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Facile and green reduction of graphene oxide by a reduced polyoxometalate and nanohybrid formation.

Catherine Debiemme-Chouvy^{*a}, Benjamin Thomas^b, Ivan T. Lucas^a, T. T. Maï Tran^a, Jean-Marc Heintz^b, Amélie Veillère^b, and Jean-François Silvain^b

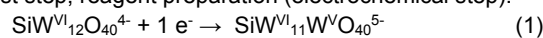
Abstract: In this communication, we report an eco-friendly chemical reduction of graphene oxide (GO) in water. The reducing agent is an electrochemically reduced Keggin-type polyoxometalate (SiW₁₂O₄₀⁵⁻). Moreover this process leads to the fabrication of SiW₁₂@rGO nanocomposite. This nanohybrid exhibits an electrochemical response which combines high faradic and capacitive currents due to high coverage of rGO sheets by the polyoxometalates, therefore it has strong potentiality for energy storage.

Graphene is the first two-dimensional atomic crystal available. Its singular structure induces exceptional properties like high mechanical strength and extremely high electrical and thermal conductivities. The potential applications of graphene are multiple ranging from electronics, flexible screen, catalyst to thermal management. However, the difficulties associated its production are a critical drawback for a mass use. Several methods have been developed using chemical and physical exfoliation of graphite such as: electrochemical exfoliation [1], intercalation of element in graphite compounds at elevated temperature [2] and liquid phase exfoliation using agents like N-methylpyrrolidone, iodine chloride or bromide.[3] Nevertheless, the most common method toward a large scale production of graphene is the moderate oxidation of graphite through the modified Hummers method [4], followed by its exfoliation (graphene oxide, GO) and its reduction to obtain graphene (reduced graphene oxide, rGO).[4-6] The last step involves commonly products like hydrazine hydrate or formaldehyde which are known as hazardous to health and the environment. In order to remove this kind of components, an alternative method based on UV-assisted photoreduction of GO in the presence of polyoxometalates (POMs) and of a sacrificial organic reagent has been proposed.[7] POMs are a class of inorganic metal–oxygen cluster anions with redox properties.[8] These clusters (so-called isopoly- and heteropolyanions (HPAs)) contain highly symmetrical core assemblies of MO_x units (M = V, Mo, W). They can have various structures containing for example 6, 12 or 18 metal atoms in their high oxidation state. For HPAs, the structure with 12 metal atoms is called Keggin structure. In the method just mentioned the POMs act also as anionic stabilizer avoiding the aggregation of rGO and

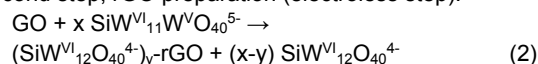
leading to the formation of POM@rGO nanocomposites. However, only small amount of rGO could be obtained under such conditions due to localized laser irradiation and also an organic reagent has to be used. It has also been shown that the hydrothermal reduction of GO in the presence of H₃PMo₁₂O₄₀ (PMo₁₂) leads to the nanocomposite PMo₁₂@rGO.[9] Another route developed recently concerns the electrochemical reduction of GO assisted by POMs [10].

Herein we propose an environmentally friendly two-step process for the preparation of reduced graphene oxide decorated with POMs (POM@rGO). In this process the first step is the electroreduction of SiW₁₂O₄₀⁴⁻ (SiW₁₂), a Keggin-type POM which is dissolved in pure water. In its fully oxidized form, all the W atoms are at the oxidation state +VI while in the reduced form a fraction of the W atoms are at the oxidation state +V (blue HPA). Then the catholyte which contains reduced SiW₁₂ is added to the GO suspension, GO is reduced by the POMs which are reoxidized and a nanocomposite is formed.

First step, reagent preparation (electrochemical step):



Second step, rGO preparation (electroless step):



Reaction (2) is rapid, being completed after one minute, the solution being stirred by Ar bubbling.

