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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 n ear y 2000 has revo ut on zed the mpact of carbo nanoforms on count ess sc ent f c d sc p nes such as organ c e ectron cs, pr ntab e c rcu ts, corros on contro /prevent on, drug de very, water pur f cat on systems, nanof u d c and advanced compos tes.[1] In th s segment, graphene ox de (*GO*) der vat ves are p ay ng a major ro e due to the r un que chem ca , mechan ca and phys ca propert es n trans at ona research top cs.[2] The grow ng popu ar ty of graphene based mater a s has soon brought to the demand of susta nab e and re ab e synthet c protoco s for the r chem ca mod f cat on n order to access tunab e funct ona t es.[3]

The current trajector es for the chem ca surface mod f cat on of *GO* der vat ves can be categor zed n two ma n areas, name y: *covalent and non covalent functionalization*, that d ffer for the nature of the chem ca nteract ons between the exposed carbon based ayers and the der vat z ng agent.[4] A though comp ementary *pro* and *cons* can be found n both approaches, the cova ent decorat ve too s are frequent y preferred, de ver ng more robust and durab e mater a s w th h gh y pred ctab e propert es. In add t on, the methodo ogy adopted n cova ent funct ona zat ons can be d ctated by the compos t on of the carbon surface; as a matter of fact, wh e ox d zed funct ona groups (*i e* a coho s, epox des, carbony s/carboxy s)[3-5] are targeted n *GO* man pu at ons, the arge y present Csp^2 doma ns are preferab y exp o ted n more reduced graphene type mater a s. Concern ng the atter approach, the emp oyment of chem ca ent t es respons b e for the generat on of h gh y react ve rad ca ntermed ates v a therma , photochem ca or e ectrochem ca means, s essent a for the format on of new C C or C X bonds.[4e,6] Th s aspect st represents a marked m tat on towards the mp ementat on of th s strategy to arger sca es, due to the ntr ns c hazard of the requ red rad ca precursors (*i e* d azon um sa ts, perox des).[7]

In pursu t of tack ng th s st pendant shortcom ng and based on our recent f nd ngs dea ng w th synthet c photochem ca methodo og es,[8] we document here a new v s b e ght ass sted ary at on of *GO* der vat ves w th ary azo su fones (**1**). Ary azo su fones, of genera formu a $ArN_2SO_2R(Ar')$, are a c ass of st underexp o ted bench stab e compounds, capab e of de ver ng ary rad ca spec es upon v s b e ght exposure.[8d,9] Add t ona y, be ng genera y deep y co ored, the use of photosens t zers (PSs) s not requ red, w th a consequent s gn f cat ve s mp f cat on of the operat ng cond t ons. The atter aspect shou d be carefu y pondered s nce the structura aff n ty of common v s b e ght PSs (π conjugate systems) and the π doma ns of the *rGO* p anes cou d cause a detr menta aggregat ve nteract on between the two spec es, prec ud ng the des red energy transfers from the PS and the ary rad ca precursors.[10] As a consequence, the use of ght for the cova ent funct ona zat on of graphene mater a s has been reported on y sporad ca y, w th a net predom nance of energet ca y demand ng UV based act vat on modes.[11]

In the present study, *rGO* nanosheets were funct ona zed w th d fferent y subst tuted arenes under (photo)cata yst free cond t ons, v a d rect v s b e ght rrad at on and us ng ary azo su fones as the source of rad ca s. F gure 1 summar zes the ma n features on the use of substrates **1**.

