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# Visible-Light Assisted Covalent Surface Functionalization of *rGO* Nanosheets with Arylazo Sulfones

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**Abstract:** We present an environmentally benign methodology for the covalent functionalization (arylation) of *rGO* nanosheets with arylazo sulfones. A variety of tagged aryl units were conveniently accommodated at the *rGO* surface via visible-light irradiation of suspensions of carbon nanostructured materials in aqueous media. Mild reaction conditions, absence of photosensitizers, functional group tolerance, and high atomic fractions (XPS analysis) represent some of the salient features characterizing the present methodology. Control experiments for the mechanistic elucidation (Raman analysis) and chemical nanomanipulation of the tagged *rGO* surfaces are also reported.

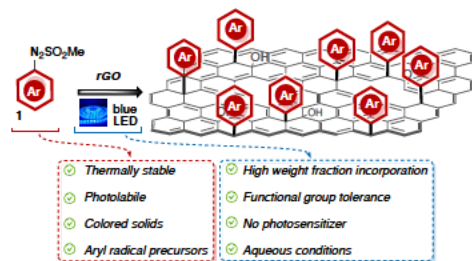
The advent of graphene in early 2000 has revolutionized the impact of carbon nanoforams on countless scientific disciplines such as organic electronics, printable circuits, corrosion control/prevention, drug delivery, water purification systems, nanofabrication and advanced composites.<sup>[1]</sup> In this segment, graphene oxide (GO) derivatives are playing a major role due to their unique chemical, mechanical and physical properties in transistors, research topics.<sup>[2]</sup> The growing popularity of graphene-based materials has soon brought to the demand of sustainable and reliable synthetic protocols for their chemical modification in order to access tunable functionalities.<sup>[3]</sup>

The current trajectories for the chemical surface modification of GO derivatives can be categorized in two main areas, namely: *covalent and non covalent functionalization*, that differ for the nature of the chemical interactions between the exposed carbon-based layers and the derivatizing agent.<sup>[4]</sup> Although complementary *pro* and *cons* can be found in both approaches, the covalent decorative tools are frequently preferred, delivering more robust and durable materials with highly predictable properties. In addition, the methodology adopted in covalent functionalizations can be dictated by the composition of the carbon surface; as a matter of fact, where oxidized functional groups (i.e. alcohols, epoxides, carbonyls/carboxylic acids)<sup>[3-5]</sup> are targeted in GO manipulations, the already present  $\text{Csp}^2$  domains are preferably exploited in more

reduced graphene type materials. Concerning the latter approach, the employment of chemical entities responsible for the generation of highly reactive radical intermediates via thermal, photochemical or electrochemical means, is essential for the formation of new C-C or C-X bonds.<sup>[4e,6]</sup> This aspect still represents a marked motivation towards the implementation of this strategy to larger scales, due to the intrinsic hazard of the required radical precursors (i.e. diazonium salts, peroxides).<sup>[7]</sup>

In pursuit of tackling this still pendant shortcoming and based on our recent findings dealing with synthetic photochemical methodologies,<sup>[8]</sup> we document here a new visible light assisted arylation of GO derivatives with arylazo sulfones (1). Arylazo sulfones, of general formula  $\text{ArN}_2\text{SO}_2\text{R}(\text{Ar}')$ , are a class of still underexplored bench stable compounds, capable of delivering aryl radical species upon visible light exposure.<sup>[8d,9]</sup> Additionally, being generally deeply colored, the use of photosensitizers (PSs) is not required, with a consequent significant improvement of the operating conditions. The latter aspect should be carefully pondered since the structural affinity of common visible light PSs ( $\pi$  conjugate systems) and the  $\pi$  domains of the *rGO* planes could cause a detrimental aggregative interaction between the two species, precluding the desired energy transfers from the PS and the aryl radical precursors.<sup>[10]</sup> As a consequence, the use of light for the covalent functionalization of graphene materials has been reported only sporadically, with a net predominance of energetic demand using UV based activation modes.<sup>[11]</sup>

