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Communication

Light-responsive nanocomposites combining graphene oxide with POSS based on host-guest chemistry

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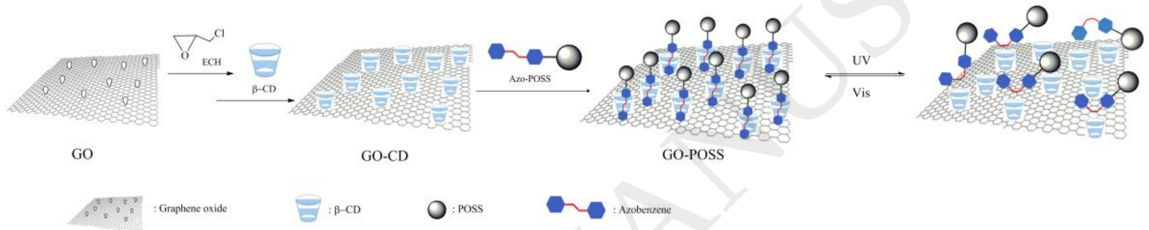
Graphical Abstract



A facile methodology has been proposed to construct light-responsive nanocomposites composed of GO and POSS based on host-guest inclusion of CD/Azo. Through manipulating photo-irradiation conditions, GO and POSS moieties in GO-POSS exhibited impressive and reversible supramolecular assembly/disassembly behaviors and had remarkable effect on oxygen barrier property of PVA-coated films, which would have potential application for smart gas barrier materials in packaging.

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ABSTRACT

Based on the reversible host-guest inclusion/exclusion of cyclodextrin-functionalized graphene oxide (GO-CD) and azobenzene-terminated polyhedral oligomeric silsesquioxane (Azo-POSS), a novel kind of light-responsive nanocomposites GO-POSS was developed under mild condition. 1H-NMR, FT-IR, TG, TEM and UV-vis spectroscopy were conducted to characterize the chemical composition and photo-responsive performance of obtained GO-POSS nanocomposites. The results demonstrated that nanocage-structured POSS and nanosheet GO components in GO-POSS exhibited pronounced supramolecular assembly/disassembly behavior upon UV/vis irradiation. Moreover, GO-POSS nanocomposites showed good water dispersity and had remarkable impact on oxygen permeability of conventional PVA-coated films under varied light irradiation conditions, which would be valuable for developing smart gas barrier materials in packaging.

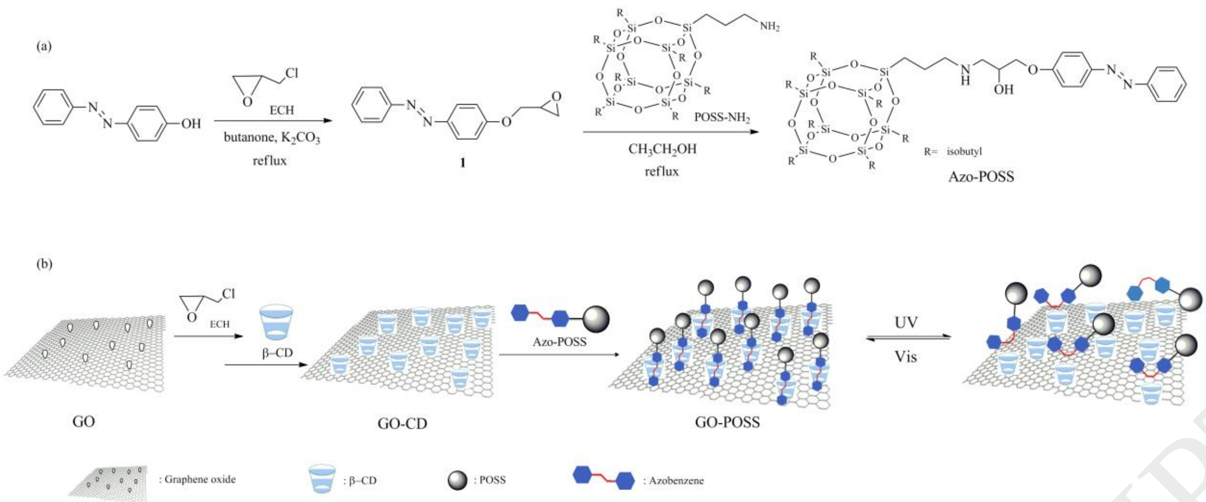
Keywords: Graphene oxide POSS Light-responsiveness Host-guest inclusion Oxygen permeability