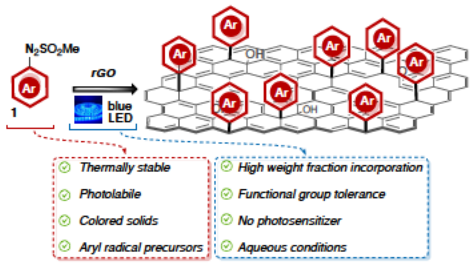


Figure 1. Schematic representation of the present visible-light assisted covalent arylation of *rGO* with arylazo sulfones **1**

At the outset of our investigation, we focused our attention on reduced graphene oxide (*rGO*) due to the larger abundance of π domains present in the surface layers, with up to 75% of sp^2 hybridized C, as highlighted by the C 1s XPS signal analysis. Aiming at the combination of high reproducibility and high atom incorporation on the *rGO* surface, a survey of reaction conditions (stoichiometric ratio, light source/power, irradiation time and reaction medium) was carried out in the conjugation of deep yellow (*p*-C_6H_4)N_2SO_2Me **1a** and *rGO*.[12]

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

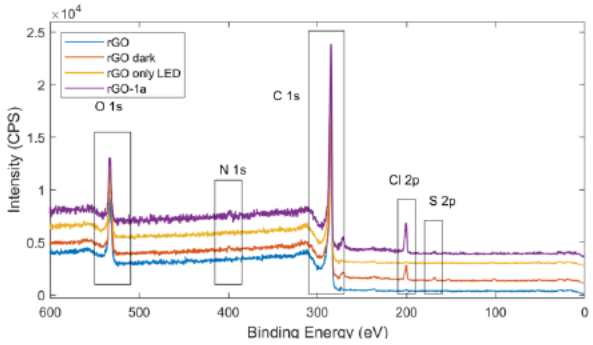


Figure 2. XPS survey spectra of reaction condition: pristine *rGO* (blue line); *rGO* (*rGO* dark orange line); *rGO* with no reagent and only LED (*rGO* only LED yellow line); *rGO*-**1a** (purple line); inset: XPS Cl 2p signal. Constant was added to each spectrum for clarity.

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 ≈ 10 cm, Figure 3b) was employed to exploit the absorption *tail* of **1a** in the visible light blue region (400–500 nm, nπ*).[9a,14]

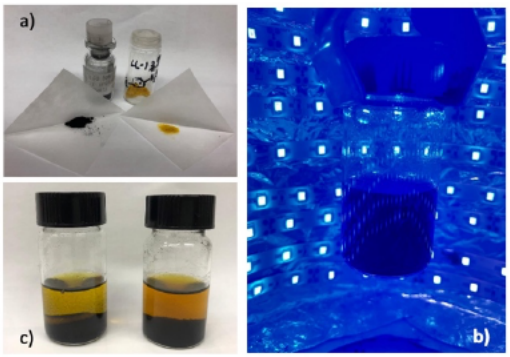


Figure 3. a) *rGO* (left) and arylazo sulfone **1a** (right) adopted as model substrates; b) The irradiation of the reaction mixture in the "*photochemical-well*" (blue-LED stripes 23 W); c) The reaction mixtures before (left) and after (right) irradiation

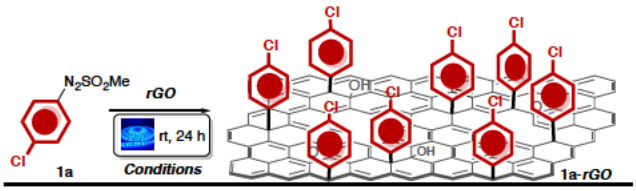
Under these conditions ([**1a**] = 0.05 M, **1a**: 0.1 mmol/6 mg *rGO*, rt, 24 h), **1a *rGO*** was recovered with a covalent incorporation of chlorine atoms with an atomic fraction = 2.8% ± 0.2 (entry 2, Table 1) and without appreciable overall reduction of the carbon matrix (O/C = 0.14 ± 0.01) with respect to the pristine material (entries 1 and 6).[15] 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 hypothesis).[9d] In particular, while the S $2p_{3/2}$ signal found in the range of 168.1 – 168.8 eV, is in agreement with the SO_2 C group,[16a] the N 1s signal at 399.4 eV is in perfect agreement with the C N=N C unit.[16b]

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_3CN) was found to maximize reproducibility and probe incorporation ([C] = 4.8% ± 0.2). This result can be rationalized by taking into account the capability of water to induce colloidal *rGO* suspensions.[17] Based on this chlorine atomic fraction and since **1a** has 6 carbon atoms and 1 C atom (atomic fraction = 7), we could calculate the surface content of the *p*-C phenyl rings to be as high as 34% ± 3 (see SI for further details).