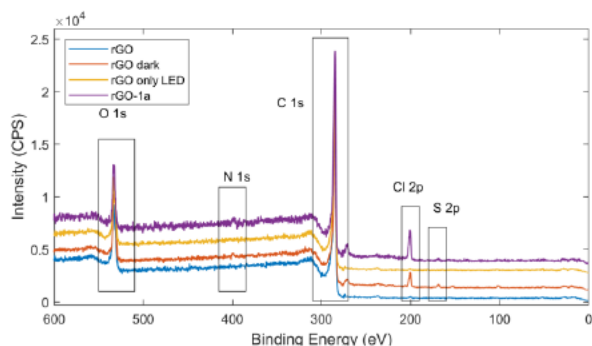
In the present study, *rGO* nanosheets were functionalized with differently substituted arenes under (photo)catalyst free conditions, via direct visible light irradiation and using arylazo sulfones as the source of radicals. Figure 1 summarizes the main features on the use of substrates 1.



**Figure 1.** Schematic representation of the present visible-light assisted covalent arylation of *rGO* with arylazo sulfones **1**

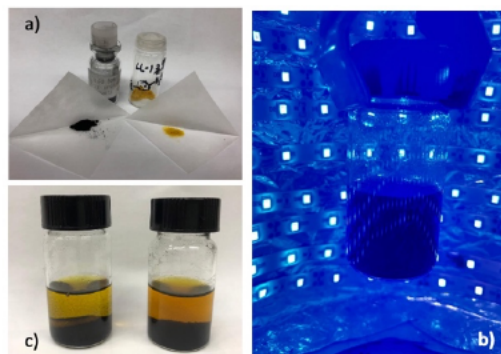
At the outset of our investigation, we focused our attention on reduced graphene oxide (*rGO*) due to the larger abundance of  $\pi$  domains present in the surface layers, with up to 75% of  $sp^2$  hybridized C, as highlighted by the C 1s XPS signature analysis. Amongst the combination of high reproducibility and high atomic incorporation on the *rGO* surface, a survey of reaction conditions (stoichiometric ratio, light source/power, irradiation time and reaction media) was carried out in the conjugation of deep yellow (*p*-C<sub>6</sub>H<sub>4</sub>)N<sub>2</sub>SO<sub>2</sub>Me **1a** and *rGO*.<sup>[12]</sup>

Conveniently, the incorporation of the *p*-chlorophenyl unit onto the *rGO* surface (O/C =  $0.16 \pm 0.01$ , C (%) =  $0.2 \pm 0.01$ , F (%) = , N (%) = , S (%) = , Figure 2 blue line) was quantitatively determined via XPS analysis (C 2p<sub>3/2</sub> energy binding energy = 200.2 eV).<sup>[13a]</sup>



**Figure 2.** XPS survey spectra of reaction condition: pristine *rGO* (blue line), *rGO* (*rGO* dark (orange line), *rGO* with no reagent and only LED (*rGO* only LED (yellow line), *rGO*-**1a** (purple line). Inset XPS Cl 2p signal. Constant was added to each spectrum for clarity.

Acetonitrile was initially chosen as the reaction medium to guarantee a complete solubilization of **1a** with consequent maximization of the photoabsorption. A blue LED stripe, ("photochemical well" mode, 461 nm, 23 W, irradiation distance  $\approx 10$  cm, Figure 3b) was employed to exploit the absorption tail of **1a** in the visible light blue region (400–500 nm,  $n\pi^*$ ).<sup>[9a,14]</sup>



**Figure 3.** a) *rGO* (left) and arylazo sulfone **1a** (right) adopted as model substrates. b) The irradiation of the reaction mixture in the "photochemical-well" (blue-LED stripes 23 W). c) The reaction mixtures before (left) and after (right) irradiation.

