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Light-driven Integration of Graphitic Carbon Nitride into Polymer Materials †

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Abstract: As a metal-free polymeric semiconductor with an absorption in the visible range, carbon nitride has numerous advantages for photo-based applications span from hydrogen evolution, CO_2 reduction, ion transport, organic synthesis and organic dye degradation. Combination of g-C_3N_4 and polymer networks grants mutual benefit for both platforms, networks are upgraded with photoactivity or formed by photoinitiation, and g-C_3N_4 is integrated into novel applications. In the present contribution, some of the recently published projects regarding g-C_3N_4 and polymeric materials will be highlighted. At first, organodispersible g-C_3N_4 will be incorporated into a highly commercialized porous resin called poly(styrene-co-divinylbenzene) through suspension photopolymerization and performances of resulting beads were investigated as recyclable photocatalysts. In the other study, g-C_3N_4 nanosheets were embedded in porous hydrogel networks and so-formed hydrogels with photoactivity were transformed either into a 'hydrophobic hydrogel' or pore-patched materials via secondary network introduction, where both processes were accomplished via visible light . Since g-C_3N_4 is an organic semiconductor exhibiting sufficient charge separation under visible light illumination, a novel method for the oxidative photopolymerization of EDOT was successfully accomplished as last. Thanks to the absence of dissolved anions during polymerization, so-formed neutral PEDOT is a highly viscous liquid that can be processed and post-doped easily, as well as granting facile coating processes.

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1. Introduction

In this proceeding, recently published projects based on the combination of metal-free semiconductor graphitic carbon nitride (g-C_3N_4) and polymers will be summarized. Proceeding will briefly focus on how graphitic carbon nitride is successfully integrated into different reaction environments, such as in dispersion or as a heterogeneous photo initiator, to evolve the properties and synthesis of polymer materials.

Despite being a quite old material, g-C_3N_4 is a polymeric semiconductor as discovered in 2009. Its synthesis is based on thermal polymerization (around 550 °C) of abundant and nitrogen-rich molecules such as urea and melamine that results in a semiconductor with a photoactivity in the visible and UV range.[1] Thermal reaction mechanism can be considered as recondensation of decomposed gaseous molecules of precursors to form a thermodynamically stable matter at elevated temperatures. It is different than a typical solid state condensation reactions, therefore reaction conditions such as temperature ramp and applied atmosphere play curial role to form desired and reproducible g-C_3N_4. Since it is a product of a type of polymerization, condensation degree can be also tuned by the variability of reaction conditions (mainly temperature). Moreover, further modifications such as edge functioning and tuning repeating motifs are just some possibilities to form diverse g-C_3N_4's. g-C_3N_4 exhibits high stability in acidic and basic environments as well as thermal stability up to 620 °C.

Selected precursor and preparation methods directly affect all final properties such as surface area, morphology, surface charge, crystallinity and optical properties. Photophysical feature of resulting g-C_3N_4 may vary depending on performed techniques. Synthesized g-C_3N_4s in powder form demonstrate slightly negative surface charge, however synthesis of g-C_3N_4 thin films and membranes are known in literature as well.[2, 3] Furthermore, as a typical semiconductor g-C_3N_4 exhibits reductive and oxidative pathways upon photoformed electrons and holes which are taking a vital role for photoredox based science. g-C_3N_4 has been a haven for photocatalysis and has been integrated into many appealing applications by acting as a heterogeneous photocatalyst.[4] Furthermore, under light irradiation, it can form radical species which can be harnessed to conduct radical photopolymerization techniques. From polymer perspective, g-C_3N_4 was employed as a heterogeneous photoinitator for free radical and controlled radical polymerization methodologies.

However, some drawbacks based on dominant π-π interactions between g-C_3N_4 sheets cause problems like processability and dispersion preparation which hinders further possibilities. Recently, surface modification of g-C_3N_4 materials introduced dispersible g-C_3N_4 colloids which addressed both in aqueous and organic environments, that are attractive for new possibilities.[5, 6] There are numerous well-established techniques that deal with the integration of g-C_3N_4 colloids in soft materials, membranes and polymer particles to form hybrid materials. Yet, there are still many materials to be explored that are based on g-C_3N_4 and polymer materials.