The genuinely light driven process was proved by running the reaction under the aforedescribed 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 significantly lower extents (2.4%).

In addition, the impact of the irradiation time on the *p*-C 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% ± 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[a]	Conditions	O/C[b]	Atomic fraction [%][b]	
			Cl	N/S
1	Pristine *rGO*	0 16	0 2 ± 0 1	-/-
2	23 W (461 nm) CH_3CN	0 14	2 8 ± 0 2	1 3/0 7
3	40 W (456 nm) CH_3CN	0 16	2 8 ± 0 2	0 9/0 6
4	23 W (461 nm) CH_3CN/H_2O	0 12	4 8 ± 0 2	0 8/0 4
5	dark CH_3CN/H_2O 24 h	0 18	2 4 ± 0 1	0 9/0 6
6	23 W (461 nm) CH_3CN/H_2O 24 h[c]	0 16	0 2 ± 0 1	--/--
7	23 W (461 nm) CH_3CN/H_2O 1 h	0 15	3 2 ± 0 2	0 8/0 7
8	23 W (461 nm) CH_3CN/H_2O 48 h	0 14	5 0 ± 0 2	0 9/0 5
9	23 W (461 nm) CH_3CN/H_2O 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 1 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] n absence of **1a**

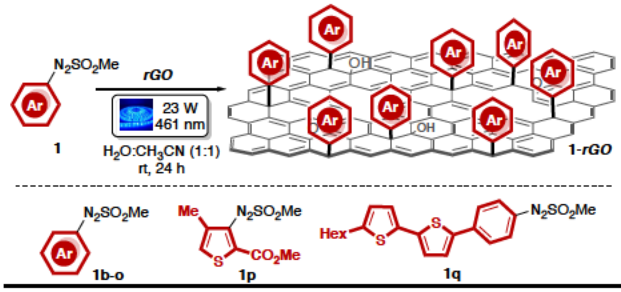
Once hav ng estab shed opt ma cond t ons, the genera ty of the methodo ogy was proved by subject ng a range of funct ona zed ary azo su fones (**1b q**) to b ue ed rrad at on n a suspens on of *rGO* (H_2O:CH_3CN 1:1, Tab e 2). In part cu ar, photoact ve compounds featur ng probe atoms for the XPS ana ys s such as ha ogens, n trogen and su fur, were e ected n order to assess the cova ent graft ng at the surface, quant tat ve y.

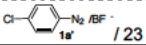
The success of ary funct ona zat on on *rGO* surface was conf rmed by XPS ana yses, fo ow ng the s gna s re at ve to the character st c b nd ng energy: C 2p, F 1s (Ar CF_3 at 687.8 eV and Ar **F** at 686.8 eV),[13b] Br $3d_{5/2}$ (Ar **Br** at 70.1 eV,[6d] N 1s (pyr d ne N at 398.8 eV) and I $3d_{5/2}$ (Ar **I** at 620.6 eV).[13c] W th concern to the S $2p_{3/2}$ s gna , the th ophene ke C **S** C was dent f ed from peak at 163.8 eV[13d] we separated from the N SO_2 C res dues (168 eV). A survey spectra are reported n the SI. Further conf rmat on of ary funct ona zat on can be found from the C 1s ana ys s, that ev denced pecu ar chem ca sh fts of carbon atoms bonded to ha ogens (see SI).

From the data co ected n Tab e 2 some conc us ons can be drawn. The degree of ox dat on of the *rGOs* conf rmed not be affected by the present photo nduced process, w th a O/C rat o a ways rank ng n the range of 0.13 0.19. The ncrease of oxygen atom content n entry 15 (O/C = 0.24) can be rat ona zed n terms of cova ent graft ng of the th eny un t **1q** carry ng the ester mo ety. Ana ogous y, the forma *rGO* reduct on recorded w th compound **1q** (entry 16) s ascr bab e to the arge number of carbon atoms present n the tagg ng tr ary un t.