Stimulus-responsive smart materials, inspired by great nature, have been widely investigated and successfully applied in many cutting-edge fields such as switching surface wettability, controlled release/drug delivery, membrane separation, electrical switch and actuators [1-6]. Among the representative stimuli (such as pH, temperature, humidity, electric field, *etc.*), light stimulus attracted much more attentions because light has own distinct advantages: noncontact process, precise area selectivity, no waste products and high spatial-temporal remote controlling. In the past decades great effort has been devoted to design and synthesize novel light-responsive materials [7, 8]. Azobenzene (Azo) was one of typical photosensitive molecules, which could undergo photo-isomerization and reversibly convert between *trans* and *cis* form under UV/vis irradiation[9]. Introducing Azo molecular moieties has been regarded as an effective and easy strategy to endow conventional materials with attractive light-responsive properties. For example, Chun *et al*. coated Azo-based polymer on conventional PCTE membrane to prepare a selective photoactive ion channel systems [10]. Upon UV/vis irradiation the system showed distinct electrical signals, which came from the variation of pore diameter of PCTE membrane and caused by the photo-isomerization of Azo molecules. Ke *et al.* covalently bonded Azo groups into PEG main chain and synthesize an amphiphilic polymer, which could not only self-assembly into different micelles but also disaggregate upon exposure to photo stimulus[11].

Host-guest chemistry has gained wide attention from all over the world since Nobel Prize was awarded to Lehn, Cram and Pederson in 1987. The most typical host-guest chemistry is the molecular inclusion of cyclodextrin (CD) with Azo [12-14]. Upon varied UV-vis irradiation the molecular interaction between CD and Azo could be reversibly controlled due to the switchable *trans* and *cis* isomer of Azo: the rodlike *trans*-Azo could form stable inclusion complex with CD, while the bent *cis*-Azo would exclude from CD cavity. Recently, Shi and coworkers [15] have reported to construct one cell assembly based on light-induced reversible interaction of CD and Azo and investigated the cell-cell assembly/disassembly behavior through manipulating photo-irradiation. Inspired by such idea, we paid our attention to imparting conventional nanomaterials with reversible light-responsive properties and prepared novel light-responsive nanocomposites to improve the gas barrier properties of conventional packaging films.

Graphene, as one emerging 2D carbon nanomaterial, has attracted considerable attention due to its intrinsic ultrathin structure, high specific surface, superior mechanical strength, remarkable electronic and gas impermeable properties in wide applications [16, 17]. Designing and preparation of novel graphene-based nanocomposites with attractive properties was always of importance and interest from both industrial and academic point of view. Polyhedral oligomeric silsesquioxane (POSS), a molecular level organic-inorganic hybrid ($R_8Si_8O_{12}$), is constituted by inner inorganic Si–O framework and outer organic substituents. POSS has been regarded as the smallest possible particles of silica due to its cage-like nanostructure (the diameter approximately 1.5 nm) [18, 19]. Recently, Liu and coworkers developed a novel graphene oxide/POSS (GO/POSS) hybrid *via* irreversible covalent bonds for dielectric materials [20]. However, to the best of our knowledge, there is no report about integrating graphene oxide (carbon material) with POSS (silica material) through reversible interaction to prepare nanocomposites with impressive light-responsive properties.

In this paper, we presented a facile strategy to construct novel GO/POSS nanocomposites with remarkable light-responsive properties. Through CD/Azo host-guest chemistry, GO/POSS nanocomposite could undergo reversible assembly and disassembly behavior upon photo-irradiation, which would potentially control gas impermeable layers dispersion and have significant impact on gas permeability for smart gas barrier materials in packaging.



Scheme 1. Illustration of a) synthetic route of Azo-POSS and b) preparation procedure of light-responsive GO-POSS nanocomposites.

Scheme 1 presented the preparation procedure and illustrated the self-assembly/disassembly behaviors of light-responsive GO-POSS nanocomposites under irradiation. As one typical representative of promising carbon and silicon materials, GO and POSS-NH_2 were selected for starting reactants and then functionalized with CD and Azo, respectively, to obtain host components GO-CD and guest components Azo-POSS. Through high efficient two-step reactions, Azo-POSS was synthesized and the chemical compositions were verified by ^{1}H-NMR (Fig. S1 in Supporting information). Due to the presence of Azo group, Azo-POSS showed remarkable photo-responsive property under irradiation (Fig. S2 in Supporting information). Upon 365 nm UV irradiation the absorption band around 342 nm corresponded to the π-π^* transition of *trans* isomer of Azo-POSS was obviously blue-shifted and decreased dramatically, while the band around 440 nm assigned to the n-π^* transition of *cis* isomer of Azo-POSS increased slightly. In contrast, the *cis* isomer could reconverted to the *trans* isomer again under visible illumination (sun light) for 24 h, resulting in a remarkable increase of π-π^* absorption and slight decrease of n-π^* absorption. Such phenomenon implied the reversible conversion between *trans* and *cis* state of azobenzene group in Azo-POSS under different irradiation conditions, which was beneficial to construct following light-responsive nanocomposites.

