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# Gram-Scale Synthesis of Aligned C<sub>3</sub>N<sub>4</sub>-Polypyrrole Heterojuction Aerogel with Tunable Band Structures as an Efficient Visible and Near Infrared Light -Driven Metal-Free Photocatalyst

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The assembly of aligned porous materials from simple building blocks is of widespread interest for engineering materials with enhanced and synergistic properties. To date, however, how to develop 3D heterojuction aerogels with aligned porosity based on 2D semiconductor materials and 1D conducting polymer for solar energy conversion in the visible and near-infrared (NIR) light region still remains a significant challenge. Here a new class of gram-scale 3D aligned heterojuction aerogels of polypyrrole (PPy)/C<sub>3</sub>N<sub>4</sub> nanosheets (NSs) were designed and synthesized by directional freezing of polypyrrole (PPy)/polyvinyl alcohol (PVA) and C<sub>3</sub>N<sub>4</sub> NSs aqueous suspension. The synthesis of aligned C<sub>3</sub>N<sub>4</sub>-PPy heterojuction aerogel can be achieved at large scale. The formed aerogel expresses stable and uniform dispersion of the two building blocks, long-range channel aligned structures along the whole monolithic sample, and additional special complementary optical properties between PPy and C<sub>3</sub>N<sub>4</sub> NSs. Based on the above unique structure and optical property, this novel metal-free heterojunction aerogel exhibits excellent photocatalytic activity and long-term stability for direct arylation of heteroaromatics under visible and near infrared (NIR) light irradiation at room temperature, far exceeding those of the singleand two-component systems. Our work therefore not only provides a new approach to obtain aligned heterojuction aerogels based on metal free semiconductors but also paves a way to develop gram-scale aerogel as a new type of highly efficient visible and NIR light induced heterogeneous photocatalyst.

### 1. Introduction

The assembly of functional materials with aligned aerogels from simple building blocks has gained extensive attention in applications such as electrochemical energy storage, solid phase supports for catalysis, membrane separation, bio-engineering, etc..<sup>1-4</sup> Especially, aligned channel structures in porous materials are fundamentally important for gaining a better understanding of self-assembly processes in biological systems and mimicking natural aligned tissues. Directional freezing-driven 0D nanoparticles (NPs) assembly has been successfully applied to align the building blocks in the form of 2D oriented flat patterns or further 3D porous structures.<sup>5-7</sup> Recently, composite structures of various kinds of array, such as polymer-inorganic nanocomposites,<sup>8</sup> porous microfibres and biaxially aligned networks,<sup>9</sup> aligned gold microwires and microwire networks,<sup>6</sup> were synthesized using this simple technique. However,

such technique has little use to construct aligned heterostructures based on 2D materials with optical activity and conducting polymer which are of considerable interest in photocatalysis.

In principle, multifunctional 3D architectures based on 2D materials, especially graphene and its analogues, provide new possibilities in electronics, catalysis, and energy conversion and storage.10,11 The chemical activity of such architectures and their hybrids exhibits unprecedented flexibility, which is dependent on the ability to control the electronic states of the crystal surface by changing the work function,12,13 the formation of monolithic structures based on different 2D crystals, and the construction of nanoreactors in the space among different 2D crystals.<sup>14</sup> As a widely investigated 2D catalyst, it was found that graphitic  $C_3N_4$  (g- $C_3N_4$ ) presents promise in photo- and electro-catalysis as well as conventional heterogeneous catalysis, due to its unique electronic structure and rich Lewis basic functions.<sup>15</sup> Generally, combining g-C<sub>3</sub>N<sub>4</sub> with other materials can further enhance the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> owing to the synergistic effect of different active sites or the increase of the active sites.16 g-C3N4 with the band gap of ~2.7 eV shows an intrinsic semiconductor-like absorption in the short-wavelength region of the visible spectrum. In addition, the most g-C<sub>3</sub>N<sub>4</sub> based catalysts were found to be very efficient under visible light, but not under near-infrared (NIR)-light.<sup>17</sup> The ability to

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develop aligned heterostructures based on g-C<sub>3</sub>N<sub>4</sub> for photocatalysis under the visible-NIR light provides new opportunities.

Recently, intergating semiconductor nanomaterials with a conducting polymer (CPy) has been considered to be an effective method to promote charge carrier separation and improve visible-light activity.<sup>18, 19</sup> Among well known  $\pi$ -conjugated conducting polymers, polypyrrole (PPy) has attracted much attention because of its easy preparation, high electrical conductivity and large surface area.<sup>20-22</sup> Tremendous efforts have been devoted to create heterojunction materials containing PPy layer and inorganic layer, polymer intercalation in 2D nanomaterials, and assembly 2D nanomaterials on multi-dimensional polymers.<sup>23-25</sup> Despite numerous efforts, there is still only limited information on the synthesis of aligned heterostructures based on g-C<sub>3</sub>N<sub>4</sub> and PPy.