A types of ha ogen atoms proved to be effect ve y tagged to the *rGO* surface v a the ary nkage. Add t ona y, the pos t on of the ha ogen atom d d not s gn f cant y affect the graft ng, w th the on y except on of 2,4,6 $Br_3(C_6H_2)N_2SO_2Me$ (**1l**, entry 11) and 2 $I(C_6H_4)N_2SO_2Me$ (**1n**, entry 13).

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



Run[a]	Ar (**1**)	O/C[b]	Atomic fraction % [X][c]	Overall aryl [%] content[d]
1	3-Cl(C_6H_4) (**1b**)	0 14	6 3 ± 0 4 [Cl]	38 ± 4
2	2-Cl(C_6H_4) (**1c**)	0 14	6 2 ± 0 5 [Cl]	37 ± 5
3	3 5-Cl_2(C_6H_3) (**1d**)	0 14	11 1 ± 0 8 [Cl]	33 ± 3
4	3-F(C_6H_4) (**1e**)	0 16	4 4 ± 0 3 [F]	31 ± 3
5	4-F(C_6H_4) (**1f**)	0 16	3 0 ± 0 3 [F]	21 ± 3
6	4-CF_3(C_6H_4) (**1g**)	0 15	9 3 ± 0 5 [F]	31 ± 3
7	3 5-$(CF_3)_2$(C_6H_3) (**1h**)	0 16	11 0 ± 0 8 [F]	26 ± 3
8	4-Br(C_6H_4) (**1i**)	0 15	5 8 ± 0 4 [Br]	40 ± 4
9	3-Br(C_6H_4) (**1j**)	0 17	4 4 ± 0 3 [Br]	31 ± 3
10	2-Br(C_6H_4) (**1k**)	0 13	5 3 ± 0 5 [Br]	37 ± 4
11	2 4 6-Br_3(C_6H_2) (**1l**)	0 19	5 1 ± 0 4 [Br]	15 ± 2
12	4- (C_6H_4) (**1m**)	0 17	3 4 ± 0 3 [I]	24 ± 3
13	2- (C_6H_4) (**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	 / 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 1 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 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 S)

In these cases, the correspond ng **1l** *rGO* and **1n** *rGO* were so ated w th s ght y ower surface funct ona zat ons (5.1% ± 0.5 of Br and 1.5% ± 0.2 of I, that correspond to 15% and 10% of overa ary content, respect ve y). Add t ona y, not on y monosubst tuted but a so d subst tuted arenes (*i e* 3,5 C_2(C_6H_3)

1d and 3,5 $(CF_3)_2(C_6H_3)$ **1h**) were adequate y accommodated onto the *rGO* surface w th sat sfy ng overa atom c fract ons (11.1% of C and 11.0% of F, correspond ng to 33% and 40% of overa ary content, respect ve y).

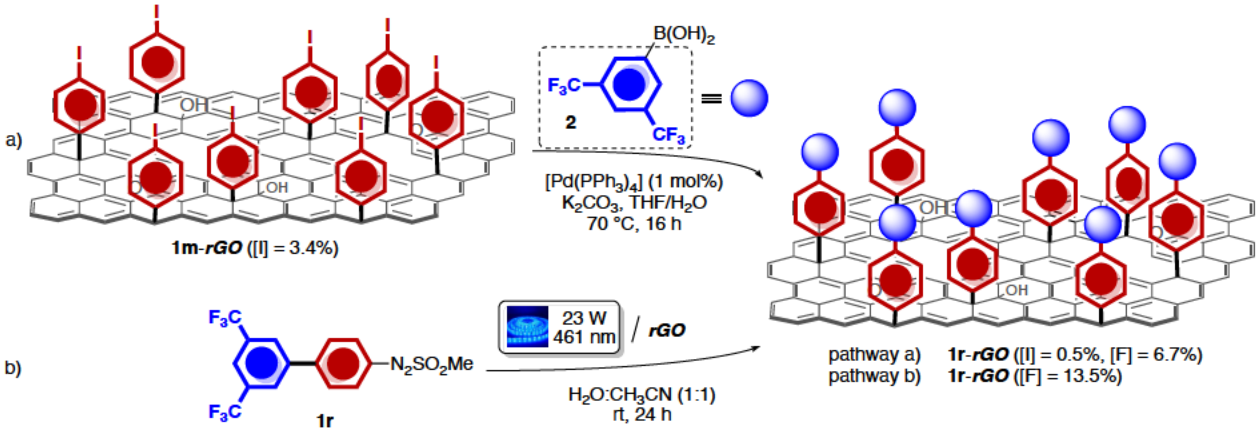
Worth ment on ng, the 3 pyr dy r ng was a so effect ve y anchored to the *rGO* surface w th a f na 3.9% ± 0.5 N atom abundance (overa ary fract on = 23%) n the presence of 3 ((methy su fony)d azeny)pyr d ne **1o** (entry 14). F na y, to further exp ore the poss b ty to conjugate the *rGO* matr x w th funct ona heteroary un ts, funct ona zat on exper ments were carr ed out n the presence of th eny and b th eny azo su fones **1p** and **1q**. Sat sfy ng y, the ncorporat on of the th oary scaffo ds occurred n moderate to good extents (1.3 6.9%, entr es 15 and 16).[18]