In Figure S1, the optical images of the solutions of GO, GO + SiW₁₂ and GO + reduced SiW₁₂ show clearly that GO is reduced in the presence of reduced SiW₁₂. Black particles are indeed visible in the GO + reduced SiW₁₂ solution whereas with oxidized SiW₁₂ no change is observed as compared to the initial GO suspension.

After washing with pure water and isolation by centrifugation, the final products were characterized by XPS, Raman, TEM, thermogravimetry analysis (TGA) and electrochemistry. In order to confirm the proposed mechanism (reaction (2)), we reproduced all the experiments with the fully oxidized POMs (sample named GO-SiW₁₂).

The reduction of GO by partially reduced SiW₁₂ anions and the nanocomposite formation (reaction (2)) were evaluated using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra depicted in Figure 1A evidence that after addition of SiW₁₂ or reduced SiW₁₂ in the GO solution, W is detected (see Table S1) with a much higher intensity for the sample prepared with the reduced SiW₁₂ *i.e.* for the reduced GO.

To estimate the effectiveness of the reduction process of GO, the C/O ratios of the three samples were determined from C1s and O1s high resolution XPS spectra without taking into account the O atoms associated to SiW₁₂O₄₀⁴⁻. GO, GO-SiW₁₂ and SiW₁₂@rGO give ratios of 2.5, 2.7 and 6.1, respectively (see Table S1). Moreover the C1s photopeaks were deconvoluted with five contributions corresponding to five types of carbon with

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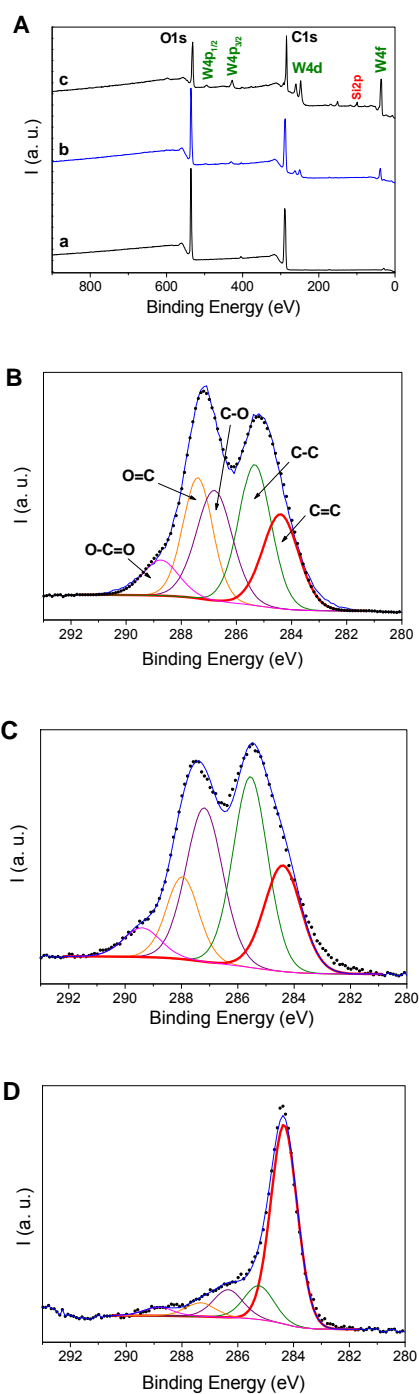


Figure 1. XPS spectra. A: Survey spectra from (a) GO, (b) SiW₁₂ + GO, (c) reduced SiW₁₂ + GO samples. B, C and D: C1s spectra from GO, SiW₁₂ + GO and reduced SiW₁₂ + GO samples, respectively.

different chemical states, C=C, C-C, C-O, C=O, O-C=O (Figures 1B-D). For each sample, the contributions of the different C bonds to the total C1s XPS signal are reported in Table S2. From this table it is clear that rGO is deeply reduced as the C=C bonds increase from 19% in GO to 70% in the nanocomposite ; the carbon-oxygen contributions being drastically lower for the GO treated with reduced SiW₁₂ in comparison with the pristine GO or with the sample treated with the fully oxidized SiW₁₂. The O1s

spectra depicted in Figure S2 confirm the presence of SiW₁₂O₄₀⁴⁻ with a new contribution that is detected at a lower binding energy (530.5 eV). The W4f_{7/2} peak located at 35.6 eV is symmetric (see Figure S3) indicating that all the W atoms are at the same oxidation state, *i.e.* +VI, and confirming that the reduced SiW₁₂ species are oxidized at the graphene oxide surface (reaction (2)). Besides, the integrity of the POMs is confirmed by the detection of a Si2p contribution around 102 eV (Figure S4) and also by the electrochemical studies (see below).