On the other hand, arylated heteroarenes are widely used in drugs.26 biomedical applications, peptide mimetics and Photocatalysis has provided a valuable alternative to the direct arylation of heteroarenes by C-H bond activation without requiring preactivation of the heteroarenes.<sup>27-29</sup> Nowadays, direct arylation of heteroaromatics generally use metal nanomaterials/metal complexes as photoredox catalysts. However, metallic catalysts suffer from corrosion or aggregation in photocatalytic reaction so as to limit their practical applications. Elegantly, König reported that Eosin Y can be directly used as homogeneous photoredox catalyst under visible light,<sup>30</sup> while they have not considered the reusability. Therefore, inexpensive metal-free alternative heterogeneous photocatalysts for rapid and direct arylation of heteroaromatics under sufficient irradiation are desirable.

In this study, we demonstrate that C<sub>3</sub>N<sub>4</sub> nanosheets (NSs) can be assembled with conductor polymer, and thereby preparing aligned heterojuction aerogel by directional freezing of polypyrrole (PPy)/polyvinyl alcohol (PVA) composites and C<sub>3</sub>N<sub>4</sub> NSs. The resultant heterojunction aerogel (denote as CNPVPy) has several remarkable features, including (i) long-range channel aligned structures along the whole monolithic sample, enabling mass transport and efficiently contact between the reaction substrates and catalysts, (ii) broad absorption from UV to NIR-range, (iii) high stability in solution, (iv) efficient charge separation, and (v) tunable band structure by changing the mass ratio of C<sub>3</sub>N<sub>4</sub> and PPy. We demonstrate that CNPVPy macrosturctures are highly efficient under visible as well as NIR light for the direct arylation of heteroaromatics at 25 °C. Interestingly, we find that CNPVPy heterojuction aerogel exhibits high photocatalytic activity, far exceeding those of the single- and mixed-component systems, as a result of the interaction between C<sub>3</sub>N<sub>4</sub> and PPy to form p-n junction thus to cause the enhanced charge separation. Furthermore, this photocatalyst is very stable in repeated cycling. To the best of our knowledge, this finding constituted the first experimental evidence of the photocatalytic activity of aligned metal-free heterojuction aerogel under visible and NIR light for synthesis of fine chemicals.

#### 2. Experimental

#### 2.1. Chemicals

Pyrrole, urea, and catalytic substrate reagents were purchased from Alfa Aesar. Polyvinyl alcohol (PVA, 99% hydrolyzed, MW = 170000) and urea were obtained from Tianjin Med. All chemicals

were used without further purification. The  $H_2O$  during the whole experimental process was deionized  $H_2O$ . DOI: 10.1039/C7TA08389K

#### 2.2. Measurements

The morphology of the samples was investigated by field-emission scanning electron microscope (FE-SEM, FEI, Sirion 200) and transmission electron microscope (TEM, JEOL, JEM-2100, 200kV). X-ray powder diffraction (XRD) patterns of the nanomaterials were recorded on a Bruker AXS D8-Advanced diffractometer with Cu Ka radiation ( $\lambda = 1.5418$ Å). N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K after heating the samples at 120 °C for 8 h to remove any moisture and solvent molecules presented in the pores with Micromeritics TriStar II 3020 analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S<sub>BET</sub>). By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5702 multifunctional spectrometer using Al Ka radiation. The XPS profiles were fitted by the Gaussian-Lorentzian method after background subtraction using Shirley's method.<sup>32</sup> Raman spectra were collected using a confocal microprobe Raman system (Renishaw, RM2000). FT-IR spectra were recorded on a Nicolet FT-170SX spectrometer. UV-vis-NIR diffuse reflectance spectra were carried out on an Agilent Cary 5000 UV-Vis-NIR Spectrophotometer. Pd contents are determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian VISTA-MPX). Photocalysis was performed using a white LED lamp (30 W). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectrums were gathered on a JEOL ESC 400M instrument. The morphology of the samples was investigated by field-emission scanning electron microscope (FE-SEM, FEI, Sirion 200) and transmission electron microscope (TEM, JEOL, JEM-2100, 200kV). X-ray powder diffraction (XRD) patterns of the nanomaterials were recorded on a Bruker AXS D8-Advanced diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$ Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5702 multifunctional spectrometer using Al Ka radiation. The XPS profiles were fitted by the Gaussian-Lorentzian method after background subtraction using Shirley's method. Raman spectra were collected using a confocal microprobe Raman system (Renishaw, RM2000). FT-IR spectra were recorded on a Nicolet FT-170SX spectrometer. UV-vis-NIR diffuse reflectance spectra were carried out on an Agilent Cary 5000 UV-Vis-NIR Spectrophotometer. Photocalysis was performed using a Xenon lamp (HSX-F300). 1H-NMR and <sup>13</sup>C-NMR spectrums were gathered on a JEOL ESC 400M instrument.

