Synthesis-in-place of highly-conjugated oligothiophene micropatterns *via* photo-activated Ullmann coupling on copper surface†

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In contrast to the traditional thermally-activated Ullmann coupling, a photo-activated Ullmann coupling for facile synthesis of oligothiophene and polythiophene films and micropatterns is reported.

The Ullmann coupling reaction is one of the most popular routes for aryl–aryl bond formation and is widely used by materials chemists for the synthesis of α–α' connected polythiophenes and oligothiophenes.[1–3] In the case of *unsubstituted* polythiophenes and oligothiophenes with long conjugation lengths (PTh), the bulk materials cannot be processed into useful device structures such as thin films or micropatterns due to their intractability. This has been a limiting factor in applications of PTh although it has good environmental and thermal stability. It is therefore highly desirable to develop an *in-situ* Ullmann coupling chemistry suitable for the production of thin films and patterns directly in the place of application.

In a typical Ullmann coupling reaction, a thienyl halide reactant is dissolved in a solvent and refluxed for several hours at high temperature (typically >100 °C) in the presence of Cu, Ni and Pd or their compounds.[3,4] This thermally activated process is convenient for bulk synthesis of PTh; but it is not directly applicable for fabrication of PTh films and micropatterns. In solution, the intermediate species formed at the Cu surface dissolves into the solution leading to polymer formation in the bulk. Also, conventional lithographic techniques cannot be easily integrated with the thermally-activated chemistry to fabricate micropatterns of PTh. The Ullmann coupling reaction can be carried out in the absence of solvent *via* reaction of the active metal surface with reactant molecules adsorbed from the gas phase. This has been demonstrated on clean Cu surfaces under ultra-high vacuum (UHV) conditions.[5] This UHV approach can produce a monolayer-thick short oligothiophene film; but it cannot produce PTh films thick enough for technical applications. The critical requirement to attain nano-scale thickness PTh films and micropatterns is to spatially localize the Ullmann reaction within a $\sim$100 nm thick monomer film deposited on the target substrate.

This paper demonstrates the use of a photo-activated Ullmann coupling reaction for synthesis-in-place of PTh thin films and micropatterns in ambient conditions. We utilize selective photodissociation of the C–I bond in 2,5-diiodothiophene to generate thienyl radicals in a thin monomer film ($\sim$140 nm). These radicals react with the Cu substrate producing thienyl–Cu intermediates. The photochemical activation allows us to generate the radicals at room temperature and thus thermal evaporation of monomer molecules is prevented. The thienyl–Cu intermediates contained in the monomer film react with the monomer and produce PTh. The photochemical activation also makes it easy to fabricate PTh micropatterns *via* UV irradiation of the monomer film through a photomask.

Experimental details are provided in the supplementary information.† In brief, 2,5-diiodothiophene (mp $\approx$ 34 °C) was thermally evaporated and deposited on target substrates held at room temperature. The clean copper surface was prepared by removing oxide layers with a nitric acid treatment.[6,7] For comparison, clean silicon oxide and gold surfaces were also used as a model inert substrate. The deposited monomer film was irradiated with UV for 3 minutes in argon. The synthesized films were analyzed with photoluminescence (PL) spectroscopy, fluorescence microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). For micropatterning, the deposited monomer layer was irradiated through a TEM grid. A fluorescence microscope image of square patterns of PTh on Cu is shown in the inset of Fig. 1 as an example.

The consequence of Ullmann coupling reactions in the photochemical synthesis of PTh on Cu is a longer conjugation length of PTh produced on Cu compared to the oligothiophene produced on the inert substrates *via* direct coupling reactions of the photogenerated radicals. Fig. 1 compares the PL emission spectra of the polymer films photochemically synthesized on Cu and SiO_2. The PL spectrum of the photochemically synthesized films on Au is essentially the same as the one on SiO_2 (see the supplementary information†). The PL emission maximum can be used to estimate the degree of α–α' coupling or conjugation of π electrons in the

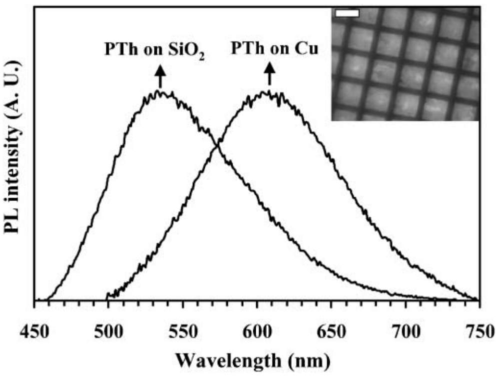

Fig. 1 PL spectra of polymer films photochemically synthesized on SiO_2 and Cu. The excitation source is 435 ± 2 nm. A fluorescence microscope image of PTh on Cu is shown in the inset (scale bar = 30 μm).