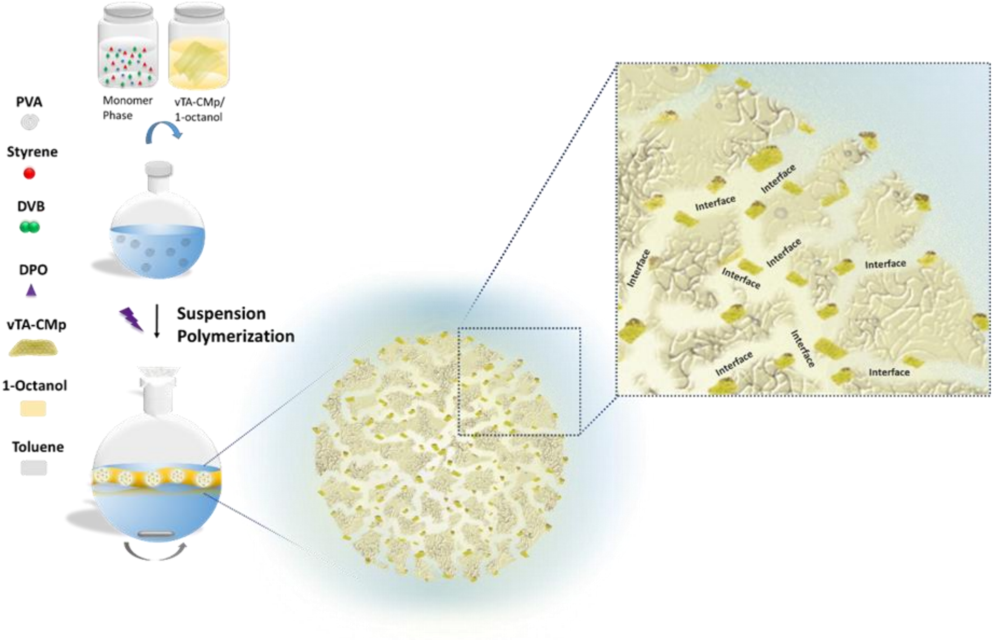
Herein, following proceeding will highlight three recently published reports based on g-C_3N_4 and polymer combination. It will start with an organic dispersion of g-C_3N_4 to form crosslinked porous polymer beads named poly(styrene-co-divinylbenzene) through suspension polymerization to sculpt photoactive bead materials. Aqueous dispersion of g-C_3N_4 will be employed for porous hydrogel synthesis, and the embedded g-C_3N_4 nanosheets will act as anchoring points for further light-induced modifications, i.e. pore substructuring and synthesis of 'hydrophobic hydrogel'. At last, g-C_3N_4 will be utilized as a heterogeneous photoinitiator to polymerize 3,4-ethylenedioxythiophene (EDOT) to form non-doped oligoEDOT material that is prone to processing prior to doping.

2. Results

2.1 Upgrading poly(styrene-co-divinylbenzene) Beads Through Suspension Photopolymerization via Carbon Nitride

Metal-free semiconductor graphitic carbon nitride (g-C_3N_4) can act as a heterogeneous photoredox polymer initiator. This study introduces g-C_3N_4 integration into inner surface (interfaces) of porous poly(styrene-co-divinylbenzene) beads via one-pot suspension photopolymerization (Scheme 1).

Regarding suspension polymerization principles, reaction conditions such as crosslinking ratio (25, 35, 50 wt.% divinylbenzene), presence of porogens (toluene as co-solvent, 1-octanol as dispersion agent of vTA-CMp), mechanical agitation (slow and medium) are investigated. According to results, 25 wt.% divinylbenzene, presence of toluene along with 1-octanol, and medium agitation speed were elucidated as optimal conditions.



Scheme 1. Schematic overview of organomodified g-C_3N_4 (vTA-CMp) incorporation into PS-DVB beads via suspension photopolymerization.[7]

As shown in Figure 1, bead morphology was investigated via SEM, and resulting images revealed a highly porous structure (**Figure 1a**). In addition, EDX investigation exhibiting homogeneous nitrogen distribution indicated successful vTA-CMp corporation since none of the reaction ingredients, except vTA-CMp, bear nitrogen (**Figure 1b**).