#### 2.3. Synthesis of polypyrrole polyvinyl alcohol nanocomposites (PPy/PVA NCs)

PVA (3 g) was dissolved in H<sub>2</sub>O (60 ml) at 100 °C, and then cooled to room temperature. FeCl<sub>3</sub>·6H<sub>2</sub>O (3.78 g) was added into the aqueous PVA solution. After 1 h stirring, pyrrole (420  $\mu$ l) was introduced dropwise into the PVA/FeCl<sub>3</sub> aqueous solution at 0 °C, and equilibrated for 4 h. After completion of polymerization, the resulting dark green seriflux was purified through the dialysis (MWCO = 300 kDa) in H<sub>2</sub>O for 1 week to remove excess FeCl<sub>3</sub>, oligomers, and contaminants. The final dark green colloidal dispersion (PPy/PVA, 24 mg/mL) was collected as stock solution.

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#### 2.4. Formation of aligned CNPVPy heterojuction aerogels

Different volumes of  $C_3N_4$  suspension synthesized according to previous work with modification<sup>31</sup> were added into PPy/PVA suspension (1 ml), then additional H<sub>2</sub>O was added until 3 ml volum, and the mixtures were ultrasonicated for 30 min at r.t.. To produce aligned self-assembly composites (CNPVPy) between  $C_3N_4$  and PPy/PVA, the mixtures were slowly put into liquid nitrogen, and then freeze-dried using a Heto Lyolab 3000 freeze-dryer. (We denoted the final architecture CNPVPyx, x is the ratio of PPy/PVA weight to  $C_3N_4$  weight)

To form orderly aligned self-assembly composites (CNPVPx) between  $C_3N_4$  and PVA, the same proportion of materials were used except using PVA solution to replace PPy/PVA suspension.

#### 2.5. Synthesis of aryldiazonium salts

The aryldiazonium salts were prepared according to the literature with slight modification.<sup>27</sup> The corresponding aniline (0.02 mol) was dissolved in a mixture of ultrapure water (8 ml) and 50% fluoroboric acid (7 ml). After the temperature fell below zero, 3 mL sodium nitrite solution (1.38 g) was added slowly. The mixture was stirred for 40 minutes in ice bath, and the resulting precipitate was collected and washed several times with CH<sub>2</sub>Cl<sub>2</sub>. The resulting solid was recrystallized by acetone and CH<sub>2</sub>Cl<sub>2</sub>.

# 2.6. General procedure for direct arylation of heteroaromatics catalyzed by CNPVPy

CNPVPy (5 mg), heteroaromatics **1** (1 ml), aryldiazonium tetrafluoroborate **2** (0.1 mmol), and EtOH (2 ml) were added into a 10 ml glass tube. The reactor was evacuated and refilled with  $N_2$ , and then stirred under visible light or NIR light irradiation (distance 10 cm) for 1h. After reaction finished, the catalyst was filtered and separated, and ethanol was washed 3 times. The filtrate was collected and diluted to 50 ml. The yield was detected by GC. The products were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR.

For recycling test, CNPVPy was isolated by filtration, soaked with EtOH (3  $\times$  5 ml), and dried at ambient condition for next cycle. Another heteroaromatics **1** (1 ml), aryldiazonium tetrafluoroborate **2** (0.1 mmol), and EtOH (2 ml) in 10 ml glass tube were used.

#### 2.7. The apparent quantum efficiency (AQE) calculation

Under visible light irradiation (450 ± 10 nm), the catalytic suspension was irradiated by a 300 W Xe lamp equipped with 450 ± 10 nm band-pass filter for 1h. During the reaction with only monosubstituted product in the initial stage of reaction, which is reasonable for parallel calculation. The average intensity of irradiation was found to be 0.443 W and 0.265 W before and after the reaction flask by a power meter (Newport; 843-R). So, total absorb light energy  $\Delta E = (0.443 - 0.265) \times 3600 = 640.8$  J, Irradiation for 1h, n = 95% × 0.1 mmol = 0.095 mmol, energy per photon  $E_0 = hc/\lambda = 6.63 \times 10^{-34} \times 3 \times 10^8/(450 \times 10^{-9}) = 4.42 \times 10^{-19}$  J, molar of photons  $n_p = \Delta E/(E_0 \times N_A) = 640.8/(4.42 \times 10^{-19} \times 6.02 \times 10^{23}) = 24.083 \times 10^{-4}$  mol = 2.4083 mmol, AQE(initial) = n/  $n_p = (0.095/2.4083) \times 100\% = 3.94\%$ . With the same method, we can calculate the initial AQE 0.95% and 5.15% for UV light irradiation (300 ± 10 nm) and NIR light irradiation (900 ± 10 nm), respectively.

