Let a Hundred Polymers Bloom: Tunable Wetting of Photografted Polymer-Carbon Nitride Surfaces

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ABSTRACT: Sunlight is widely used by plants to produce chemical energy fundamental for all life, a process that also serves as an inspiration for science. Recently, light-harvesting semiconductor materials, here, carbon nitrides, have been widely used in photochemistry to catalyze reactions under visible light illumination. We exploited photoactive carbon nitride thin films as a metal-free platform for one-step photografting from polymers on the surface. Here, we observe photoswitchable wetting properties of polystyrene-grafted carbon nitride, which are independent of any classical photoswitchable groups. Dense and thick polymer brush formation with a tunable thickness (up to 700 nm) was obtained, allowing for tailor surface properties. Furthermore, exploiting the reciprocal insolubility of water–dimethylacrylamide and pentane–styrene solutions, we provide a general method for the synthesis of centimeter-scale carbon nitride-based Janus asymmetric films. It is thought that the simple experimental design based on cheap and common chemicals provides a novel dimension of carbon nitride materials with advanced surface properties.

INTRODUCTION

The increasing consideration of sustainability and the search for metal-free catalysts led to the rediscovery of polymeric graphitic carbon nitride (pCN), a metal-free semiconductor absorbing in the visible light range. Such photocatalysts are usually prepared via thermal condensation of abundant, nitrogen-rich precursors, such as urea or melamine, which leads to a polymerized structure with repeating tri-s-triazine units, while photophysical properties of pCN can be easily tuned via altering precursors or postmodification techniques. As a powder with strong π-π stacking and slight negative surface charge, pCN is applied as a heterogeneous photocatalyst in a variety of fields such as CO₂ reduction, water splitting, or photovoltaics, only to name a few. Well-defined films of pCN could be particularly interesting for broadening the applications; however, film formation formerly relied on vapor techniques, such as vapor deposition polymerization, thermal vapor condensation and microcontact printing, or spray-coating of organo-modified pCN, both leading in most cases to non-self-supporting and highly defective materials. The formation of well-defined, defect-free pCN thin films via the chemical vapor deposition method (CVD) was just recently described, for instance with melamine as a precursor. The thickness-tunable and highly homogeneous CVD method paves the way to employ pCN thin film structures in various applications. Among them, pCN thin films can be used as a metal-free heterogeneous photocatalytic surface for radical polymerization reactions. The generation of polymer brushes grafted from a flat interface is a powerful approach to tailor the chemical and physical surface properties. In this context, very recently, Grill and Hecht have launched a quest for new materials and new approaches toward covalent on-surface polymerization that can be met by pCN thin films. Covalent on-surface polymerization is of great interest for miniaturized devices for electronics and optoelectronics, but also lab-on-a-chip applications.

The controlled growth of polymer brushes grafted from a substrate is a key step to developing smart surfaces, i.e., surfaces that respond to an external stimulus, such as light. For this purpose, it is necessary to find the right substrate–polymer system. Stimuli responsive materials modify their surface free energy or morphology, and surface properties like wettability change accordingly. Various methods have been exploited to control surface wettability, including electric potential, temperature, mechanical stress, pH, and light irradiation.
instance, photoresponsive surfaces that change surface wettability with light find application as antifogging, self-cleaning, and lubricating films, but also in microfluidic optical pumps and valves free of moving parts.26−28 Photosensitive semiconductors such as ZnO, TiO2, V2O5, SnO2, and other inorganic oxides have shown UV-photoinduced hydrophilicity.29 On the other hand, photoswitchable wettability in organic materials relies mostly on the use of photoinduced isomerization of dyes, such as azobenzenes and spiropyranes.26,30,31 In these cases, functional polymers are chemically or physically immobilized on the surface of different materials.32 Along those lines, Zong and co-workers have recently prepared cotton fabrics dip-coated with a random copolymer containing fluorine and azobenzene functional groups. Upon illumination with UV and Vis light, the cotton fabric shifts from superhydrophilic to superhydrophobic, respectively, due to the UV-triggered isomerization of the azobenzenes groups.30 As another example, Wang et al. prepared a patterned surface via atom transfer radical polymerization of a spiropyran monomer on silicon substrate in which, upon illumination with UV and visible light, the contact angle (CA) shifts from 138.8° to 42.7°.33 However, in all cases, the light-triggered surface properties change requires the presence of photoisomerizable groups on the surface and rather complex chemistry.