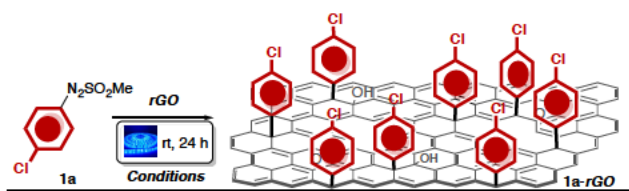
Under these conditions ([**1a**] = 0.05 M, **1a**: 0.1 mmol/6 mg *rGO*, rt, 24 h), **1a**/*rGO* was recovered with a covalent incorporation of chlorine atoms with an atomic fraction =  $2.8\% \pm 0.2$  (entry 2, Table 1) and without appreciable overall reduction of the carbon matrix (O/C =  $0.14 \pm 0.01$ ) with respect to the pristine material (entries 1 and 6).<sup>[15]</sup> Additionally, XPS analysis supports the presence of minor N and S contents, key deriving from photo-promoted decomposition of the arylazo sulfone (*vide infra* for mechanistic hypotheses).<sup>[9d]</sup> In particular, while the S 2p<sub>3/2</sub> signal found in the range of 168.1–168.8 eV, is in agreement with the SO<sub>2</sub> C group,<sup>[16a]</sup> the N 1s signal at 399.4 eV is in perfect agreement with the C=N–N–C unit.<sup>[16b]</sup>

Furthermore, exposure to a stronger irradiation source (40 W, 456 nm) did not provide any significant variation on the chemical outcome (entry 3), while the introduction of water in the reaction mixture (1:1 mixture with CH<sub>3</sub>CN) was found to maximize reproducibility and probe incorporation ([C] =  $4.8\% \pm 0.2$ ). This result can be rationalized by taking into account the capability of water to induce colloidal *rGO* suspensions.<sup>[17]</sup> Based on this chlorine atomic fraction and since **1a** has 6 carbon atoms and 1 Cl atom (atomic fraction = 7), we could calculate the surface content of the *p*-C<sub>6</sub>H<sub>4</sub> rings to be as high as  $34\% \pm 3$  (see SI for further details).

The genuinely light-driven process was proved by running the reaction under the aforementioned conditions but in the dark (entry 5). Here, fixation of **1a** on the *rGO* surface probably via physisorption (*vide infra* for Raman analysis) worked in a significantly lower extent (2.4%).

In addition, the impact of the irradiation time on the *p*-C<sub>6</sub>H<sub>4</sub> phenyl group incorporation was assessed by prolonging the reaction time up to 72 h (entries 7–9). However, the slight increase in % atomic fraction of chlorine atom detected ( $5.0/5.1\% \pm 0.2$ ) testified that the covalent tagging occurred predominantly at the early stage irradiation time (entry 7).

**Table 1.** Optimization of the reaction conditions for the visible-light assisted covalent functionalization of *rGO* (for sake of clearness a single layer *rGO* was represented)



Run <sup>[a]</sup>	Conditions	O/C <sup>[b]</sup>	Atomic fraction [%] <sup>[b]</sup>	
			Cl	N/S
1	Pristine rGO	0.16	0.2 ± 0.1	-/-
2	23 W (461 nm) CH <sub>3</sub> CN	0.14	2.8 ± 0.2	1.3/0.7
3	40 W (456 nm) CH <sub>3</sub> CN	0.16	2.8 ± 0.2	0.9/0.6
4	23 W (461 nm) CH <sub>3</sub> CN/H <sub>2</sub> O	0.12	4.8 ± 0.2	0.8/0.4
5	dark CH <sub>3</sub> CN/H <sub>2</sub> O 24 h	0.18	2.4 ± 0.1	0.9/0.6
6	23 W (461 nm) CH <sub>3</sub> CN/H <sub>2</sub> O 24 h <sup>[c]</sup>	0.16	0.2 ± 0.1	-/-
7	23 W (461 nm) CH <sub>3</sub> CN/H <sub>2</sub> O 1 h	0.15	3.2 ± 0.2	0.8/0.7
8	23 W (461 nm) CH <sub>3</sub> CN/H <sub>2</sub> O 48 h	0.14	5.0 ± 0.2	0.9/0.5
9	23 W (461 nm) CH <sub>3</sub> CN/H <sub>2</sub> O 72 h	0.14	5.1 ± 0.2	1/0.5

[a] All the reactions were carried out in reagent grade solvents under air [1a] = 0.01 mmol/6 mg of rGO [1a] = 0.01 mM. When a solvent mixture was utilized a 1:1 mixture was employed. [b] O/C was determined via XPS from O 1s and C 1s signals. O/C ratios are expressed ± 0.01. Errors on N and S were ± 0.1. [c] in absence of 1a.