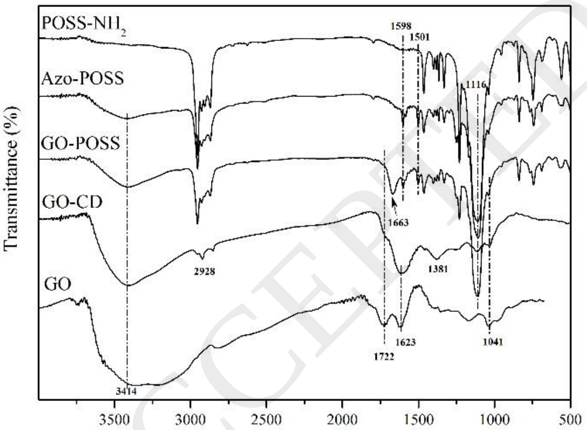


Fig.1 FT-IR spectra of GO, GO-CD, POSS-NH_2, Azo-POSS and GO-POSS.

On the other hand, in order to form strong inclusion complex between POSS and GO, *β*-CD was introduced into GO and GO-CD was prepared in the presence of ECH. Detailed synthetic process was presented in Supporting Information. Different from depending on hydrogen bonds in previous literatures [21], ECH could easily bridge *β*-CD and firmly attach to GO sheets via covalent bonds due to the presence of large number of hydroxyl groups for both *β*-CD and GO. To confirm the surface functionalization of GO, FI-IR spectroscopy were employed to verify the chemical compositions (Fig.1). Characteristic absorptions at ~3327 cm^{-1} (O-H), 1722 cm^{-1} (C=O), 1623 cm^{-1} (C=C) and 1041 cm^{-1} (C-O) were observed for GO, which indicated there were a large number of oxygen-containing groups present in graphite sheet after oxidation treatment. When *β*-CD was bonded into the surface of GO, GO-CD exhibited typical *β*-CD absorption features of O-H stretching vibrations at ~3409 cm^{-1}, CH/CH$_2$ stretching and bending vibrations at ~2928, 2853 and 1381 cm^{-1}, as well as the coupled C-O-C/C-OH stretching vibrations at ~1116 cm^{-1}. Moreover, in comparison with GO, a much stronger band at ~1623 cm^{-1} and a relative smaller absorption at 1722 cm^{-1} (attributed to sp^2 C=C and C=O of GO, respectively) were found in GO-CD, which suggested that the reaction between GO and *β*-CD in the presence of ECH consumed a lot of oxygen-containing groups, restored graphite lattice and finally reduced GO to some extent. Similar phenomenon has been reported in other literatures [21]. Thermogravimetric analysis (TGA, Fig. S3 in Supporting information) indicated that the relative amount of CD molecules on the surface of GO was determined to be 26.7 wt% (about one CD per 260 carbon atoms), suggesting that a high number of CD was bonded on the surface of GO.