Figure 2 shows the Raman spectra of GO, GO-SiW₁₂ and SiW₁₂@rGO samples collected with a blue excitation laser ($\lambda_{exc} = 473$ nm). The most prominent features, D (1350 cm⁻¹) and G (1580 cm⁻¹) bands, are assigned to disorder-induced breathing modes of sp² atoms in carbon rings and to stretching modes from the sp² carbon pairs respectively.^[11] The similarity between the GO-SiW₁₂ and GO spectra attests that no GO reduction took place during contact of GO solution with SiW₁₂ in its pristine state (oxidized). SiW₁₂@rGO spectrum is however considerably altered with a dominant intensity of the D band over the G band. From the ratio of D and G band intensities, I_D/I_G, a measure of the inter-defect distance or the average size of the sp² domains can be estimated.^[11, 12] In a large number of papers relative to chemical reduction of GO, this ratio is observed to increase from 0.8-1 to about 1.1-1.2. ^[5, 7, 13] In our experiment, this ratio increases from 0.81 for GO to 1.13 for SiW₁₂@rGO which confirms the effectiveness of the reduction process using reduced SiW₁₂. It can be interpreted by the creation during the GO reduction process of numerous new graphitic domains (sp²) smaller in size as compared to the ones present in the exfoliated GO.^[14]

Figure 3 shows a HR-TEM micrograph of SiW₁₂@rGO. Other TEM or HR-TEM micrographs of typical microstructure of GO, GO with SiW₁₂, and reduced GO with SiW₁₂ are shown in Figures S5, S6, S7, respectively. Typical TEM contrast associated to GO can be observed in Figure S5. For GO materials after contact with fully oxidized SiW₁₂ (GO-SiW₁₂), a few darker contrasts can be observed on the sample surface in the TEM micrograph of Figure S6. These darker dots (sizes ranging from 20 to 40 nm) can be associated with W based clusters. The HR-TEM micrograph taken on the edge of the material shows two typical areas. On the pure edge (black rectangle), the space between two wave lines is closed to 0.34 nm which can be

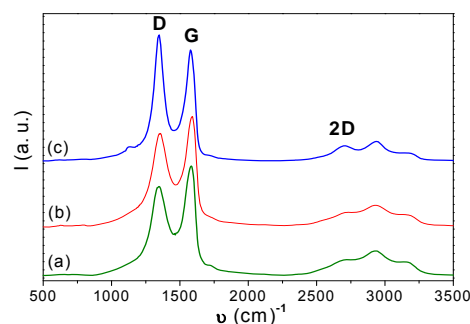


Figure 2. Raman spectra ($\lambda_{exc} = 473$ nm) of pristine GO (a), GO-SiW₁₂ (b) and SiW₁₂@rGO nanocomposite (c) highlighting the effectiveness of the GO reduction process through the strong D/G ratio increase. All spectra were normalized to the G band intensity.

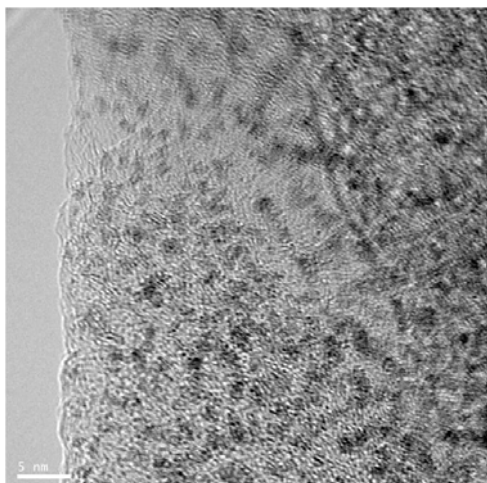


Figure 3. HR-TEM micrograph of the SiW₁₂@rGO nano-composite. Scale bar: 5 nm.

