (current density= $74 \text{ mA g}^{-1}$ ).

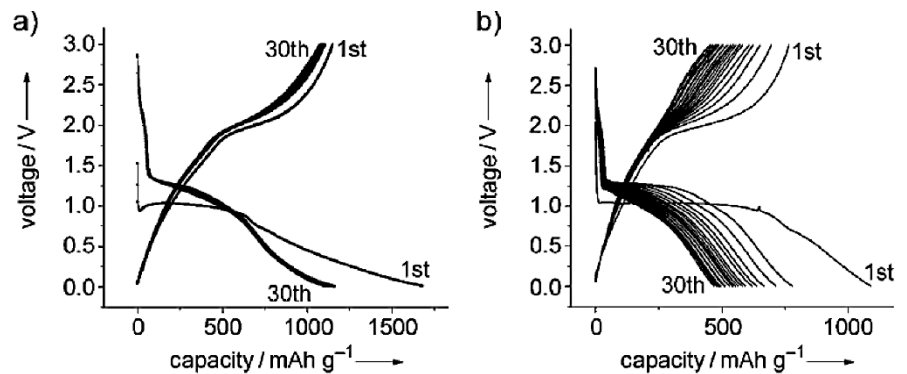
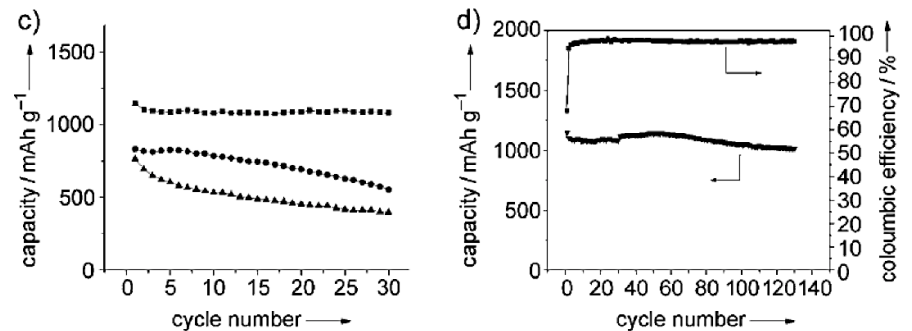


Fig 2: Comparison of c) cycle performance of GE- $\text{Co}_3\text{O}_4$  (rectangle), mixed  $\text{Co}_3\text{O}_4$ /graphene composite (circle), and bare  $\text{Co}_3\text{O}_4$  electrodes (triangle) over 30 cycles, and d) cycle performance and Coulombic efficiency of the GE- $\text{Co}_3\text{O}_4$  electrode during 130 cycles (current density= $74 \text{ mA g}^{-1}$ ).



These results confirm that the proposed technology enables a good encapsulation of electrochemically active metal oxide nanoparticles by graphene sheets and results in materials with a remarkable lithium storage performance with high reversible capacity and excellent cycle performance.

These hybrid nanoparticles were patented with broadly granted substance claims in US, EP, JP, KR, CN and TW.

Granted US8611070 claims:

Claim 1: Nanoparticles comprising at least one component A selected from the group consisting of a metal, a semimetal, and metal compound and a semimetal compound; and at least one coating of graphene.



Claim 15: An electrochemical cell or a supercapacitor, comprising the nanoparticles according to claim 1.

Even though a third party opposed against the granting of the EP and JP patents, these patents were granted with broad substance claims.

Meanwhile the BASF shares in the patent portfolio were completely transferred to Max-Planck-Society, so that we are the only assignee owning the patents which enables us to grant an exclusive worldwide patent license.

As the patented graphene coated nanoparticles will probably be used for introducing high performance batteries into the market in the near future, we are of the opinion that the offered patent portfolio - besides the superior performance of the patented materials - is also of high patent strategic interest for companies in this field.

## Literature

[1] L. L. Perreault et al: "Spray-Dried Mesoporous Mixed Cu-Ni Oxide@Graphene Nanocomposite Microspheres for High Power and Durable Li-Ion Battery Anodes", Adv. Energy Mater. 2018, 8, 1802438

[2] <https://news.samsung.com/global/samsung-develops-battery-material-with-5x-faster-charging-speed>

[3] In Hyuk Son et al: "Graphene balls for lithium rechargeable batteries with fast charging and high volumetric energy densities", NATURE COMMUNICATIONS 1 8: 1561

[4] <http://www.samsungsdi.com/sdi-news/1803.html>

[5] K. Müllen, X. Feng, S. Ivanovici, S. Yang: "Fabrication of Graphene-Encapsulated Oxide Nanoparticles: Towards High-Performance Anode Materials for Lithium Storage.", Angew. Chem. Int. Ed. 2010, 49, 8408–8411.  
Highly cited paper with > 750 citations (source: web of science)

## Patent Information

EP priority patent application filed 14.05.2010.  
WO2011141486 and TW201206712 filed in 10.05.2011,  
WO2011141486 nationalized in EP, US, JP, KR, CN.  
US8611070, TWI562898B, CN102917981B, KR101809771B1, JP6403705B2 granted.  
EP2569249B1 granted, nationalized in DE, FR, GB, BE.

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