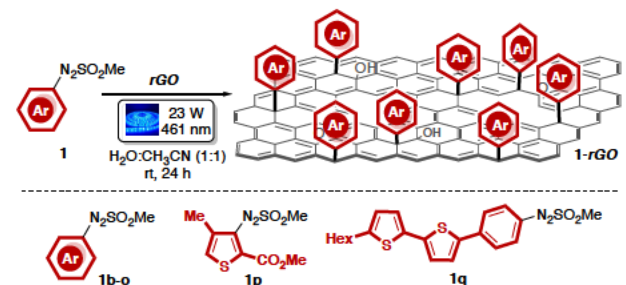
Once having established optimal conditions, the generality of the methodology was proved by subjecting a range of functionalized aryl azosulfones (1b-q) to blue LED irradiation in a suspension of rGO (H<sub>2</sub>O:CH<sub>3</sub>CN 1:1, Table 2). In particular, photoactive compounds featuring probe atoms for the XPS analysis such as halogens, nitrogen and sulfur, were selected in order to assess the covalent grafting at the surface, quantitatively.

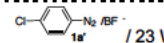
The success of aryl functionalization on rGO surface was confirmed by XPS analyses, following the signature relative to the characteristic binding energy: C 2p, F 1s (Ar CF<sub>3</sub> at 687.8 eV and Ar F at 686.8 eV),<sup>[13b]</sup> Br 3d<sub>5/2</sub> (Ar Br at 70.1 eV,<sup>[6d]</sup> N 1s (pyridine N at 398.8 eV) and I 3d<sub>5/2</sub> (Ar I at 620.6 eV).<sup>[13c]</sup> With concern to the S 2p<sub>3/2</sub> signature, the thiophene-like C-S-C was identified from peak at 163.8 eV<sup>[13d]</sup> well separated from the N-SO<sub>2</sub>-C residues (168 eV). A survey spectra are reported in the SI. Further confirmation of aryl functionalization can be found from the C 1s analysis, that evidenced peculiar chemical shifts of carbon atoms bonded to halogens (see SI).

From the data collected in Table 2 some conclusions can be drawn. The degree of oxidation on the rGOs confirmed not to be affected by the present photo-induced process, with a O/C ratio always ranking in the range of 0.13-0.19. The increase of oxygen atom content in entry 15 (O/C = 0.24) can be rationalized in terms of covalent grafting of the thiophene unit 1q carrying the ester moiety. Analogously, the former rGO reduction recorded with compound 1q (entry 16) is ascribable to the large number of carbon atoms present in the tagging triaryl unit.

Ar types of halogen atoms proved to be effectively tagged to the rGO surface via the aryl linkage. Additionally, the position of the halogen atom did not significantly affect the grafting, with the only exception of 2,4,6-Br<sub>3</sub>(C<sub>6</sub>H<sub>2</sub>)N<sub>2</sub>SO<sub>2</sub>Me (1l, entry 11) and 2-I(C<sub>6</sub>H<sub>4</sub>)N<sub>2</sub>SO<sub>2</sub>Me (1n, entry 13).