Depending on the reversible host-guest inclusion/exclusion of CD/Azo, novel light-responsive GO-POSS nanocomposites could be successfully fabricated when Azo-POSS was blended with GO-CD under irradiation. Upon visible illumination (sun light), *trans*-Azo-POSS would dominate and could assembly with GO-CD to form GO-POSS. Fig.1 compared the FT-IR spectra of Azo-POSS, GO-CD and GO-POSS. It found that GO-POSS nanocomposites not only possessed all characteristic absorptions of Azo-POSS, but also exhibited typical features of GO-CD. Moreover, due to the formation of host-guest inclusion complex, the C=O and C=C absorptions derived from GO components in GO-POSS became undetectable and shifted from 1623 cm^{-1} to 1663 cm^{-1}, respectively, which suggested strong interactions between GO and POSS moieties occurred and successful supramolecular assembly took place between GO-CD and Azo-POSS. When UV irradiation was applied, *trans*-Azo-POSS would convert to *cis*-Azo-POSS and host-guest inclusion between GO-CD and Azo-POSS could not take place. As expected, UV-Vis spectra of GO-POSS under 365 nm UV irradiation (shown in Supporting Information, Fig. S4) demonstrated that the absorption band of GO-POSS at 342 nm (attributed to *trans*-Azo-POSS) remarkably decreased, while the band around 440 nm (ascribed to *cis*-Azo-POSS) slightly increased with the increase of irradiation time. It suggested that the photoisomerization of Azo-POSS component in GO-POSS took place, resulting in the disassembly and separation of Azo-POSS from GO-CD. To further confirm light-responsive properties and visualize assembly/disassembly behaviors of GO-POSS, TEM was carried out and the images of GO, GO-CD and GO-POSS under different condition were compared in detail. As presented in Fig.2, the prepared GO was fully exfoliated in water and exhibited characteristic wrinkled flake-like topology. After β-CD was covalently bonded into GO, a large amount of small grey spots attributable to CD aggregates appeared and dispersed uniformly on the surface of GO sheet, which favored the following host-guest inclusion of Azo-POSS. When adding Azo-POSS into GO-CD under visible illumination, it was found that the formed GO-POSS showed dense layers and some small dark spots above GO sheet. This was because under visible light Azo-POSS molecules were strongly trapped in GO-CD through host-guest inclusion and uniformly coated on the surface of GO sheet. No obvious dark POSS aggregates were observed. In contrast, when UV light was applied to irradiate the GO-POSS for 20 min, a large number of dark POSS aggregates appeared. It implied that under UV irradiation Azo-POSS components in GO-POSS gradually disassembled from GO-CD due to the photo-isomerization and could move freely to form POSS aggregates. If GO-POSS was again illuminated under sun light for 24 h, dark POSS aggregates disappeared and the morphology of GO-POSS returned to that of before UV irradiation, which suggested host-guest inclusion took place again and further verified photo-responsive reversible assembly/disassembly behavior of GO-POSS. Moreover, when GO-POSS was photo-irradiated by UV followed by CH$_2$Cl$_2$ extraction, no POSS aggregates were found in GO surface and similar morphology with GO-CD was observed. This was because Azo-POSS molecules disassembled under UV were thoroughly removed through following organic solution extraction. All the results from UV-Vis and TEM proved that novel GO-POSS nanocomposites prepared based on host-guest chemistry possessed remarkable photo-responsive properties under irradiation.

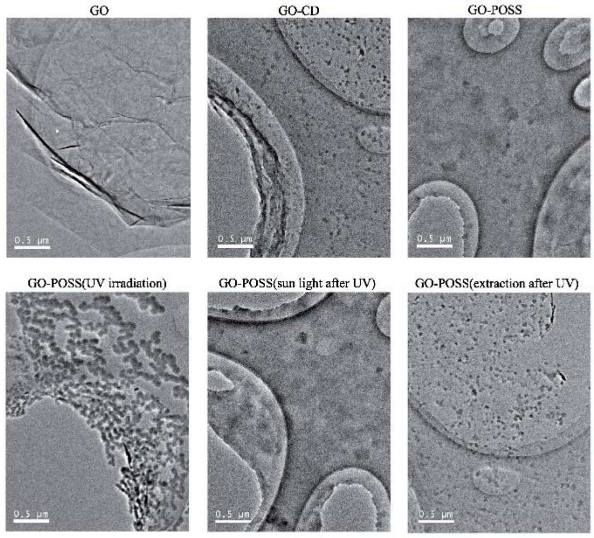


Fig.2 TEM images of GO, GO-CD and GO-POSS under different irradiation conditions.

The dispersion stability of light-responsive GO-POSS in water and organic solvents was compared in Fig. S5 in Supporting information. As we know, GO has good dispersity in water because of large number of oxygen-containing groups on the surface of graphene sheet. The strong hydrogen bonds between GO and H_2O have efficiently prevented the aggregation of graphene sheet. Compared with light yellow GO solution, GO-CD solution became brown dark. According to above FT-IR analysis, attachment of β-CD into GO consumed many oxygen-containing groups, restored graphite lattice and reduced GO to some extent. Although oxygen-containing groups decreased, the presence of large number of hydrophilic *β*-CD molecules (26.7 wt%) on the surface of graphene sheet made GO-CD disperse well in water and kept dispersion stable after 24 h. To our delight, when hydrophobic Azo-POSS was incorporated into the surface of graphene sheet, GO-POSS still retained excellent dispersity and exhibited impressive stability in water even placing for 24 h. It was deduced that hydrophibic Azo-POSS were completely trapped in hydrophilic β-CD moiety and had little adverse effect on dispersity of GO-POSS. Moreover, not only in water, GO-POSS also dispersed well and kept homogeneous in many organic solvents.