#### 3. Results and discussion

#### DOI: 10.1039/C7TA08389K 3.1. Preparation and Characterization of CNPVPy heterojuction aerogel

Scheme 1 and Scheme S1 showed the structural evolution of CNPVPy heterojuction aerogel from 2D C<sub>3</sub>N<sub>4</sub> NSs and PPy/PVA composites. Cooper's work has suggested that the PVA plays a crucial role as a structuring agent to produce 2D/3D aligned porous materials.<sup>6</sup> In order to obtain aligned porous structure, we first prepared PPy/PVA aqueous suspension with negative zeta potential (-7.13 mV) by one-step oxidation of pyrrole using ferric ions in PVA solution.<sup>32</sup> C<sub>3</sub>N<sub>4</sub> NSs aqueous suspension with positive zeta potential (+18.9 mV) was deliberately prepared according to the literature with little modification.<sup>17,33</sup> The above two aqueous suspensions were mixed thoroughly and then the directional freezing arrangement generation aligned CNPVPy heterojuction aerogel. In addition, by adjusting the mass ratio of PPy/PVA and C<sub>3</sub>N<sub>4</sub>, we can get a series of assemblies containing different amounts of C<sub>3</sub>N<sub>4</sub>.



Scheme 1. Synthetic route and proposed formation mechanism of CNPVPy heterojuction aerogel.

The formation of CNPVPy heterojuction aerogel from the  $C_3N_4$ and PPy/PVA was confirmed by FT-IR spectra. As shown in Figure 1a and Figure S2, the  $C_3N_4$  spectrum contained several main bands range from 1205 cm<sup>-1</sup> to 1640 cm<sup>-1</sup>, which are belonging to the characteristic vibrational modes of CN heterocycles.<sup>17</sup> While the bands at 1240 and 1320 cm<sup>-1</sup> are corresponding to the stretching vibrations of C–N–C (partial condensation) and the connected units of N–(C)3 (full condensation), respectively. A FT-IR spectrum of PPy/PVA showed pyrrole ring stretching band at 1550 cm<sup>-1</sup>, =C–H in-plane vibration band at 1315 and 1185 cm<sup>-1</sup>, conjugated C–N stretching band at 1450 cm<sup>-1</sup>, and =C–H out-of-plane vibration band at 915 cm<sup>-1</sup>.<sup>32</sup> After formation of CNPVPy aerogel, the C<sub>3</sub>N<sub>4</sub> and PPy signals appeared simultaneously. But with the increase of PPy/PVA component, the C<sub>3</sub>N<sub>4</sub> signals gradually weakened, while PPy signals gradually became strong.

In Figure 1b, XRD powder analysis of  $C_3N_4$  revealed a weak (100) diffraction peak at 13.5° for the inter-planar structural packing, and a sharp (002) diffraction peak at 27.9° for interlayer stacking of aromatic systems.<sup>17,33</sup> In addition, a broad signal at 22.4° belongs to amorphous carbon, which is similar to that of PPy/PVA. After formation of CNPVPy macrosturctures, the characteristic peaks belonging to  $C_3N_4$  are weakened, while the broad signals for amorphous carbon are enhanced (Figure S3). Similarly, X-ray photoelectron spectroscopy (XPS) depth analysis indicated the existence of N, C, and O species in CNPVPy (Figure 1c). We also discovered that the intensity of O and C in the CNPVPy increased and the intensity of N decreased with the increase of PPy/PVA component. In addition, the high-resolution XPS survey spectra of C1s, N1s, and O1s also confirmed that CNPVPy has the same

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chemical bond as PPy/PVA and C<sub>3</sub>N<sub>4</sub> (Figure S4 and S5). We firstly explored the absorption of PVA in Figure S6 and found no interferential signal peaks, suggesting that PVA just acted as guiding role matrix. The UV-vis-NIR spectra of C3N4, PPy/PVA, and CNPVPy were compared in Figure 1d. C<sub>3</sub>N<sub>4</sub> expressed strong absorption in the UV-vis range (300~700 nm), and PPy/PVA expressed obvious absorption at NIR range (600~1050 nm). After formation of CNPVPy, the absorption intensity in the whole UV-vis-NIR range was enhanced. Also, the absorption intensity increased with the increase of PPy/PVA content in CNPVPy heterojuction aerogel (Figure S7a). In Figure S7b, the absorption edge is determined by the intersection point of the tangent of the curves. For bare C<sub>3</sub>N<sub>4</sub> and PPy/PVA, the absorption edge is 460 nm and 546 nm, respectively. With the increase of PPy/PVA content to C3N4 suspension, the absorption edge gradually occured red shift, indicating that the Eg of the macrosturctures gradually decrease. It is reasonable that the Eg of each component will be almost constant when the heterojunction between two components form.<sup>17</sup> That is, tunable band structure by changing the mass ratio of C<sub>3</sub>N<sub>4</sub> and PPy can be realized, and the red shift of the  $E_g$  for CNPVPyx demonstrated the intrinsic heterojunction in this macrostructures. Especially, the absorption edge at ~535 nm of CNPVPy20 is almost the same of PPy/PVA (546 nm), which encouraged us to use CNPVPy20 as enhanced photocatalyst.