Herein, we present a simple and innovative method for one-step photografting of dielectric polymers onto pCN thin films that allows to control surface properties and shows photo-
switchable wettability. Eventually, the pCN thin films were used as photoinitiators for radical polymerization reactions, under visible light illumination, for one-step photografting from with common monomers (Figure 1a). This process allows precise control of surface properties such as the contact angle. Moreover, to our surprise, polystyrene films showed photo-switchable wettability under UV illumination without any photoswitchable group, indicating selective charge transport through polystyrene, a property usually not attributed to this most simple mass polymer. Exploiting the simple method to produce covalently polymer-grafted-pCN layers to pCN films positioned at reciprocally insoluble solvent–solvent interfaces, we have realized amphiphilic pCN-based thin films. In these experiments, we prepared free-standing large area Janus sheets by one-pot grafting of hydrophilic and hydrophobic polymers at the interface of water/pentane monomer solutions (Figure 1b).

RESULTS AND DISCUSSION

The synthesis of pCN thin films using melamine as a single-source precursor was recently described.19 The as-prepared thin films are highly homogeneous over large areas and are used as substrates for polymer brushes grown using the visible photografting method. Therefore, we chose a set of vinyl monomers, such as styrene and dimethylacrylamide, as commonly available monomers for radical polymerization. The synthetic method requires coating the pCN thin film surface with a vinyl monomer and keeping it under visible illumination for 12 h, while the monomer is re-fed onto the surface every 4 h.

To prove that polymer brushes were grown and covalently grafted from the pCN thin film, the as-prepared polymer-grafted pCN samples were immersed in a suitable solvent for the grown polymer brushes, e.g., water for poly(dimethylacrylamide) and tetrahydrofuran for poly(styrene), to remove ungrafted polymers and unreacted monomer residues. Subsequently, the polymer-grafted pCN bilayers were analyzed by Fourier-transform infrared spectroscopy (FT-IR; Figure S1), and the thickness was evaluated by step-height atomic force microscopy (AFM; Figure 2a–c). The FT-IR spectra reveal in all cases the characteristic vibration modes of the respective polymers, different from the bare pCN thin films, especially in the fingerprint region (Figure S1a). In particular, for the pCN-poly(styrene) (pCN-PS), the spectrum reveals very well-defined peaks at 3034 and 2926 cm\(^{-1}\) attributed to aromatic ring C–H and aliphatic –CH\(_2\)– stretching modes, respectively, and the out-of-plane aromatic –C–H bending at 757 and 698 cm\(^{-1}\), as well as the typical pCN heptazine breathing mode at 810 cm\(^{-1}\) (Figure S1b).\(^{19,34}\) The AFM step-height measurements of peeled-off samples deposited on a glass slide reveal that the bare pCN thin film has a thickness of about 330 nm, which increases above 1000 nm after surface photopolymerization for pCN-PS and pCN-PDMA (Figure 2a–c; details of the step height are reported in the insets and in Figure S2). As expected, the grafted polymers do not significantly affect the optical absorption spectrum of pCN thin films, since they are highly transparent above the 350 nm wavelength (Figure S3). The sample surface was further investigated by means of scanning electron microscopy (SEM; Figure 2d–f) to evaluate the morphology of the bare pCN and the polymer brushes. Analysis of the bare pCN thin film deposited on glass (Figure 1d) shows that the deposition occurs homogeneously and pinhole-free over large surfaces. Watching closely, the film reveals a microstructure that we attribute to different thermal expansion coefficients of pCN and glass, causing a different shrinking rate between the film and the substrate during cooling from 550 °C. The surface morphology appears very different after the light-induced grafting of PS (Figure 2e) and PDMA (Figure 2f). With regard to PS-grafted-pCN, the surface looks homogeneously covered and crack-free after the washing step. The small droplet patches present on the surface we attribute to minor impurities of free polystyrene chains being expelled from the grafts (Figure 2e). The PDMA-grafted-pCN surface (Figure 2f) is “skin-like” and more rough but nevertheless tight and in the long range homogeneous.