Table 2. Generality of the protocol (for sake of clearness a single layer rGO was represented)



Run <sup>[a]</sup>	Ar (1)	O/C <sup>[b]</sup>	Atomic fraction % [X] <sup>[c]</sup>	Overall aryl [%] content <sup>[d]</sup>
1	3-Cl(C <sub>6</sub> H <sub>4</sub> ) (1b)	0.14	6.3 ± 0.4 [Cl]	38 ± 4
2	2-Cl(C <sub>6</sub> H <sub>4</sub> ) (1c)	0.14	6.2 ± 0.5 [Cl]	37 ± 5
3	3,5-Cl <sub>2</sub> (C <sub>6</sub> H <sub>3</sub> ) (1d)	0.14	11.1 ± 0.8 [Cl]	33 ± 3
4	3-F(C <sub>6</sub> H <sub>4</sub> ) (1e)	0.16	4.4 ± 0.3 [F]	31 ± 3
5	4-F(C <sub>6</sub> H <sub>4</sub> ) (1f)	0.16	3.0 ± 0.3 [F]	21 ± 3
6	4-CF <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> ) (1g)	0.15	9.3 ± 0.5 [F]	31 ± 3
7	3,5-(CF <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>3</sub> ) (1h)	0.16	11.0 ± 0.8 [F]	26 ± 3
8	4-Br(C <sub>6</sub> H <sub>4</sub> ) (1i)	0.15	5.8 ± 0.4 [Br]	40 ± 4
9	3-Br(C <sub>6</sub> H <sub>4</sub> ) (1j)	0.17	4.4 ± 0.3 [Br]	31 ± 3
10	2-Br(C <sub>6</sub> H <sub>4</sub> ) (1k)	0.13	5.3 ± 0.5 [Br]	37 ± 4
11	2,4,6-Br <sub>3</sub> (C <sub>6</sub> H <sub>2</sub> ) (1l)	0.19	5.1 ± 0.4 [Br]	15 ± 2
12	4-I(C <sub>6</sub> H <sub>4</sub> ) (1m)	0.17	3.4 ± 0.3 [I]	24 ± 3
13	2-I(C <sub>6</sub> H <sub>4</sub> ) (1n)	0.17	1.5 ± 0.2 [I]	10 ± 2
14	3-pyridyl (1o)	0.15	3.9 ± 0.5 [N]	23 ± 3
15	1p	0.24	1.3 ± 0.2 [S]	13 ± 2
16	1q	0.07	6.9 ± 0.4 [S]	76 ± 4
17	 1a' / 23 W	0.16	1.0 ± 0.3 [Cl]	6 ± 1

[a] All the reactions were carried out in reagent-grade solvents under air [1] = 0.01 mmol/6 mg of rGO [1] = 0.01 mM. [b] Determined via XPS from O 1s and C 1s signal. O/C ratios are expressed ± 0.01. [c] Atomic abundance was obtained from Cl 2p, F 1s, Br 3d, N 1s and S 2p signals. [d] Overall aryl [%] content was calculated by multiplying the atomic abundance of X by the number of atoms composing the molecular probe attached to rGO and divided by the number of X atoms inside the correspondent molecule (see SI).

In these cases, the corresponding 1l rGO and 1n rGO were so treated with slightly lower surface functionalizations (5.1% ± 0.5 of Br and 1.5% ± 0.2 of I, that correspond to 15% and 10% of overall aryl content, respectively). Additionally, not only monosubstituted but also disubstituted arenes (i.e. 3,5-C<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>))



**1d** and **3,5**-(CF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>) **1h**) were adequately accommodated onto the *r*GO surface with satisfying overall atomic fractions (11.1% of C and 11.0% of F, corresponding to 33% and 40% of overall content, respectively).

Worth mentioning, the 3-pyridyl ring was also effectively anchored to the *r*GO surface with a final 3.9% ± 0.5 N atom abundance (overall fraction = 23%) in the presence of 3-((methylsulfonyl)diazene)pyridine **1o** (entry 14). Finally, to further explore the possibility to conjugate the *r*GO matrix with functional heteroaryls, functionalization experiments were carried out in the presence of thienyl and benzimidazolones **1p** and **1q**. Satisfyingly, the incorporation of the thienyl scaffolds occurred in moderate to good extents (1.3–6.9%, entries 15 and 16).<sup>[18]</sup>