associated with the distance between two graphene sheets (3.35 Å). Therefore, this part corresponds approximately to 15 graphene layers. Inside the black circle, on the same micrograph, spot contrasts can be observed. The distance between these spots is close to 0.14 nm which is the distance between 2 carbon atoms in a graphene plane (1.42 Å). For the SiW₁₂@rGO composite, TEM and HR-TEM contrasts are quite different from the previous ones (see Figures 3 and S7). The presence of very small clusters can be observed. The size of these clusters is similar to the size of SiW₁₂ (1.1 nm).^[15] The interplanar distances, measured on the HR-TEM micrograph (inside the black circles in Figure S7), are close to 0.19 nm, which can be associated to the {611} plane of the SiW₁₂ compound.

TGA coupled with mass spectrometry were carried out in order to study the stability of the samples for temperatures ranging from 20°C to 1000°C, in air atmosphere. Figure 4 shows the TGA curves recorded for H₄SiW₁₂O₄₀ (a), GO (b), GO-SiW₁₂ (c) and SiW₁₂@rGO (d) whereas Table S3b reported the mass loss percentage for 4 temperature range areas (TRAs) and the total mass loss at 1000°C. The 4 temperature range areas are called TRA1 (20 °C - 160°C (excepted for H₄SiW₁₂O₄₀ where final temperature is 108°C)), TRA2 (160°C – 290°C), TRA3 (290°C – 545°C to 610 °C) and TRA4 (545°C to 610°C – 1000°C). For TRA1, mass loss is mostly associated with OH and H₂O whereas for the 3 other TRAs, mass losses can be associated with the combustion of carbonaceous matter. It has to be mentioned that no weight loss can be attributed to the thermal decomposition of the SiW₁₂ species for temperature up to 1000°C, as curve (a) in Figure 4 shows that H₄SiW₁₂O₄₀ is stable until 1000°C. For the GO and the GO-SiW₁₂ materials, the percentage loss for the 4 TRAs is almost similar. The total loss for GO is 100% and it is close to 98% for GO-SiW₁₂ (the 2% remaining mass can be related to the presence of W type clusters shown by TEM and XPS). For the SiW₁₂@rGO sample the mass loss percentages for the various TRAs are quite different than those determined for the GO and GO-SiW₁₂ samples. Indeed, it is smaller for the 3 first TRAs leading to a remaining mass closed to 40%. This remaining material can be

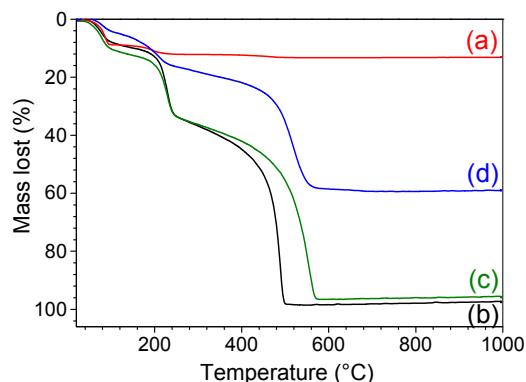


Figure 4. TGA in air of (a) H₄SiW₁₂O₄₀, (b) GO, (c) GO-SiW₁₂, (d) SiW₁₂@rGO samples.

associated with the POM clusters detected by TEM and XPS. Between 20 and 108°C (TRA1), a mass loss of 7.5% is observed which is mainly due to OH and H₂O as indicated by the mass spectroscopy analyses (Figure S8 and Table S4). Therefore the real initial mass corresponding only to rGO + SiW₁₂ is 2.139 mg (see Table S3(a)). After annealing until 1000°C, the remaining sample mass which corresponds to the POMs is 0.914 mg. Thus we can estimate the amount of SiW₁₂ immobilized onto the rGO sheets that is 0.26 mmol SiW₁₂/g GO. This coverage is high, it is higher than the one obtained by hydrothermal reduction of GO in the presence of H₃PMo₁₂O₄₀ that is 0.18 mmol PMo₁₂/g GO.^[9]