The complementarity of the presented methodology with the known diazonium salt based analogou[6] was f na y ascerta ned by treat ng a suspens on of *rGO* w th *p* ch oropheny d azon um sa t **1a'** under convent ona B ue LEDs rrad at on (entr es 17). Interest ng y, s gn f cant ower tagg ng (1.0%) of the ha ogenated ary fragment was recorded prov ng the h gher eff c ency of our protoco .

F na y, the nanoman pu at on of odo funct ona zed **1m** *rGO* was effect ve y proved by subject ng a **1m** *rGO* suspens on (THF/H_2O) to a pa ad um cata yzed Suzuk M yaura cross coup ng n the presence of commerc a y ava ab e boron c ac d **2** (Scheme 1a).

XPS ana ys s of the recovered nanostructured mater a **1r** *rGO* (F gure 4) revea ed an a most comp ete d sappearance of the od ne s gna (0.5 ± 0.1) n favor of the f uor ne one (6.9%, F 1s at 688.3 eV), generated by the format on of the b s(tr f uoromethy) b pheny group. The atter f nd ngs contr bute to e ect the methodo ogy as a va uab e converg ng synthet c too for the preparat on of ta or made funct ona brushes on carbon based nanomater a s.

To further corroborate th s chem ca nterpretat on, we emp oyed $(CF_3)_2$ b ary azo su fone **1r** n the photochem ca der vat zat on of *rGO* (Scheme 1b). Grat fy ng y, XPS ana ys s of recovered **1r** *rGO* showed a f uor ne F 1s s gna at 687.6 eV that s w th n the same range of the one recorded on **1r** *rGO* obta ned v a Suzuk coup ng. Here, the h gher atom c fract on of F = 13.5% *vs* 6.9% can be reasonab y accounted by cons der ng a part a de od nat on of **1r** *rGO* dur ng the Pd med ated nanoman pu at on.



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 *rGO* with preformed compound **1r**