Modifying surfaces of pCN thin films via grafting with different polymers will modify the surface wettability according to the surface energy of the polymers. For this reason, we prepared surfaces modified with pCN-poly(allylamine) (pCN-PAAA), pCN-poly(methyl methacrylate) (pCN-PMA), pCN-poly(N-isopropylacrylamide) (pCN-PNIPAM), and pCN-poly(N-vinylimidazole) (pCN-PVI), in addition to the already mentioned pCN-PS and pCN-PDMA. The surface morphology was determined also for the systems pCN-PAA and pCN-PDMA, showing features similar to the previous cases (Figure S4). The bare pCN thin film has a water contact angle (WCA) of 52.0°, which by modification is tuned in the range of 10.9° for pCN-PDMA (hydrophilic) up to 132.3° for pCN-PS (hydrophobic; Figure 3a). This confirms the high flexibility of the proposed method, allowing for growing a wide range of polymer brushes from vinylic monomers and by that control the surface properties.

The as-prepared samples’ water wettability ranking was determined using the sessile drop method: pCN-PDMA < pCN-PAAA < pCN-PVI < pCN-PNIPAM < pCN < pCN-PN < pCN-PVI < pCN-PS (listed in Figure 3b, WCA images in Figure 3).

![Figure 3. Tunable contact angle of pCN-polymer-grafted surfaces. (a) Water contact angles (WCA) of pure pCN film, pCN-PDMA, and pCN-PAA; (b) list of the WCA obtained for different pCN-grafted surfaces, ranked from the most wettable to the least wettable. Scale bar 1 mm.](https://dx.doi.org/10.1021/acs.chemmater.6b00796)
Yet, the density of grafting and chain growth is often low. Usually, polymer brushes grafted on surfaces are in the efficient growth can be attributed to the high photoactivity of pCN films that act as initiators for the growth of the dielectric polymer: under light illumination the initiating species, i.e., electrons and holes, are formed in the semiconductor and move to surface sites of the pCN. We assume that the first anion and cation radicals very effectively clean the polymerization medium, while the polymerization occurs at rather low radical concentrations and—by geometric constraints of the brush—without the ability to terminate in a simple fashion. The initiating radicals are formed on the surface, and directional growth continues along the final film thickness in a way providing “clean” polymer growth. In order to confirm our assumptions, we have performed the polymerization on the surface in the presence of a RAFT agent (2-cyano-2-propyl benzodithioate), expecting that the resulting chain length is reduced in the presence of competing species. Indeed, AFM confirms only a minor change in surface thickness of the PS film, growing only about 50 nm (Figure S8), supporting the proposed mechanism. Initiating radicals are taken away from the pCN surface by transfer agents, such as the RAFT agent, in a similar way to that previously observed also for dispersed bulk pCN, resulting in a smaller PS brush size. Therefore, we attribute the radial polymerization governed by holes, as previously reported in our investigations considering carbon nitrides for polymer syntheses.

To support a quasi-living character of the radical polymerization on the surface environment, we analyzed the role of polymerization time, i.e., the illumination time of the pCN film coated with the vinyl monomer, on the PS brush thickness, at 1, 2, and 4 h of illumination. As expected, the polymer brush thickness increases with the polymerization time, and a similar trend is followed also by the WCA (Figure 4a). After 1 h, the PS-grafted film thickness grows only a few nanometers, causing only a minor change in the pCN contact angle. Between 2 and 4 h, the PS-grafted brush thickness increases dramatically from about 50 to 380 nm, accelerated by the increased local viscosity at higher monomer conversion. The WCA increases accordingly, from 75.4 to 90.0°, thus providing another method to control the surface properties over a wide range, simply by the polymerization time given to the styrene on the pCN surface (Figure S9).