Figure 1. (a) FT-IR, (b) XRD, (c) wide scan XPS, and (d) UV-vis-NIR spectra of C<sub>3</sub>N<sub>4</sub>, PPy/PVA, CNPVPy3.5, and CNPVPy20. (i, ii, iii, and iv represent C<sub>3</sub>N<sub>4</sub>, PPy/PVA, CNPVPy3.5, and CNPVPy20, respectively).

The microstructures of the formed CNPVPy heterojuction aerogel were further confirmed by TEM, EDX, high angle annular dark field scanning transmission electron microscopy (STEM-HAADF) image, and the element mapping images. Figure 2a and S8 showed that C<sub>3</sub>N<sub>4</sub> exhibited nanoscale sheets approximately 200 nm. In Figure 2b and S9, the mean diameter of PPy microspheres was uniformly at ~110 nm. After the formation of CNPVPy, PPy microspheres and C<sub>3</sub>N<sub>4</sub> nanosheets were uniformly distributed in PVA matrix, and the C<sub>3</sub>N<sub>4</sub> distributed around the PPy microspheres and closely contacted with PPy (Figure 2c~d). The STEM-HAADF image and element mapping images indicated that O, N and C uniformly dispersed in the CNPVPy heterojuction aerogel (Figure 2e~h).



Figure 2. Typical TEM images of (a) C<sub>3</sub>N<sub>4</sub>, (b) PPy/PVA, (c) CNPVPy20 and (d) the corresponding high-magnification images of blue range in c. (e) HAADF image and the corresponding STEM-EDS elemental mapping images of (f) carbon, (g) nitrogen, (h) oxide in CNPVPy20 composites.

The morphology and hierarchical porous structure of the aligned CNPVPy heterojuction aerogel were investigated by SEM. Typically, C<sub>3</sub>N<sub>4</sub> exhibits stacked nanosheets in Figure 3a and S10. The PPy/PVA exhibits aligned 3D macroscopic structures after directional freezing (Figure 3b and S12). Direct freezing of the mixed colloidal solution of PPy/PVA and C<sub>3</sub>N<sub>4</sub> followed by freezedrying resulted in CNPVPy macrostructures (Figure 3c~3i), which showed long-range channel aligned structures along the whole monolithic sample that was similar to the PVA (Figure S11) and PPy/PVA materials (Figure 3b and S12). Compared with the smooth surface of PVA materials (Figure S11), the surface of CNPVPy was rougher because of the doped C<sub>3</sub>N<sub>4</sub> nanosheets and PPy macrospheres in PVA matrix. From lateral view of CNPVPy aerogels, the SEM image of such composite material exhibited numerous unique interconnected honeycomb structures with an average pore size of 2~5 µm (Figure 3d). Also, we explore the effect of the doping amount of C<sub>3</sub>N<sub>4</sub> nanosheets on the morphology of the formed CNPVPy heterojuction aerogel. As can be seen in Figure 4

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and S13, under the low doping of  $C_3N_4$ , aligned 3D macrostructurs were generated (Figure 4). However, when the amount of  $C_3N_4$ increased, the structure became fluffier, and a large number of detached fragments presented (Figure S13), indicating that PVA matrix play an important role to form aligned macrostructures.



**Figure 3.** Typical SEM image of (a)  $C_3N_4$ , (b) PPy/PVA, (c) simulated image of CNPVPy20, (e) the photographs of CNPVPy20, (d) vertical view and (f) lateral view of CNPVPy20, (g, h, i) High-magnification images of red range i, ii, iii in f. The insets are the corresponding enlarged images of blue ranges.