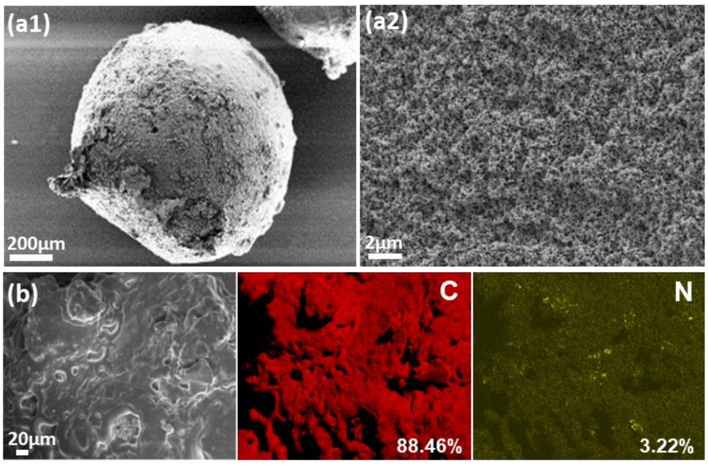


Figure 1. Scanning electron microscopy (SEM) images (a1-2) of Model bead and and Elemental mapping of Model bead via EDX (b).[7]

Photocatalytic properties of selected beads were investigated by performing aqueous Rhodamine B dye degradation experiment under visible light illumination and dark conditions (**Figure 2a-b**). Among as-synthesized beads, g-C_3N_4 photo-initiated bead (CBT5m) exhibited 89% degradation efficiency in 5 hours within R^2 value of 0.971 (**Figure 2c**). Moreover, cyclic photocatalytic cycles run up to 7 cycle and resulted in moderate loss of activity, 55.6% (**Figure 2d**). Lastly, pH effect on photodegradation explicated stability of applied beads with no host degradation. In addition, dye adsorption/desorption properties were tested in both aqueous and organic dyes.