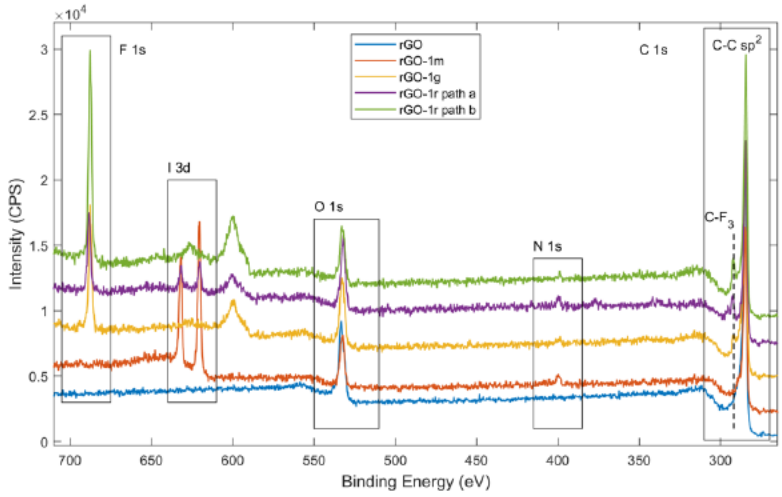
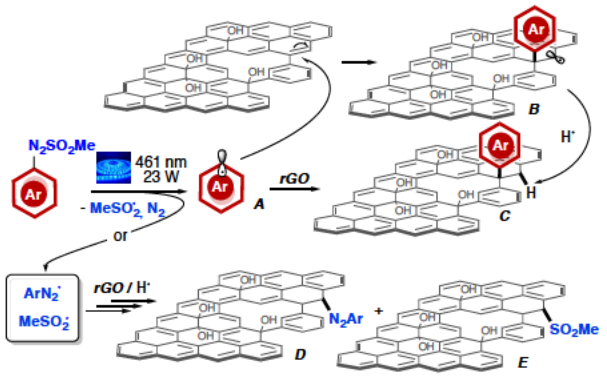


Figure 4. XPS survey spectra of reaction path proposed in Scheme 1 Pristine *rGO* (blue line) **1m**-*rGO* (orange line) **1g**-*rGO* (yellow line) **1r**-*rGO* path a (purple line) and **1r**-*rGO* path **b** (green line) F 1s 3d O 1s N 1s and C 1s regions are highlighted by rectangles C 1s region presents clear evidence of CF_3 carbon at 292 eV c a chemically shifted from Csp^2 at 284 6 eV Auger signal from F KLL is present in 650-600 eV region

Mechan st ca y, the rad ca process dep cted n Scheme 2 s proposed. In part cu ar, the n t a rrad at on of ary azo su fones w th B ue LEDs wou d ead to the correspond ng ary (**A**, Ar•) and methanesu fony rad ca s v a homo yt c c eavage of the N S bond and subsequent y n trogen extrus on from the f rst y generated ary d azeny rad ca .[9] Add t on of the ary rad ca **A** to the π π unsaturat on of the *rGO* surface wou d generate the cova ent graft ng of the ary un t and consequent format on of a cont guous rad ca center **B**.[19] D rect hydrogen abstract on from the med um wou d resu t n the tagged carbon spec es type **C**. A ternat ve y, trapp ng of e ther the methanesu fony rad ca or the e ectroph c ary d azeny rad ca before n trogen oss by *rGO* can para e the ary at on event, generat ng new heterofunct ona zed "defects" on the nanostructure ary ated att ce (see spec es **D** and **E**).

The afore proposed hypothes s was part a y ver f ed by app y ng opt ma cond t ons to the decorat on of samp es of GO w th su fone **1a** (see SI for deta s). The amount of C*sp*^{2} measured by XPS (C 1s s gna) ncreases from 40% n *GO* to 75% n *rGO*. As expected, the man pu at on of graphene ox de, that features a ower content of C*sp*^{2} doma ns, ed to a s gn f cant ower atom c fract on of C ncorporat on (1.4%) accompan ed by a s gn f cant reduct on of the carbonaceous mater a (see SI for deta s).[15]