Finally, the SiW₁₂@rGO composite was characterized with electrochemical techniques. For this purpose, a drop of the nanocomposite in suspension in ethanol was deposited on a glassy carbon electrode. After solvent evaporation, the electrochemical responses were recorded in an acidic aqueous solution (0.5 M H₂SO₄). Faradic current due to reduction/reoxidation of the POMs immobilized on the rGO sheets and capacitive current due to the high surface area of the nanocomposite are detected in the current-potential curves (Figures 5 and S9), confirming the presence of SiW₁₂ on the rGO surface and the good electronic conductivity of the nanocomposite as no binders nor conductive additives were used. For comparison the response obtained with the pristine GO is also reported in Figure 5 (curve(d)).

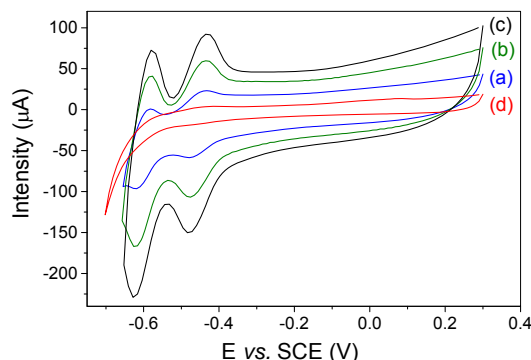


Figure 5. Cyclic voltammograms in 0.5 M H₂SO₄ solution of (a-c) SiW₁₂@rGO deposited on a GC electrode, at various potential scan rates (v): (a) 100, (b) 200, (c) 300 mV s⁻¹; (d) GO deposited on a GC electrode, v=100 mV s⁻¹.

In summary, a rapid and easy route for the preparation of an hybrid nanocomposite made of reduced graphene oxide

decorated with electroactive inorganic clusters is presented in this work. The partly reduced SiW₁₂ species prepared by an electrochemical route react with the initial GO leading to a nanocomposite homogeneously decorated with SiW₁₂ with a final concentration of 0.26 mmol per g of rGO. This materials has many potential applications such as energy storage (supercapacitors)^[9] or electrocatalysis^[16].

Acknowledgements

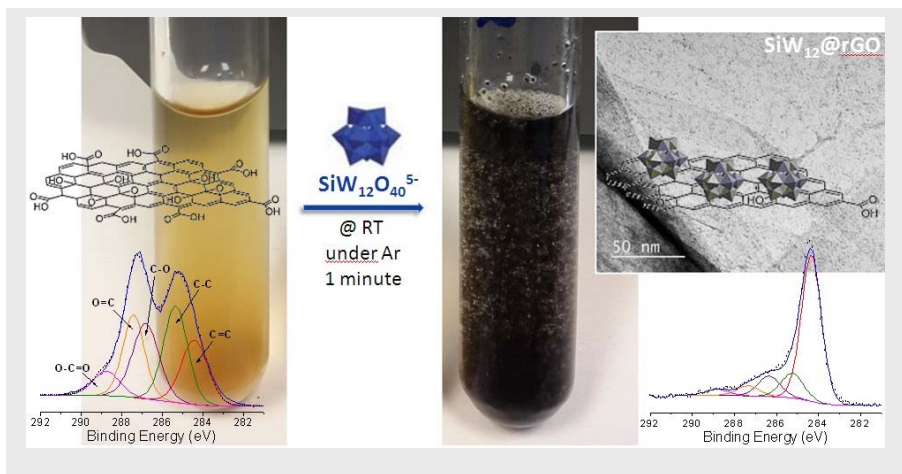
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Keywords: Graphene oxide • Polyoxometalate • Nanocomposite • Electrochemistry • Reduced graphene oxide

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