Furthermore, pCN thin films have been used as light-powered membranes for ion transport. The ion transport...
mechanism was investigated and attributed to the change in surface charge of pCN, allowing dissolved ions to selectively cross the membrane in the light direction. Inspired from the light-induced generation of surface charges, we have investigated the effect of UV light illumination on the WCA of the pCN-PS system. As polystyrene is a dielectric material, we expected the charges to “reach through” the PS layer, accounting for its thickness according to the Coulomb law. When exposed to UV illumination, the pCN-PS wettability increases considerably after only 20 s, as shown by the drop of the WCA from 132.3° to 75.0°; switching off the UV light leads to recovery of the hydrophobic properties in about 3 min (Figure 4b), and it can be seen even by the naked eye (Video S1). To the best of our knowledge, this is the first time that photoswitchable wettability is shown on PS, which we attribute to the aromatic structure of PS grown directly from the pCN surface. On the one hand, to our surprise, similar experiments to the aromatic structure of PS grown directly from the pCN surface. On the other hand, the effect of the covalent binding of PS on the pCN surface was investigated comparing the results of pCN-PS with a sample obtained by spin-coating commercial PS on a pCN film surface, and thus without covalent bonds between pCN and PS. As previously mentioned, the spin-coated PS film on pCN WCA increases to 88.8° (Figure S6), in good agreement with previous results on PS thin films, however, significantly lower with respect to pCN-PS.49 The high WCA obtained for pCN-PS obtained by photografting, with respect to the PS spin-coated sample, supports our previous assumption that the grafted polymer brushes grow in a more elongated, stretched conformation. In this regard, Walker and Li have shown that increasing the polymer radius of gyration increases the hydrophobicity.49 Therefore, we can assume that photografted PS brushes on pCN have a higher gyration radius; i.e., the polymer growth leads to a more elongated conformation, causing higher surface hydrophobicity. Moreover, in this case, no change in WCA was observed upon UV light illumination (Video S4), confirming once more that the change in WCA arises only when covalent bonds between PS and pCN are formed. All these observations exclude a simple interface charging and action via Coulomb law, further supported by measuring the contact angle change under UV illumination with salty water of pCN-PS: as expected, no change in the contact angle occurs due to the extra ions passivating the interfacial charges (Video S5).

Therefore, our only possible explanation is that covalent grafting of aromatic polymer brushes on the pCN surface improves charge transfer over the interface, leaving the polystyrene temporarily oxidized, carrying a radical cation on the aromatic rings. This charge transfer builds up slowly (20 s) and recombines even more slowly (180 s), all time scales which are well above ordinary excited state dynamics. In this model, bare pCN recombines too quickly, while all non-aromatic polymers cannot stabilize the radical cation and are thereby not oxidized.49 In other words, the covalent binding of an otherwise insulating plastic layer, such as PS, on our photoactive semiconductor results in directional charge separation and in temporary changes of surface properties with a memory in the minute region.

In the previous part, we exploited the surface photocactivity of pCN films, and we showed different methods to control the surface properties, i.e., by grafting different polymers, polymerization times, and for pCN-PS also reversible light-induced wettability. However, the pCN thin films deposited on glass slides can be peeled from the substrate after soaking in water. Eventually, these films possess two surfaces available for photografting from polymers, allowing for creating asymmetrical superstructures with opposite properties on the two surfaces, e.g., Janus surfaces. To prepare pCN-based large area Janus surfaces, with two different polymer layers, the peeled-off pCN thin film was placed at the interface between two reciprocally insoluble liquids containing a high monomer concentration, e.g., dimethylacrylamide in water (50 vol %) and styrene in pentane (50 vol %). Similarly to the previous case, the grafting of polymer brushes onto the pCN thin film is achieved by illuminating the pCN film at the interface for 24 h (Figure 1b). The Janus superstructure, constituted of poly-(dimethylacrylamide)-pCN-polystyrene (PDMA-pCN-PS), was cut and folded to show both surfaces and the pCN edge, the PDMA on top and the PS below, respectively, and analyzed by SEM (Figure 5a,b). The sharp edge of the folded layer localizes the stiff pCN film, as highlighted also by energy dispersive X-ray spectroscopy (EDX; Figure S10) where a high intensity signal of the nitrogen element is shown. In the SEM images both sides look very homogeneous but with different morphologies at the two surfaces, and very different from the bare pCN one, with wrinkles, waves, and droplets, typical of polymer layers. This confirms that the method is effective to obtain double surface grafting with different monomers, and therefore the 2D-Janus film over large areas even around 10 cm² (Figure S11).