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synthesized polymer. As the degree of conjugation increases, the PL emission maximum shifts to a longer wavelength. The PL spectrum of the polymer film synthesized on Cu is peaked at ~605 nm (orange red) while those of the films synthesized on other substrates are at ~545 nm (greenish yellow). These PL results clearly indicate that the PTh film synthesized on Cu has a longer conjugation length than those synthesized on other inactive substrates such as SiO_2 and Au. From comparison with the literature,[6] the average conjugation length of PTh on Cu is estimated to be ~7, whereas those on other substrates are ~4.

The PTh films synthesized on Cu and Au were further analyzed with surface enhanced Raman spectroscopy (SERS). In Fig. 2, The peaks at 691 cm^{-1}, 1043 cm^{-1}, and 1215 cm^{-1} are attributed to C–S–C ring deformation, C_β–H bending, and C_α–$C_{\alpha'}$ inter-ring stretching, respectively.[8] The presence of these peaks confirms that the thienyl ring structure is preserved during the photochemical reaction. For the PTh film synthesized on Cu, the ring C_α=C_β symmetric peak is at ~1450 cm^{-1}, the asymmetric peak appears as a shoulder at ~1510 cm^{-1} and the I_{asym}/I_{sym} intensity ratio is ~0.30. For the PTh film syntheszed on Au, the symmetric and anti-symmetric peaks are located at 1440 cm^{-1} and 1520 cm^{-1}, respectively, and the I_{asym}/I_{sym} ratio is ~1. These peak positions and intensity ratios can also be used to estimate the degree of conjugation.[9,10] As the number of thiophene ring units in α–α′ oligothiophene increases from 3 to 8, the C_α=C_β asymmetric stretching peak location gradually shifts from 1530 cm^{-1} to 1502 cm^{-1} and the I_{asym}/I_{sym} intensity ratio decreases gradually to ~0.2. From this comparison, the average conjugation length of the PTh synthesized on Cu is estimated to be 6 or 7 and that on Au is estimated be 3 or 4, which is consistent with the PL data.

The increased conjugation length of PTh synthesized on Cu indicates that the Ullmann coupling reaction is actively occurring during the photochemical polymerization. The photogenerated thienyl radicals (I–Th•) react with the Cu, forming the I–Th–Cu intermediate.[7,11] These intermediates react with the neighbouring monomers/oligomers at the 2 or 5 position forming exclusively α–α′ linking. But, in the absence of active metals for the Ullmann reaction, the photogenerated I–Th• radicals directly react with the neighbouring unreacted monomer forming both α–α′ linking and α–β mislinking. The presence of these mislink defects reduces the conjugation length, hence the PTh formed on non-reactive substrates have a short conjugation length.[12] In the presence of Cu, Ullmann coupling reactions aid α–α′coupling, so the PTh synthesized on copper has a longer conjugation length of ~7.

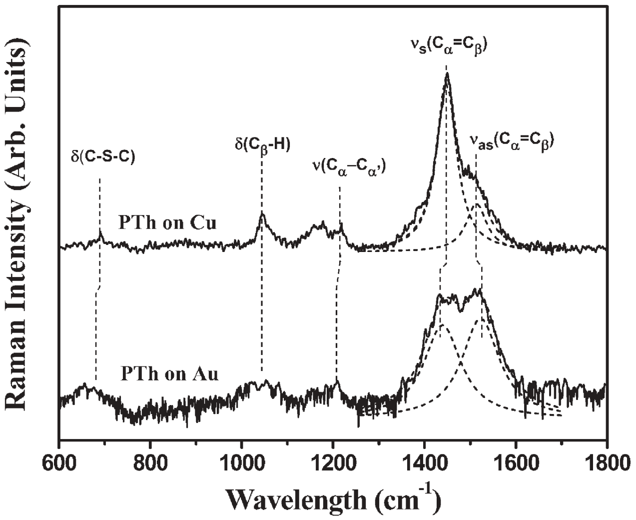

Fig. 2 Surface enhanced Raman spectrum of photochemically synthesized PTh film on Cu and on Au.