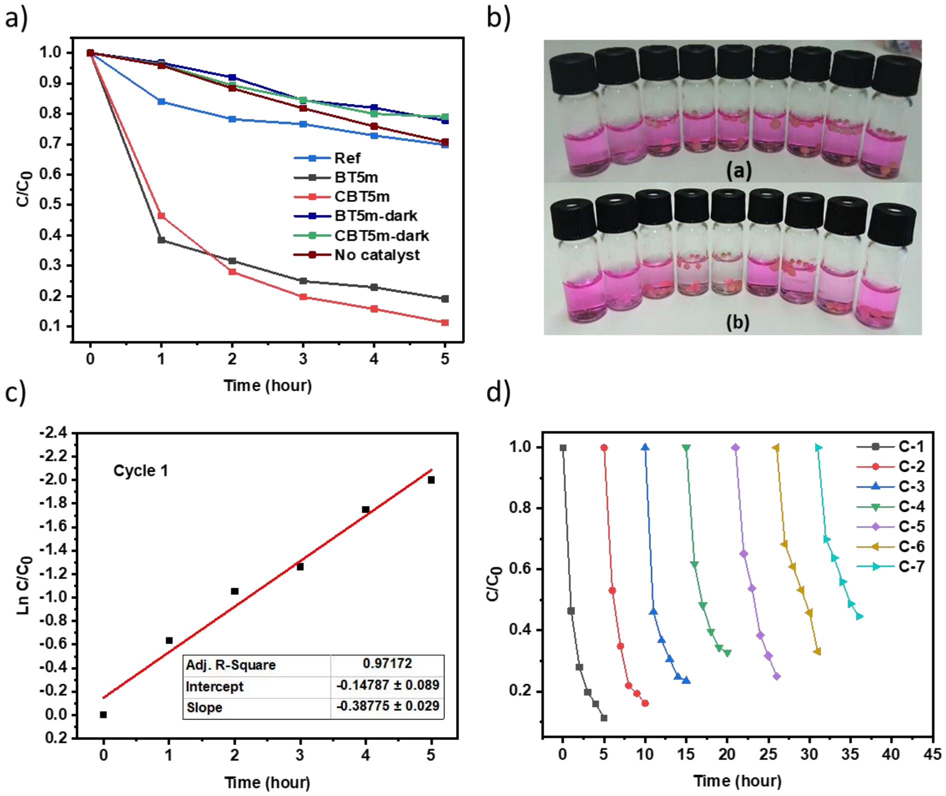


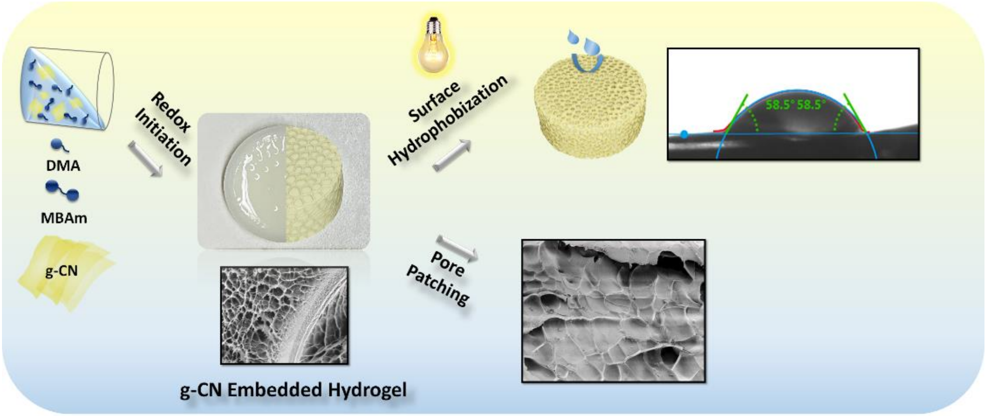
Figure 2. RhB dye degradation of BT5M, CBT5m, reference and RhB dye solution (no catalyst) under visible light irradiation (BT5m-dark and CBT5m-dark were not exposed to visible light) (a). Digital images of PS-co-DVB derived beads in RhB solution, from left to right: RhB Dye, REF, B5m, BT5m, CBT5m, BT5s, B7m, BT7m, BT10m before and after 5 hours visible light irradiation (b). Pseudo-first order kinetic fitting data of cycle 1 (pH:6.3, T=25° C, bead/RhB:0.055/0.0015 g.L-1) (c). Cyclic photocatalytic RhB dye degradation with several run cycles in the presence of CBT5m under visible light irradiation (d).[7]

Afterwards, g-C_3N_4 incorporated beads were subjected to a photoinduced surface modification by employing vinylsulfonic acid (VSA) and 4-vinyl pyridine (VP) under visible light irradiation. According to results, VSA photografting was analyzed successfully by elemental mapping via EDX along with elemental analysis via detected sulfur content. On the other hand, VP photografting was confirmed via combustive elemental analysis together with FT-IR successfully.

In other words, beads donated with photoactivity via metal-free semiconductor g-C_3N_4 integration can be exploited for dye photodegradation and as an acid-base catalyst after post-functionalization through a simple photoinduced surface modification.

2.2. Synthesis of g-C_3N_4 Integrated Hydrogels and Subsequent Post-Modifications

As a particular class of hydrophilic polymers, hydrogels possess high-water content through their crosslinked porous networks. A facile synthesis of a hydrogel can be simply described as a combination of water-soluble monomer and multi-functional crosslinker in the presence of initiator (mainly radical-based systems). In this context, firstly, g-C_3N_4 embedded hydrogel synthesis thereafter its further subsequent visible light assisted post modifications will be described (Scheme 2).



Scheme 2. Schematic overview of g-C_3N_4 embedded hydrogel fabrication and its subsequent photoinduced post-modifications.[8]

Template g-C_3N_4 embedded hydrogel was formed by free-radical polymerization in the presence of redox couple (ascorbic acid-hydrogen peroxide), water-soluble monomer (N,N-Dimethylacrylamide, DMA) with crosslinker (N,N′-methylenebisacrylamide, MBA) in aqueous dispersion of g-C_3N_4. Gelation proceeded in 3 hours and resulting hydrogel furtherly employed surface hydrophobization by being immersed into 4-methyl-5-vinylthiazole (vTA) under visible light irradiation. Drastic morphology change over pore closure observed via SEM investigation (**Figure 3a**) and sulfur detection via EDX measurement were supportive evidences of performed surface photomodification (**Figure 3b**). Moreover, resulting hydrophobized hydrogel shown enhanced water contact angle result (58.5º over 40 seconds) unlike initial hydrophilic hydrogel (**Figure 3c**). Besides, sustained cation release performance by investigating several cations in both samples, was confirmed based on controlled release after surface hydrophobization (**Figure 3d**).