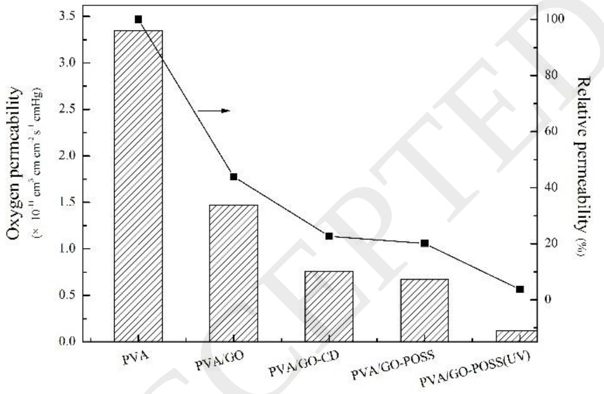


Fig.3 Oxygen permeability coefficient and relative permeability of PVA-coated films containing GO, GO-CD and GO-POSS.

Oxygen barrier polymer materials have great demand in modern electronic and packaging fields. Especially for intelligent packaging, the ideal material was that oxygen transmission rate and permeability could be controlled and adjusted depending on external circumstances. Both GO and POSS are regarded as good gas impermeable nanofillers and have already been used as key components to improve the gas barrier properties of polymer packaging films [22-25]. So it was anticipated that the light-responsive GO-POSS composed of GO and POSS would exert the synergistic effect of GO and POSS and could have some unique impact on gas transmission rate of materials under irradiation. Due to excellent dispersity of GO-POSS in water, we introduced GO-POSS nanocomposite into PVA matrix through solution blending and then casted on commercial PET films to investigate the effect of GO-POSS under different irradiation conditions on the oxygen permeability of packaging films. Fig.3 presented the preliminary results of oxygen barrier properties of PVA-coated films. It was obvious that incorporation of as-prepared GO-POSS dramatically decreased the oxygen transmission rate of films. The oxygen permeability coefficient of PVA/GO-POSS coated film was only 0.67×10^{-11} $cm^3\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$ and just one-fifth of pristine PVA-coated film, while the values for PVA/GO and PVA/GO-CD coated films were 1.47 and 0.76×10^{-11} $cm^3\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$, respectively. This demonstrated that on one hand GO-derived nanofillers were efficient gas barrier materials and could greatly decreased oxygen transmission rate of polymer film, while on the other hand even compared with hot nanofiller GO, as-prepared GO-POSS was still the most efficient nanofiller and exhibited impressive oxygen barrier behaviors. We think the main reason was the coexistence of two efficient gas barrier nano-components (GO and POSS) in one supramolecular assembly. The presence of impermeable nanofillers prolonged gas diffusion path and decreased the gas permeability. Moreover, to our delight, undergoing UV irradiation before blending GO-POSS with PVA solution, the oxygen permeability coefficient of PVA/GO-POSS coated film was further decreased 82.2% compared with films without UV irradiation and almost improved oxygen barrier property 30 times than pristine PVA-coated film, which suggested that incorporation of as-prepared light-responsive GO-POSS could endow conventional packaging film with attractive ability of dynamically controlling oxygen transmission rate of polymer films, which was crucial requirement for future intelligent packaging. The mechanism behind will be specifically investigated and discussed in our next future paper.

In conclusion, an easy and convenient strategy to design and prepare novel light-responsive GO-POSS nanocomposites was proposed based on host-guest chemisty. UV-vis spectroscopy and TEM clearly indicated that depending on the reversible inclusion/exclusion of GO-CD and Azo-POSS, the prepared GO-POSS exhibited remarkable supramolecular assembly/disassembly behavior upon UV/vis irradiation. Due to the good dispersity in water and many other solvents, GO-POSS could be easily incorporated into convention polymer films and had significant impact on oxygen barrier properties of materials. Under visible illumination, the oxygen permeability coefficient of PVA/GO-POSS coated film was only 0.67×10^{-11} $cm^3\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$ and just one-fifth of pristine PVA-coated film, while upon UV irradiation before blending, the oxygen permeability coefficient of PVA/GO-POSS coated film could be further decreased 82.2% down to 0.12×10^{-11} $cm^3\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$. This kind of novel light-responsive GO-POSS would endow conventional packaging film with attractive ability of dynamically controlling oxygen transmission rate and have promising applications in future intelligent packaging.

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