Janus pCN sheets retain their high photoluminescence (Figure 5c) when subjected to UV illumination. We have investigated immersion of Janus sheets in water under UV light. Depending on the hydrophilic or hydrophobic side, Janus pCN sheets fold on the hydrophilic side (PDMA) and open again when contacting water (Video S6). The synthesis of centimeter-sized Janus pCN films, in this facile, one-step synthesis utilizing the interface-based, asymmetric, two-phase grafting polymerization, will be of great interest to develop simple sensors and micromotors with commonly available and cheap precursors51,52.

**CONCLUSION**

In summary, we presented a generic and simple method to grow different dielectric polymer brushes from vinyl-containing monomers on pCN thin films, via a one-pot photoinitiated polymer–polymer grafting method with visible light. The surface properties of pCN films can be conveniently tailored by choosing a different monomer and/or with a different polymerization time, over a wide range (from WCA of 10.9°
up to 132.3°). A very thick and dense polymer brush formation (up to 700 nm) was grown directly on the pCN surface, which indicates an efficient surface initiated photopolymerization, poor in radical recombination. Unexpectedly, the polystyrene-grafted pCN shows also UV light-responsive surface wettability, where UV light illumination grants temporary hydrophilicity, and the initial hydrophobicity is recovered, with switching times in the seconds to minute range. To the best of our knowledge, this is the first time that photoswitchable surface wettability is reported for polystyrene, without photosomizerable groups obtained by the visible photografting method directly at the pCN surface. Introducing simple methodologies to engineer surface wettability by UV light will set the base for tailoring surface properties of great interest for future smart devices, which may possess different properties with respect to the single components.

In a second set of experiments, we exploited the pCN films to generate centimeter scale Janus pCN-based large area surfaces. We believe such components and effects might allow localized solvent transport, smart micromachines, and photocatalytic films responding to different environments.

■ EXPERIMENTAL SECTION

Materials. All materials were used as purchased unless noted otherwise: 1-vinylimidazole (VI, 99%, TCI), 2-cyano-2-propyl benzothioate (97%, Sigma-Aldrich), allylamine (AA, 99%, TCI), melamine (99%, Sigma-Aldrich), methyl methacrylate (MMA, 99%, Sigma-Aldrich), N-isopropylacrylamide (NIPAM, 97%, Sigma-Aldrich), N,N-dimethylacrylamide (DMA, 99%, Sigma-Aldrich), pentane (99%, Honeywell-Fluka), styrene (99%, Sigma-Aldrich), poly(styrene) (Polymer Source Inc. Mn = 40000, polydispersity = 1.05), tetrahydrofuran (THF, 99%, Sigma-Aldrich), and toluene (99.5%, Sigma-Aldrich). 50 W LED chips (365 nm UV light and 420 nm visible light) were connected to a self-made circuit and cooling system. A 3100 Atomic Force Microscope from Veeco Instruments in the tapping mode and elaborated with NanoScope Analysis 1.9 software. SEM and EDX imaging was performed after Au/Pd sputtering of the nonconductive sample in a LEO 1550-Gemini system (acceleration voltage: 2 to 10 kV) equipped with an Oxford Instruments X-MAX 80 mm2 detector. Sessile drop contact angles of water on the coatings were measured at room temperature about 10 s after placing the drop on the surface with a DSA 10 video contact angle measuring system G10 (Krüss, Germany), and data evaluation was done with DSA version 1.80.02 software.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01798.

Video S1: Water contact angle shift of pCN-PS under UV illumination (MP4)
Video S2: Water contact angle of bare pCN under UV illumination (MP4)
Video S3: Water contact angle of pCN-PMMA under UV illumination (MP4)
Video S4: Water contact angle of pCN-spin coated PS under UV illumination (MP4)
Video S5: Contact angle of pCN-PS with salty water under UV illumination (MP4)
Video S6: Janus film bending and folding and opening at contact with water (MP4)
Additional films characterization (FTIR, AFM, UV–vis absorption, SEM and EDX), TGA, WCA, setup for preparation of Janus films (PDF)

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Author Contributions

These authors contributed equally. P.G. and B.K. conceived the idea. P.G. and R.R. prepared the pCN thin films. P.G. and made the absorbance, FTIR, and SEM measurements. B.K. made the light-induced surface polymerization. B.K. and J.Z. made the contact angle measurements. P.G., B.K., and M.A. wrote the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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