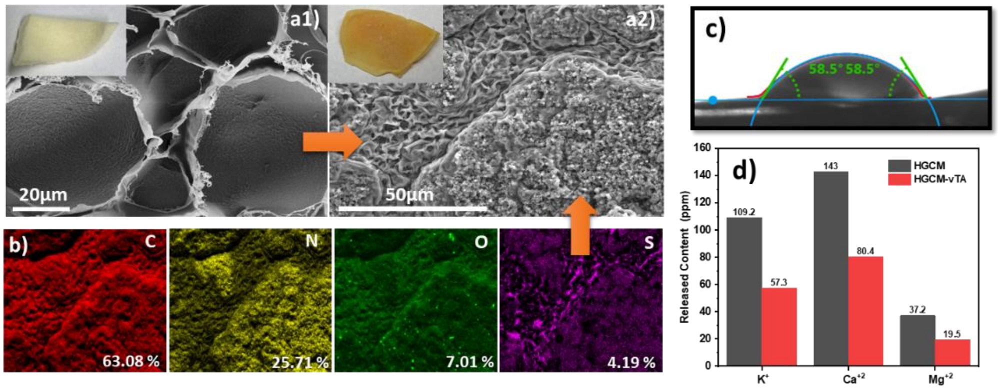


Figure 3. Scanning electron microscopy (SEM) images of HGCM (a1) and HGCM-vTA (a2) in combination with HGCM-vTA elemental mapping results via EDX. Water contact angle result of HGCM-vTA (c). Inductively coupled plasma optical emission spectroscopy (ICP-OES) results of released K^+, Ca^{2+} and Mg^{2+} content for HGCM and HGCM-vTA (d).[8]

Considering SEM results exhibiting the highly porous structure of host hydrogel, pore substructuring was performed by taking advantage of embedded g-C_3N_4 photoactivity. Regarding that, host hydrogel was swollen by various vinyl monomers and exposed to visible light. According to the SEM investigation, closure of pores via polymer layer formation was observed, and detecting functional groups via FT-IR underlines the efficient modification (**Figure 4a,b,c**).