The band gap (Eg) of a semiconductor can be calculated from the Tauc plot, the curve of converted  $(\alpha h v)^n v s h v$  from the UV-vis-NIR diffuse reflectance spectra (Figure S14), in which h, v, and  $\alpha$  are the Planck constant, light frequency, and absorption coefficient, respectively. n = 1/2 is for an indirect band gap material and n = 2 is for a direct band gap material. From Figure 5a, a standard relationship of  $(\alpha h v)^2 = A(hv - Eg)$  was then used to draw the Tauc plots for C<sub>3</sub>N<sub>4</sub> NSs, PPy/PVA, and CNCPVPy20.<sup>17</sup> Eg values of 2.24 eV and 2.77 eV for the individual PPy/PVA and C<sub>3</sub>N<sub>4</sub>, respectively, were extracted by extrapolating a straight-line of the linear part of the curve in the lowest energy area to  $(\alpha h v)^2 = 0$ . Using the same method, the Eg values of PPy/PVA and C<sub>3</sub>N<sub>4</sub> in the final CNCPVPy20 were determined to be 2.09 eV and 2.69 eV, which were close to that of individual PPy/PVA and C<sub>3</sub>N<sub>4</sub>. In order to confirm the charge separation between C<sub>3</sub>N<sub>4</sub> nanosheets and PPy in CNPVPy heterojuction aerogel, photoluminescence (PL) spectrum was performed because of its intrinsic origin from radiative recombination of free charge carriers.<sup>34</sup> Generally, suppression of e-/h+ recombination leads to a photoluminescence quenching. As shown in Figure 5b, CNPVPy20 has much lower PL intensity than free C<sub>3</sub>N<sub>4</sub> under the same C<sub>3</sub>N<sub>4</sub> content. That is to say, charge recombination process of CNPVPy20 can be greatly inhibited by coupling with PPy as a result of e-/h+ redistribution driven by the band offsets.

According to the estimated conduction, valence band edges, and Eg values of PPy and  $C_3N_4$  (Figure 5a and S15), we proposed a mechanism schematic of charge separation for CNPVPy heterojuction aerogel illustrated in Figure 5c.  $C_3N_4$  and PPy harvested light, and absorbed photon promoted electron from the ground states into an excited states. Given that the lowest

unoccupied molecular orbital (LUMO) levels of the PPy was energetically lower than that of conduction chandl (CB) 7000 km/s, electron transfers easily from PPy to C<sub>3</sub>N<sub>4</sub>. The coupling between n-C<sub>3</sub>N<sub>4</sub> and p-PPy semiconductors is believed to build up an internal electric field to form p-n junction, causing the enhanced charge separation and thus greatly suppressing e/h<sup>+</sup> recombination rate.<sup>30,35</sup> As a result, the aforementioned synergism could help to quickly separate charge and effectively retard the recombination between photo-generated e/h<sup>+</sup> pairs, so as to enhance photocatalytic activity of CNPVPy.



**Figure 4**. SEM images of orderly aligned self-assembly composites CNPVPy. (a, b) CNPVPy30, (c, d) CNPVPy25, (e, f) CNPVPy15, (g, h) CNPVPy10, (i, j) CNPVPy8, (k, l) CNPVPy5, (m, n) CNPVPy3.5, (o, p) CNPVPy2.



**Figure 5.** (a) The Tauc plots of  $C_3N_4$  nanosheets, PPy/PVA, CNCPVPy3.5, and CNCPVPy20. (b) PL spectra of different aqueous samples with the same component proportion as CNPVPy20. (c) Energy band diagram of the CNPVPy20 nanojunction system.

# **3.2.** The direct arylation of heteroaromatics under irradiation at room temperature

Based on the strong absorption band of CNPVPy heterojuction aerogel in the whole UV-vis-NIR range, We decided to utilize the catalyst to study the direct arylation of heteroarenes between diazonium salts and heteroarenes under the different wavelength light irradiation for 1 h at 25  $\pm$  1 °C using a thermostatic control device to eliminate the effect of light on the temperature of the

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reaction system. As shown in Figure 6a, under the different irradiation wavelength within 1 h, the yields and apparent quantum efficiency (AQE) of CNPVPy20 to the direct arylation of between 4nitrobenzenediazonium tetrafluoroborate (1) and furan (2) are different. The highest yield (95%) with AQE (3.94%) at the wavelength of  $450 \pm 10$  nm indicates that visible light contributed to the reaction mostly. The NIR light could also enhance the photocatalytic activity of CNPVPy, while only 27% and 10% yields were obtained when illuminated under UV light and without light illumination, respectively. The action and absorption spectra of CNPVPy20 coincided in the range of 450 nm~900 nm, which was thought that the photoinduced arylation was driven by the absorption of CNPVPy20. So we further tested the transient photocurrent density of C<sub>3</sub>N<sub>4</sub>, PPy, and CNPVPy20. In Figure 6b, the transient photocurrents were measured during repeated ON/OFF illumination cycles under visible light irradiation. The photocurrent of CNPVPy20 showed 2 times and 6.6 times as high as that of C<sub>3</sub>N<sub>4</sub> and PPy under visible light, respectively. The photocurrent enhancement of the CNPVPy20 collectively confirmed the presence of photoelectron transfer in photocatalysis, which could be attributed to the synergetic effect of C<sub>3</sub>N<sub>4</sub> and PPy.