Further evidences for Ullmann coupling can be found in XPS results shown in Fig. 3. After photochemical reactions on Cu, the Ullmann coupling by-product, CuI, is detected. The I $3d_{5/2}$ peak of the films synthesized on Au (and others) is at 620.5 eV while that of PTh synthesized on Cu is at 619.7 eV. The 620.5 eV peak is attributed to iodine covalently bonded to carbon.[13] The binding energy of 619.7 eV is attributed to the iodine anion in CuI.[14] The $L_3M_{4,5}M_{4,5}$ Auger peak of Cu detected for the photochemically synthesized PTh is in agreement with CuI (570.5 eV), not metallic Cu (568.1 eV).[15,16] The elemental analysis reveals that the Cu/I ratio is ~1. The I/C ratio is ~0.6 for PTh synthesized on Cu and ~0.1 for the film synthesized on other substrates. These results indicate that on Cu substrates iodine atoms are retained as CuI in the film. On other substrates, only iodine atoms covalently bonded to oligothiophene molecules are detected in XPS. The molecular iodine species formed *via* coupling of iodine atoms are not detected in XPS because they desorb into vacuum during XPS measurements.

In the sulfur 2p region, the well-resolved doublet peak at 163.8 eV and 165 eV is observed (data shown in supplementary information†). These peaks correspond to the S $2p_{3/2}$ and $2p_{1/2}$ of polythiophene.[17] A small shoulder at the lower binding energy side is often observed. This is attributed to the sulfide species formed by concurrent desulfurization reaction.[18] The sulfide formation is also observed in the chemical synthesis of polythiophene by the nickel-catalyzed Ullmann reaction.[19]

It should be noted that the substrate peaks are not detected in XPS of the films synthesized on other metals and SiO_2. The film thickness (~100 nm) is much larger than the escape depth of photoelectrons from the substrate (an order of 10 nm). In contrast, strong CuI peaks are observed in XPS of the ~100 nm thick PTh film produced on Cu. The detection of CuI indicates that the Cu atoms from the substrate are dissolved and diffused into the film probably in the form of organo-Cu intermediates during the photochemical reaction. CuI is insoluble in the thiophene or iodothiophene liquid. It should be mentioned that we observe the

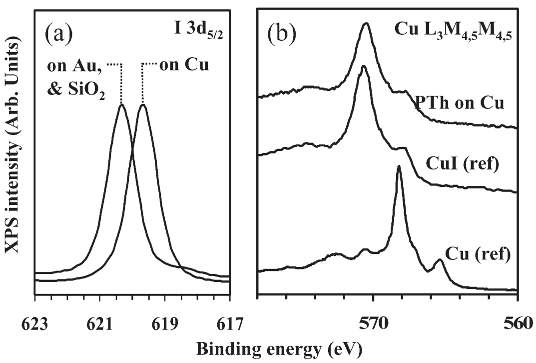

Fig. 3 (a) High-resolution XPS the spectra of the I $3d_{5/2}$ region for PTh films produced on Au and Cu. (b) Comparison of the Cu LMM Auger region of the PTh produced on Cu with those of CuI and Cu reference.[13,14]

formation of a liquid phase in the monomer film during UV irradiation. This seems due to the formation of photochemical intermediates with low melting points (note that 2-iodothiophene is liquid at room temperature). This liquid phase formation may facilitate the diffusion of organo-Cu intermediates formed at the copper surface into the monomer film. These organo-Cu intermediates initiate Ullmann coupling reactions throughout the monomer film aiding in formation of α–α' coupled polythiophene.

The photo-activated Ullmann coupling reaction can be developed as an effective technique for fabrication of thin film or micropattern devices containing unsubstituted PTh as a functional component. This approach can be extended to other conjugated molecules if proper precursors are utilized. The presence of CuI by-product in the PTh film might be advantageous in hybrid solar cell applications, as CuI is a large band-gap material that can be used as a hole acceptor.[20]

In conclusion, the selective photodissociation of the C–I bond in 2,5-diiodothiophene on Cu leads to Ullmann coupling reactions involving substrate atoms and produces PTh with an average conjugation length of $\sim$7. This photo-activated chemistry allows synthesis-in-place of unsubstituted PTh into thin film and micropattern forms, thus avoiding the intractability issues of unsubstituted PTh.

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