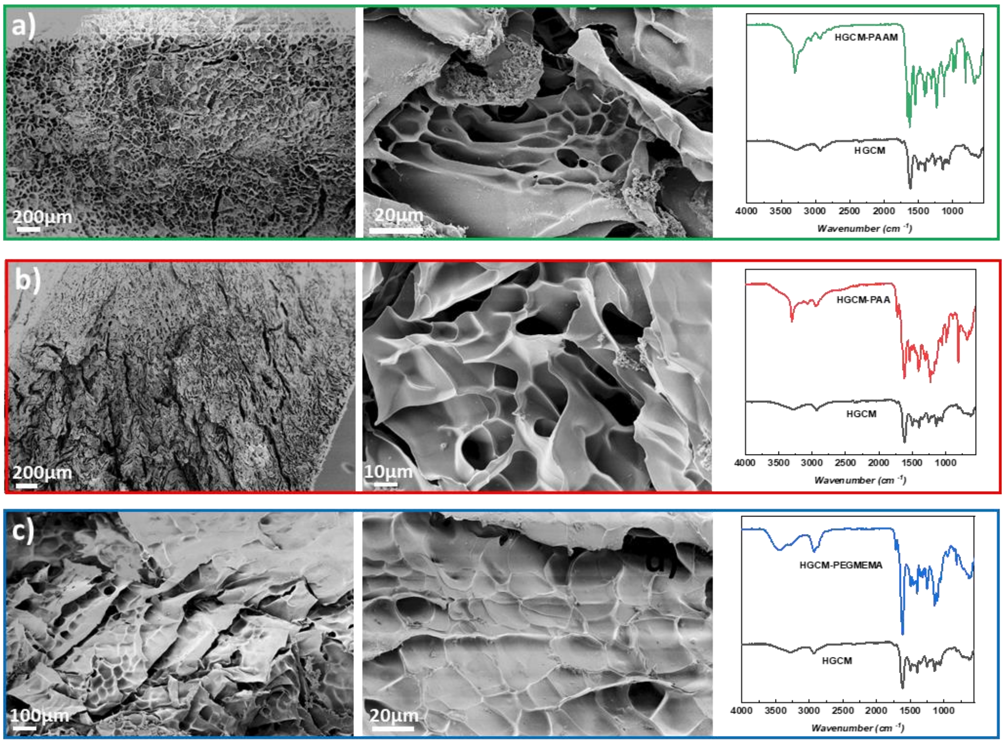


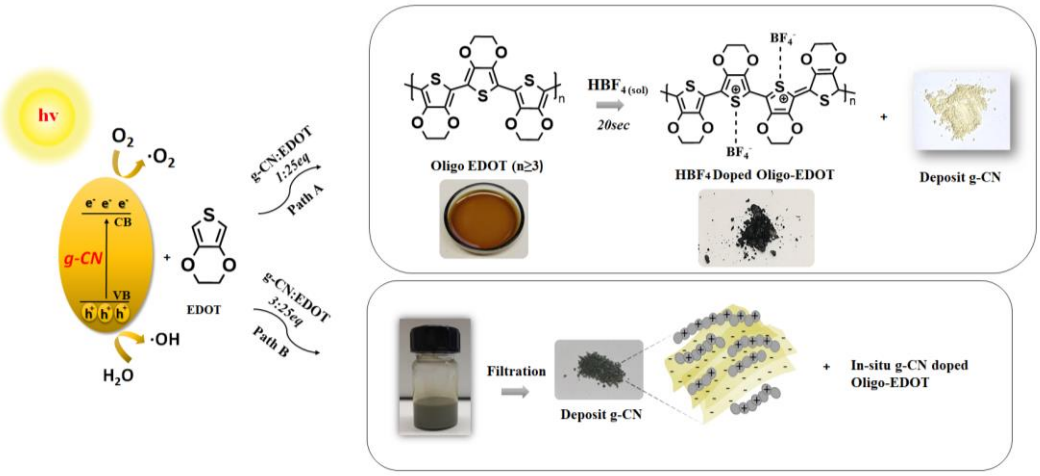
Figure 4. Scanning electron microscopy (SEM) images of HGCM-PAAM, HGCM-PAA, and HGCM-PEGMEMA in combination with their FT-IR spectra, respectively (a,b,c).[8]

Enrichment of hydrogels via embedding photoactive g-C_3N_4 nanosheets can be a promising subject with variety of target applications for the future, especially when the simplicity of post-functionalization via light illumination is considered.

2.3. Oxidative Photopolymerization of 3,4-Ethylenedioxythiophene (EDOT) via g-C_3N_4

Conductive polymers have been playing a vital role in a broad range of materials from optoelectronic to conductive composites. PEDOT as a functional polymer possessing high conductivity and stability even after doping process . However, lack of processability of PEDOT requires external factors which in return negatively influences its conductivity. As an alternative way to overcome this, g-C_3N_4 was employed as photoredox type photoinitiator to achieve oxidative photopolymerization of EDOT under visible light irradiation. One-pot reaction in the presence of oxygen allowed neutral oligo-EDOT formation (path 1) and reusable deposit g-C_3N_4, alternatively addition of excess g-C_3N_4 in the reaction led to hybrid heterojunction material which possesses deposited oligo-EDOT on g-C_3N_4 power based on surface polaron formation (path 2) (Scheme 3).

The eventual molecular weight was analyzed via UV-vis spectroscopy. According to literature, so-formed oxidative photopolymerization product explicit oligomer formation in comparison to established PEDOT products, thus named as 'oligo-EDOT' ($n \geq 3$) based upon its intensified and slightly red-shifted UV-vis spectrum (**Figure 5a**). Furthermore, enhanced viscosity within darkened color after polymerization (as EDOT is a colorless monomer) supported success in photooxidative polymerization (**Figure 5b**). Resulting viscous oligo-EDOT was furtherly post-doped with HBF_4 and final dried product was confirmed via FT-IR (**Figure 5c**). From manufacturing perpsective, a facile formation of film and coatings without further addition of chemical substances yields homogeneous conductive matter (**Figure 5d**).