Figure 6. (a) Action and absorption spectra of CNPVPy20 for C-H arylation of heteroarenes reaction under different laser irradiations for 1 h at  $25 \pm 1$  °C. The corresponding wavelength captured for AQE calculation are located at  $300 \pm 10$  nm,  $450 \pm 10$  nm,  $550 \pm 10$  nm,  $650 \pm 10$  nm,  $800 \pm 10$  nm, and  $900 \pm 10$  nm. Note: all the reaction used a thermostatic control device to eliminate the effect of light on the temperature of the reaction system. (b) Transient photocurrent density versus time plotted for C<sub>3</sub>N<sub>4</sub>, PPy, and CNPVPy20 in 0.01 M Na<sub>2</sub>S electrolyte under 400 nm~700 nm.

The activity of CNPVPy20 for the direct arylation of heteroaromatics was then investigated under visible irradiation. For our purpose, we first investigated the optimal condition for the arylation between 4-nitrobenzenediazonium tetrafluoroborate (1) and furan (2). The corresponding conversions were presented in Table S1. Among the different solvents tested (Table S1 entries 1-8), ethanol is considered the superior solvent for the photoreaction under 1 h irradiation at r.t. (Table S1 entry 2). We also found that 12% yield was obtained without irradiation (Table S1 entry 9), and the yield was only 56% when the reaction temperature was 60 °C without irradiation (Table S1 entry 10). Meanwhile, the photocatalytic activities of C<sub>3</sub>N<sub>4</sub>, PPy/PVA, simply mixed C<sub>3</sub>N<sub>4</sub> and PPy/PVA were also carried out under visible light irradiation at  $25 \pm 1$  °C. As shown in Figure 7, the photocatalytic activity of CNPVPy20 is the highest among the C<sub>3</sub>N<sub>4</sub>, PPy/PVA, simply mixed C<sub>3</sub>N<sub>4</sub> and PPy/PVA. Also, yields increased with increasing the ratio of PPy/PVA, which may be caused from the Eg decrease.(Figure S7b) However, when the ratio of PPy/PVA further increased beyond 20 (CNPVPy20), the yield decreased, because of excess PVA surrounded C<sub>3</sub>N<sub>4</sub>-PPy junction hindering effective contact with reactant. To illustrate the general

applicability of CNPVPy, the method was subsequently extended to other aryldiazonium salts derivatives, furan and thiophene Arabies showed the results of these arylations. Gratifyingly, the presence of electron-withdrawing groups as well as electron-donating groups on the benzene ring could be proceeding smoothly in good yield, especially for furan derivatives in yields up to 88% (3a-3h). However, the corresponding yields from thiophene were lower than that of furan, while they were still up to 77% (3i~3p). The CNPVPy20 catalyst is preferable to that of other reported photocatalysts.<sup>36-38</sup>



Figure 7. Optimization of the catalyst using EtOH as solvent with white LED lamp irradiation.

Table 1. Substrate scope of furan and thiophene with aryldiazonium salts.



**Reaction condition**: CNPVPy20 (5 mg), **1** (0.1 mmol), **2** (1 mL), EtOH (2 mL), irradiation with white LED lamp (30 W). Yields of products were determined by GC

3.3. Robust test and recycling of the Catalyst

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The recyclability of CNPVPy20 was then evaluated because cyclical stability is an inevitable topic of photocatalyst in green system. The arylation between 4-nitrobenzenediazonium tetrafluoroborate (1) and furan (2) was performed in each cycle under the same reaction conditions as described above except using the recovered catalyst. After each run, CNPVPy20 was isolated by filtration and soaked with EtOH, and CNPVPy20 was directly used for next cycle. It was demonstrated that the catalyst could be reused at least 8 times with above 90% yields (Figure S16). Furthermore, after the 8 times cycle, the used catalyst showed little morphology change (Figure 8a and S17), indicating CNPVPy20 still keeps long-range pore alignment. Meanwhile, the peaks and element contents of C1s, N1s, and O1s are negligible change in high-resolution XPS spectra (Figure S18), suggesting the stability of CNPVPy20 in this reaction system.



**Figure 8.** (a) Typical SEM image of reused CNPVPy20 after 8<sup>th</sup> photocatalytic cycles. (b) Reaction kinetic of formation and decomposition of azoether **4b** (R = 4-Cl) *via* detection of absorption maximum at 412 nm. (c) Postulated reaction mechanism of CNPVPy20 for photo-mediated direct C–H arylation of heteroarenes at room temperature. (d) The scheme to illustrate the proposed reaction pathway of tetrafluoroborate and heteroarenes in heterojunction aerogel.

