

Metal cluster and single atom decoration of thermally exfoliated graphite oxide

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The availability of chemically and physically produced bulk graphene is of prominent relevance in applications where a large surface area is a necessity, such as in sensors, batteries, super capacitors and hydrogen storage materials.¹ In the recent past, Thermally Exfoliated Graphite Oxide (TEGO) has been revealed particularly suitable for this kind of applications, despite the high density of structural and *in plane* defects as compared to the one produced by mechanical cleavage or epitaxially grown.

However, both the absorption of hydrogen on TEGO and the diffusion of Li and Na ions required for its application in batteries proved to be poor in the pure material. The situation sensibly changes when TEGO is decorated with transition metal clusters or even single atoms.

In this work we present the synthesis of Ni and Pt decorated TEGO. The decoration is obtained using different strategies: impregnation of TEGO with a solution of metallorganic precursors, metathesis reaction between Li-graphene and metal chlorides (NiCl₃, PdCl₂) or thermal decomposition of carbonyl metal cluster precursors. The change of different parameters during the synthesis allows to control the metal nanoparticles size distribution and even obtain a decoration with single atoms of metals (in the case of Pt) as shown in Figure 1.

The obtained decorated systems have been characterized with Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Raman spectroscopy and SQUID magnetometry.

Their interaction with atomic and molecular hydrogen was investigated using the Muon Spin Relaxation (μ SR) technique and hydrogen pressure concentration isotherms which show a strong hydrogen-graphene interaction and a 51% increase in H₂ absorption compared to other common carbon based materials².

Remarkable results were also recently obtained by using Ni decorated TEGO as negative electrode material in Li and Na batteries. In the latter it showed the highest reversible capacities of all studied batteries and graphene derivatives, with 826 mAhg⁻¹ after 25 cycles with approximately 97% coulombic efficiency.

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References

- [1] J. Zhu, D. Yang, Z. Yin, Q. Yan, H. Zhang, Graphene and graphene-based materials for energy storage applications. *Small* **10**, 3480–98 (2014).

- [2] M. Gaboardi, et al., Decoration of graphene with nickel nanoparticles: study of the interaction with hydrogen. *J. Mater. Chem. A* **2**, 1039 (2014).
- [3] J.C. Pramudita et al., Graphene and Selected Derivatives as Negative Electrodes in Sodium- and Lithium-Ion Batteries. *ChemElectroChem* **2** (2015) 600-610.

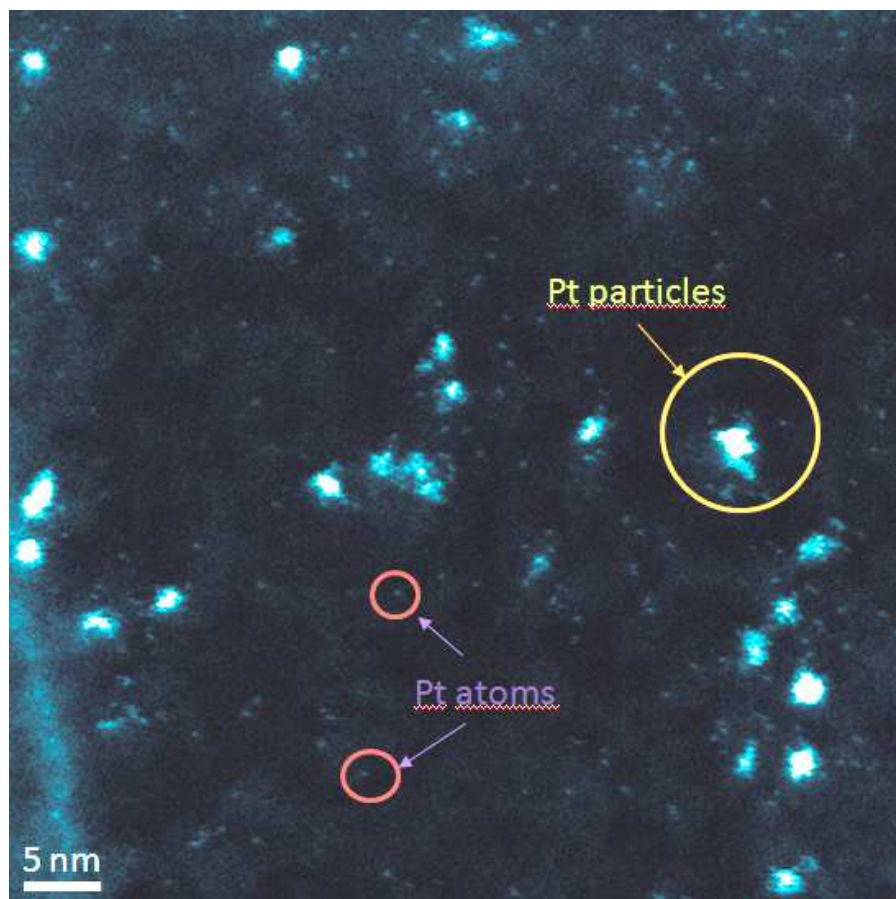


Figure 1: TEM image of Pt decorated TEGO.