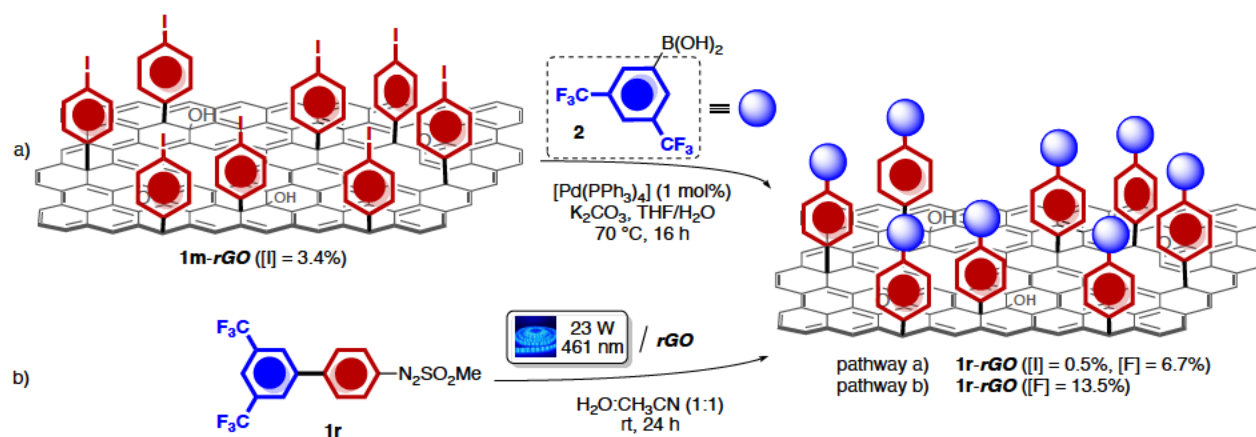
The complementarity of the presented methodology with the known diazonium salt based analogues<sup>[6]</sup> was finally ascertained by treating a suspension of *r*GO with *p*-chlorophenyl diazonium salt **1a'** under conventional blue LEDs irradiation (entries 17). Interestingly, significant overtagging (1.0%) of the heterogeneous fragment was recorded proving the higher efficiency of our protocol.

Finally, the nanomanipulation of oxidized functionalized **1m** *r*GO was effectively proved by subjecting a **1m** *r*GO suspension

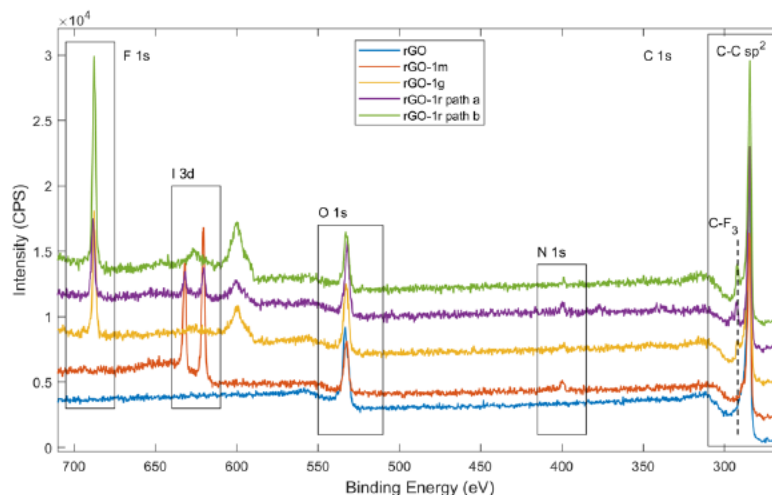
(THF/H<sub>2</sub>O) to a palladium catalyzed Suzuki–Miyaura cross-coupling in the presence of commercial available boronic acid **2** (Scheme 1a).

XPS analysis of the recovered nanostructured material **1r** *r*GO (Figure 4) revealed an almost complete disappearance of the iodine signal (0.5 ± 0.1) in favor of the fluorine one (6.9%, F 1s at 688.3 eV), generated by the formation of the bis(trifluoromethyl)benzene group. The latter findings contribute to effect the methodology as a valuable converging synthetic tool for the preparation of tailored functional brushes on carbon based nanomaterials.