Scheme 2. Simplified mechanistic sketch

The afore proposed hypothes s was ver f ed both exper menta y as we as spectroscop ca y. In part cu ar, we app ed the opt ma cond t ons to the decorat on of samp es of *GO* w th su fone **1a** (see SI for deta s). As expected, the man pu at on of graphene ox de, that features a ower content of Csp^2 doma ns, ed to a s gn f cant ower atom c fract on of C ncorporat on (1.4%) accompan ed by a s gn f cant reduct on of the carbonaceous mater a (see SI for deta s).[15] In add t on, the nvo vement of the Csp^2 doma ns n the present cova ent graft ng, was unamb guous y proved by runn ng a v s b e ght treatment on *HOPG* (h gh y ordered pyro yt c graph te) w th **1a**. The spectra of **1a**-*HOPG* samp es obta ned w th and w thout ght exposure were co ected and reported n F gure 5. **1a** *HOPG* presents a c ear D band at 1330 cm^{-1} that demonstrates the format on of sp^3 defects due the cova ent ary at on process on the Csp^2 compos ng the surface of HOPG basa p ane (change n hybr d zat on from sp^2 to sp^3). Converse y, no D peak was observed n absence of LED ght on *HOPG* contro samp e (**1a** *HOPG* dark), therefore, t m ght be c a med than cova ent graft ng observed on **1a** *HOPG* s ma n y a ght dr ven process. G band (1582 cm^{-1}) and 2D band (2686 cm^{-1}) were a so present (see SI). The rat o ntens ty of D and G band (*i e* I_D/I_G), was used as quant tat ve parameter of graft ng eff c ency, resu t ng 0.04 ± 0.01 for **1a** *HOPG*. The magn tude of I_D/I_G s compat b e w th a sub mono ayer coverage of d azon um mo ecu es grafted on *HOPG*, as prev ous y reported for e ectrochem ca graft ng[6e] and chem ca y act vated graft ng.[20]

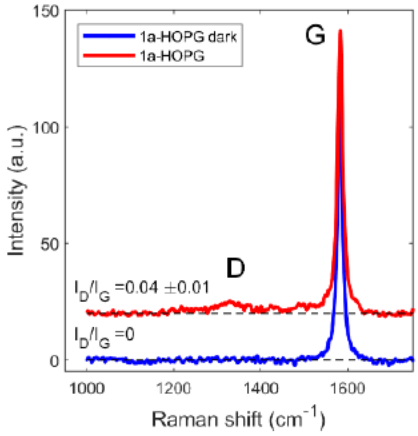


Figure 5 Raman spectrum of **1a**-HOPG dark and **1a**-HOPG Linear background was subtracted and spectra were shifted for clarity

In conc us on, we have documented a v s b e ght ass sted cova ent funct ona zat on of *rGO* v a an ary at on procedure. It s worth ment on ng that:) the absence of meta based or organ c PSs,) the very m d cond t ons emp oyed (rt, aqueous med a),) the w de funct ona group to erance; v) the dense surface decorat on, and v) the quant tat ve ana yt ca determ nat on of the tagged ary un ts v a XPS, represent a un que comb nat on of factors e ect ng the present methodo ogy as a va uab e synthet c a ternat ve to the known protoco s for the cova ent mod f cat on of reduced graphene ox de surface. The ate stage funct ona zat on of the mod f ed *rGO* and a mechan st c proposa based on both exper menta as we as spectroscop c (Raman) ana yses comp eted the study. Efforts towards the mp ementat on of the present protoco to the rea zat on of d fferent cova ent y conjugated nanostructured carbon mater a s are underway n our aborator es and w be presented n due course.

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Keywords: *rGO* • surface mod f cat on • ary azasu fones • photochem stry • Suzuk cross coup ng

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[19] Other possible quenching modalities of the radical intermediate ***B*** such as i) SET process with formation of a stabilized carbocation and subsequent restoring of the insaturation on the surface via deprotonation and ii) radical-radical coupling between ***B*** and a second Ar• species were not depicted in the Scheme 2 for clarity

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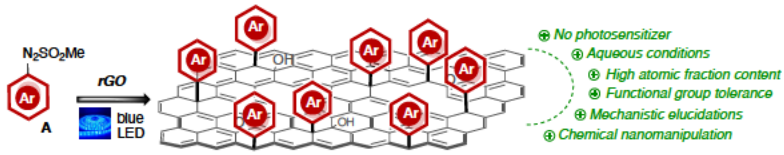
Entry for the Table of Contents



Lightning @ surface. The v s b e ght rrad at on of unharmfu and photo ab e ary azo su fones enab ed the eff c ent cova ent decorat on (*i e* ary at on) of *rGO* surfaces under m d, funct ona group to erant and photosens t zer free cond t ons (see Scheme). Nanoman pu at on of the tagged *rGO* surface v a Pd cata yzed cross coup ng was a so documented.