Scheme 3. Oxidative photopolymerization of EDOT via g-C_3N_4.[9]

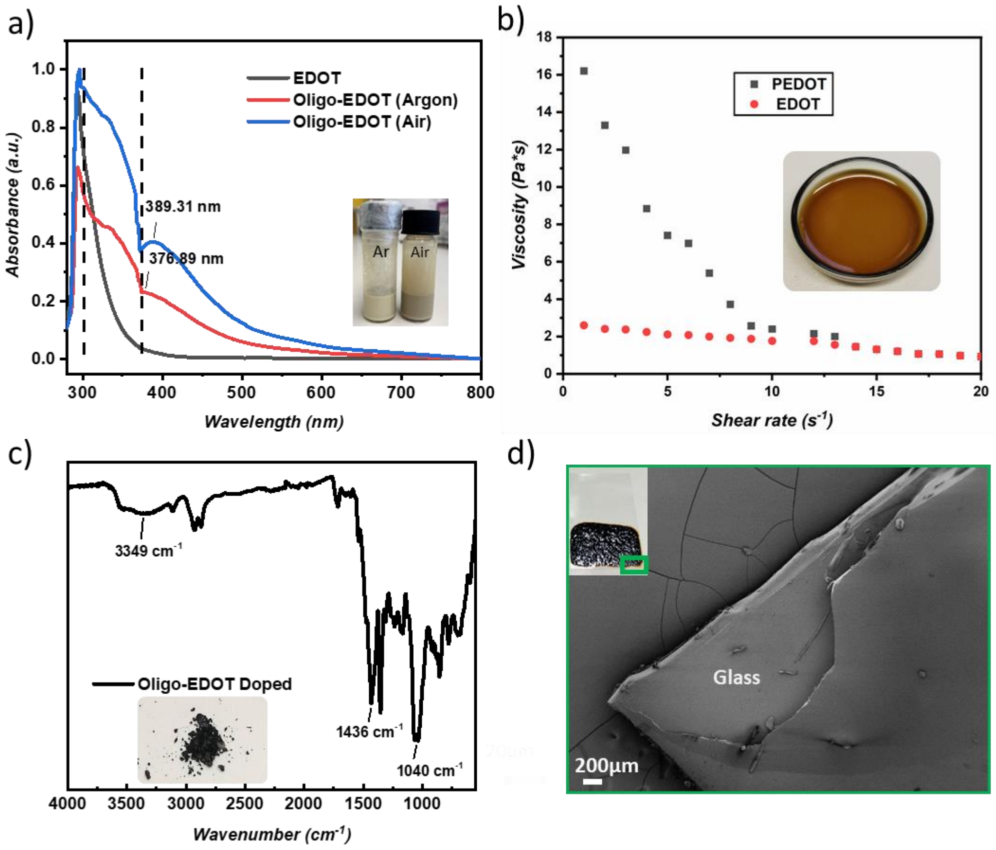


Figure 5. UV-vis spectra of EDOT, oligo-EDOT (Argon) and oligo-EDOT (Air) (after the depicted purification step, samples were prepared at 10^{-5} M, in THF (a). Viscosimetry results of EDOT and oligo-EDOT in varied shear rate (b). FT-IR spectrum of post-doped oligo-EDOT (c). Scanning electron microscopy (SEM) image of coated post-doped oligo-EDOT on a glass (d).[9]

Oxidative photopolymerization to form non-doped conducting polymers and conjugated systems that are promosing for optoelectronic and energy devices was achieved via g-C_3N_4 acting as a photocatalyst. When used in excess, surface polaron based novel hybrid materials can be accessible.

3. Conclusions

Combination of metal-free semiconductor g-C_3N_4 with polymer materials is highly exciting and offers many advanced materials, as shown in the present contribution. Photoactivity of g-C_3N_4 can be harnessed to synthesize polymers through photoredox chemistry (either forming active radicals through charge transfer processes or excited electrons or positive hole can be directly employed), alternatively g-C_3N_4 can be dispersed and embedded in polymer networks to grant photoactivity. Merging polymers with colloidal g-C_3N_4 materials is still at the infant stage, however one can distill a versatile synthetic polymer chemistry knowledge with a semiconductor science to design functional materials that can address soft materials, conducting polymers, hybrid polymer materials, agricultural delivery systems and catalysis.

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Conflicts of Interest: The authors declare no conflict of interest.

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