To further corroborate this chemical interpretation, we employed (CF<sub>3</sub>)<sub>2</sub>benzimidazolone **1r** in the photochemical derivatization of *r*GO (Scheme 1b). Gratifyingly, XPS analysis of recovered **1r** *r*GO showed a fluorine F 1s signal at 687.6 eV that is within the same range of the one recorded on **1r** *r*GO obtained via Suzuki coupling. Here, the higher atomic fraction of F = 13.5% vs 6.9% can be reasonably accounted by considering a partial degradation of **1r** *r*GO during the Pd-mediated nanomanipulation.



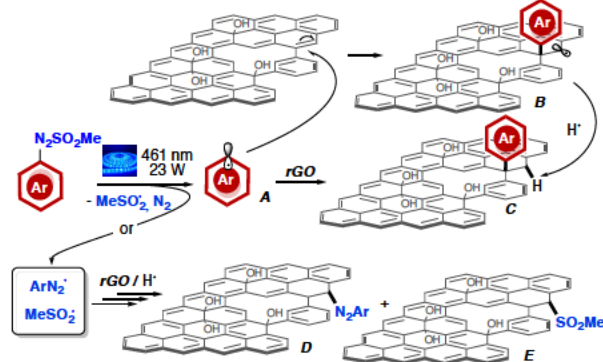
**Scheme 1.** a) Chemical elaboration of the tagged **1m-rGO** (Suzuki cross-coupling) b) Proving the consistency of the chemical elaboration of the covalently bound *p*-aryl units (Scheme 1a) via photo-irradiation of *r*GO with preformed compound **1r**



**Figure 4.** XPS survey spectra of reaction path proposed in Scheme 1. Pristine rGO (blue line), 1m-rGO (orange line), 1g-rGO (yellow line), 1r-rGO path a (purple line) and 1r-rGO path b (green line). F 1s, 3d, O 1s, N 1s and C 1s regions are highlighted by rectangles. C 1s region presents clear evidence of CF<sub>3</sub> carbon at 292 eV, which is chemically shifted from Csp<sup>2</sup> at 284.6 eV. Auger signal from F KLL is present in 650-600 eV region.

Mechanistically, the radical process depicted in Scheme 2 is proposed. In particular, the nitroaradication of aryl azosulfones with blue LEDs would lead to the corresponding aryl (A, Ar•) and methanesulfonyl radical species via homolytic cleavage of the N-S bond and subsequent nitrogen extrusion from the firstly generated aryl diazenyl radical.<sup>[9]</sup> Addition of the aryl radical A to the ππ unsaturation of the rGO surface would generate the covalent grafting of the aryl unit and consequent formation of a contiguous radical center B.<sup>[19]</sup> Direct hydrogen abstraction from the medium would result in the tagged carbon species type C. Alternatively, trapping of either the methanesulfonyl radical or the electrocyclic aryl diazenyl radical before nitrogen loss by rGO can parallel the aryl at-on event, generating new heterofunctionalized "defects" on the nanostructure arylated lattice (see species D and E).

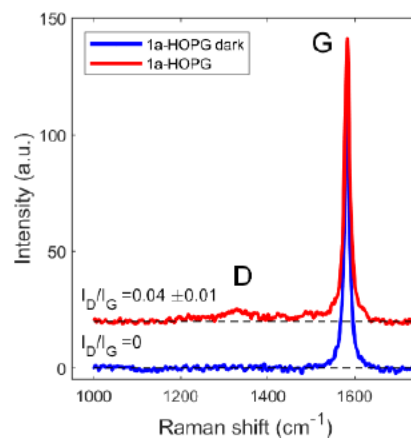
The aforeproposed hypothesis was partially verified by applying optimal conditions to the decoration of samples of GO with sulfone 1a (see SI for details). The amount of Csp<sup>2</sup> measured by XPS (C 1s signal) increases from 40% in GO to 75% in rGO. As expected, the manipulation of graphene oxide, that features a lower content of Csp<sup>2</sup> domains, led to a significant lower atomic fraction of C incorporation (1.4%) accompanied by a significant reduction of the carbonaceous material (see SI for details).<sup>[15]</sup>