#### 3.4. Mechanistic Studies

Previous studies suggested that alcohol could react with the diazonium salt to generate an intermediate azoether **4**, which exhinited a strong absorption at 412 nm, and such intermediate plays an important role to form the target products in the presence of

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photocatalysts under irradiation. To investigate the plausible mechanism of this arylation in the presence 1000 CNPVPy201 eatalyst, the standard reactions with diazonium salt 1b (R = 4-Cl) were carried out and the azoether 4 was detected by UV-vis spectroscopy.<sup>36,38</sup> As shown in Figure 8b, in the standard reaction without CNPVPy20, an absorption maximum at 412 nm could be detected after 20 min and the intensity decreased slowly for more than 40 min. When the reaction was conducted without furan, slight maximum was observed over a period of 15 min. These results indicated that diazonium salt reacted with the alcohol to form an intermediate azoether 4b, and furan as a base could help to form azoether 4b. It was hardly to detect absorption maximum over a period of 2 h in the standard reaction, which could be due to the enhanced catalytic performance of CNPVPy20 to conver azoether 4a to aryl radical 5b, which has no absorption peak at 450nm.

Based on above experiment results, we proposed a plausible mechanism for the direct arylation of heteroaromatics (Figure 8c), which is similar to that mediated by TiO2 and Fe3O4@Cu2-xS-MoS2 frameworks.<sup>36,38</sup> First, diazonium salt 1 reacts with ethanol to generate azoether 4 which then produces aryl radical 5 excited by single electron transfer (SET) excitation from the excited state of CNPVPy. The generated aryl radical 5 is easily reacted with heteroaromatic 2 to form radical intermediate 6 which is further oxidized by CNPVPy to form carbocation intermediate 7 by a radical chain transfer mechanism. In another path, the radical intermediate 6 can be also oxidized by azoether 4 to generate aryl radical 5. And finally, the intermediate 7 forms the final arylated heteroarenes 3. Moreover, CNPVPy with aligned microstructures architectures generate numerous hierarchical pore structures. In Figure S19 and Table S2, the BET surface area and pore size of CNPVPy20 are 35.3874 cm<sup>2</sup>/g and 18.3170 nm, respectively. The pore structures can be acted as nanoreactors to help the reaction substrates efficiently contact with the surface of C<sub>3</sub>N<sub>4</sub> nanosheets and PPy macrospheres.38, 39 Hierarchical structures allow scattering and multi-reflection of irradiated light sources and thus increasing quantities of photogenerated electrons and holes functioning, endowing with enhanced photocatalytic activity.40,41 Thus the photocatalytic efficiency is enhanced by the unique structure of the photocatalyst. (Figure 8d).

#### 4. Conclusion

In summary, we obtained gram-scale 3D aligned heterojuction aerogel of of PPy/C<sub>3</sub>N<sub>4</sub> NSs by directional freezing of PPy/PVC composites and C<sub>3</sub>N<sub>4</sub> NSs. In such structure, the PPy and C<sub>3</sub>N<sub>4</sub> formed p-n heterojunctions, in which the PPy directly injected the photogenerated electrons into the C<sub>3</sub>N<sub>4</sub>. In addition, tunable band structure can be realized by changing the mass ratio of C<sub>3</sub>N<sub>4</sub> and PPy. Therefore, such constructed frameworks help to synergistically promote the charge transfer abilities and retards the recombination of electronhole pairs of PPy/C<sub>3</sub>N<sub>4</sub>. Because of its long-range channel aligned structures along the whole monolithic sample and good light capture both in visible range and NIR range, the synthesized 3D aligned heterojuction aerogel of PPy/C<sub>3</sub>N<sub>4</sub> NSs catalyst exhibited unexpected photocatalytic activity and robust cycling for the direct arylation of heteroaromatics at 25 <sup>0</sup>C, superior to the single- and mixed-component systems, and recently reported photocatalysts. Our

work thereby not only provides a new approach to prepare aligned metal-free heterojunction aerogels based on the 2D semiconductor materias and 1D conducting polymers, but also opens up a new field for the development of metal free heterojuction aerogels as a new type of highly efficient visible and NIR light induced heterogeneous photocatalysts. The employment of 3D aligned heterojuction aerogel of  $PPy/C_3N_4$  NSs as a heterogeneous photocatalyst for other types of reactions and the development of other 1D/2D heterojuction aerogels as highly efficient visible and NIR light induced heterogeneous photocatalysts are currently underway in our laboratory.

#### **Conflicts of interest**

There are no conflicts to declare.

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# Gram-Scale Synthesis of Aligned $C_3N_4$ -Polypyrrole Heterojuction Aerogel with Tunable Band Structures as an Efficient Visible and Near Infrared Light -Driven Metal-Free Photocatalyst

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Gram-scale 3D aligned heterojuction aerogel of  $PPy/C_3N_4$  NSs with long-range pore alignment over the whole length of the monolithic sample and a channel structure were prepared. Such aerogel as metal free photocatalyst displayed excellent photocatalytic activity for direct arylation of heteroaromatics under visible-near infrared (NIR) light irradiation at room temperature.