**Scheme 2.** Simplified mechanistic sketch

The aforeproposed hypothesis was verified both experimentally as well as spectroscopically. In particular, we applied the optimal conditions to the decoration of samples of GO with sulfone 1a (see SI for details). As expected, the manipulation of graphene oxide, that features a lower content of Csp<sup>2</sup> domains, led to a significant lower atomic fraction of C incorporation (1.4%) accompanied by a significant reduction of the carbonaceous material (see SI for details).<sup>[15]</sup> In addition, the involvement of the Csp<sup>2</sup> domains in the present covalent grafting, was unambiguously proved by running a visible light treatment on HOPG (highly ordered pyrolytic graphite) with 1a. The spectra of 1a-HOPG samples obtained with and without light exposure were collected and reported in Figure 5. 1a-HOPG presents a clear D band at 1330 cm<sup>-1</sup> that demonstrates the formation of sp<sup>3</sup> defects due to the covalent aryl at-on process on the Csp<sup>2</sup> composing the

surface of HOPG basal plane (change in hybridization from sp<sup>2</sup> to sp<sup>3</sup>). Conversely, no D peak was observed in absence of LED light on HOPG control sample (1a-HOPG dark), therefore, the light becomes a mediator than covalent grafting observed on 1a-HOPG sample in a light-driven process. G band (1582 cm<sup>-1</sup>) and 2D band (2686 cm<sup>-1</sup>) were also present (see SI). The ratio intensity of D and G band (*I*<sub>D</sub>/*I*<sub>G</sub>), was used as quantitative parameter of grafting efficiency, resulting 0.04 ± 0.01 for 1a-HOPG. The magnitude of *I*<sub>D</sub>/*I*<sub>G</sub> is compatible with a sub-monolayer coverage of diazonium moieties grafted on HOPG, as previously reported for electrochemical grafting<sup>[6e]</sup> and chemistry activated grafting.<sup>[20]</sup>



**Figure 5.** Raman spectrum of 1a-HOPG dark and 1a-HOPG. Linear background was subtracted and spectra were shifted for clarity.

In conclusion, we have documented a visible light-assisted covalent functionalization of rGO via an aryl at-on procedure. It is worth mentioning that: i) the absence of meta-based or organic PSs, ii) the very mild conditions employed (rt, aqueous media), iii) the wide functional group tolerance; iv) the dense surface decoration, and v) the quantitative analytical determination of the tagged aryl units via XPS, represent a unique combination of factors reflecting the present methodology as a viable synthetic alternative to the known protocols for the covalent modification of reduced graphene oxide surface. The late-stage functionalization of the modified rGO and a mechanistic proposal based on both experimental as well as spectroscopic (Raman) analyses completed the study. Efforts towards the implementation of the present protocol to the realization of different covalently conjugated nanostructured carbon materials are underway in our laboratories and will be presented in due course.

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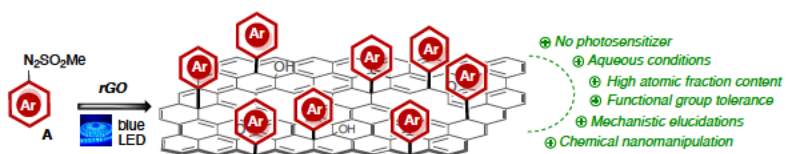
**Keywords:** rGO • surface modification • ary azasulfones • photochemistry • Suzuki cross coupling

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## Entry for the Table of Contents



**Lightning @ surface.** The visible light irradiation of unarmful and photoaberrant aryl azo sulfonates enabled the efficient covalent decoration (i.e. arylation) of rGO surfaces under mild, functional group tolerant and photosensitizer free conditions (see Scheme). Nanomanipulation of the tagged rGO surface via Pd catalyzed cross coupling was also documented.