

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

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### Experimental Details

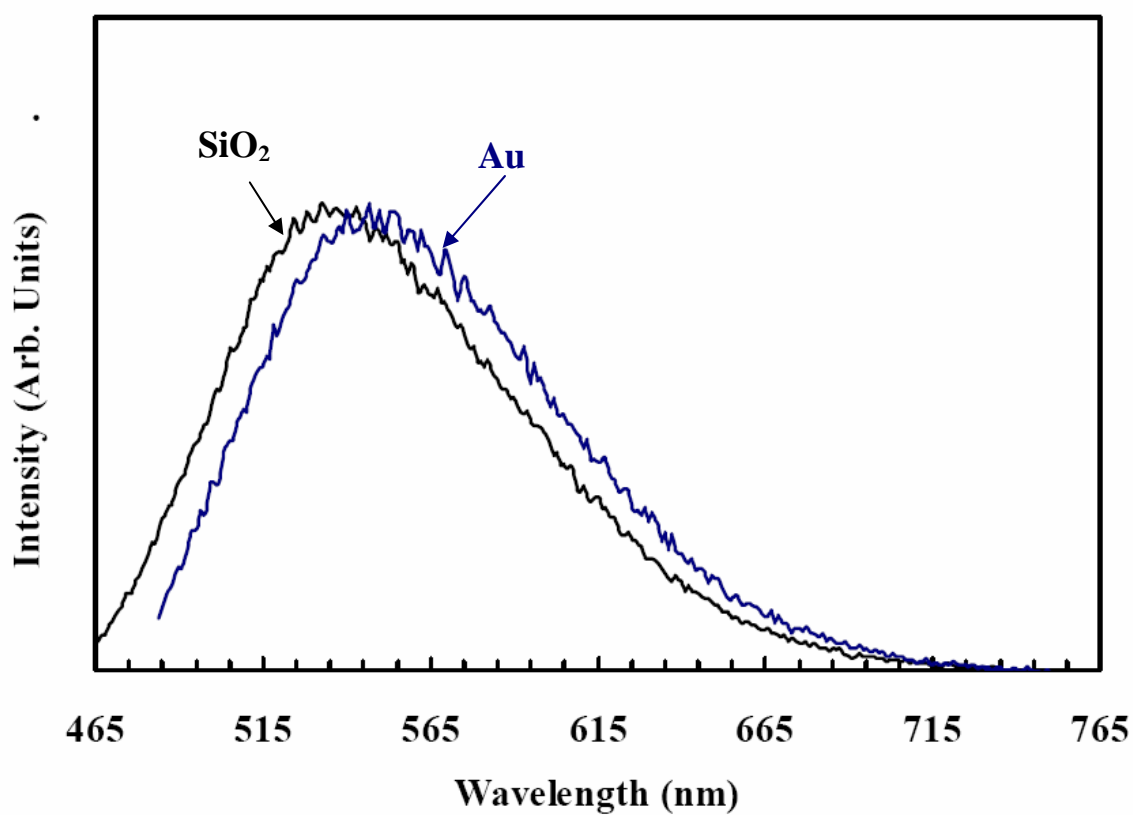
Thin films of copper, gold, platinum, and palladium substrates were prepared on silicon wafers by thermal evaporation just prior to use. In the case of copper, a thin foil (> 99.99 % purity) was also used after cleaning off oxide with nitric acid (1.5N) [M.M. Sung, K.Sung, C.G. Kim, S.S.Lee, Y.Kim, *J. Phys. Chem B*, 2000, **104**, 2237; A. Fürstner, *Angew. Chem. Int. Ed.*, 1993, **32**, 164]. A native oxide film on a Si wafer was cleaned with 5:1:1 mixture of H<sub>2</sub>O:NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub> at 70 °C. 2,5-diiodothiophene (monomer) was thermally evaporated at ~120°C in ambient conditions and deposited onto the substrate held at room temperature. The monomer deposition rate was calibrated with a quartz crystal microbalance. The deposited monomer thickness was kept constant at ~140 nm thickness in this experiment. The monomer film was irradiated with a collimated UV beam from a 200W mercury lamp (Oriol 6283) for 3 minutes in argon. The IR radiation from the UV lamp was removed using a water filter to prevent sample heating during UV irradiation. The thickness of the final polymer products was ~100 nm. The photochemically-produced polythiophene films were analyzed in ambient conditions with photoluminescence (PL), x-ray photoelectron (a monochromatic Al-K<sub>α</sub> source was used; the binding energies reported in this paper were referenced to C1s at 284.6 eV) and Raman spectroscopy (excitation radiation = 632.8 nm HeNe laser).

Copper iodide, a side product of the Ullmann reaction, has the photoluminescence activity upon excitation with UV at  $\lambda < 430$  nm [P.M.Sirimanne, T.Shirata, L.Damodare, Y.Hayashi, T.Soga, T.Jimbo, *Solar Energy Materials & Solar Cells*, 2003, **77**, 15]. In order to

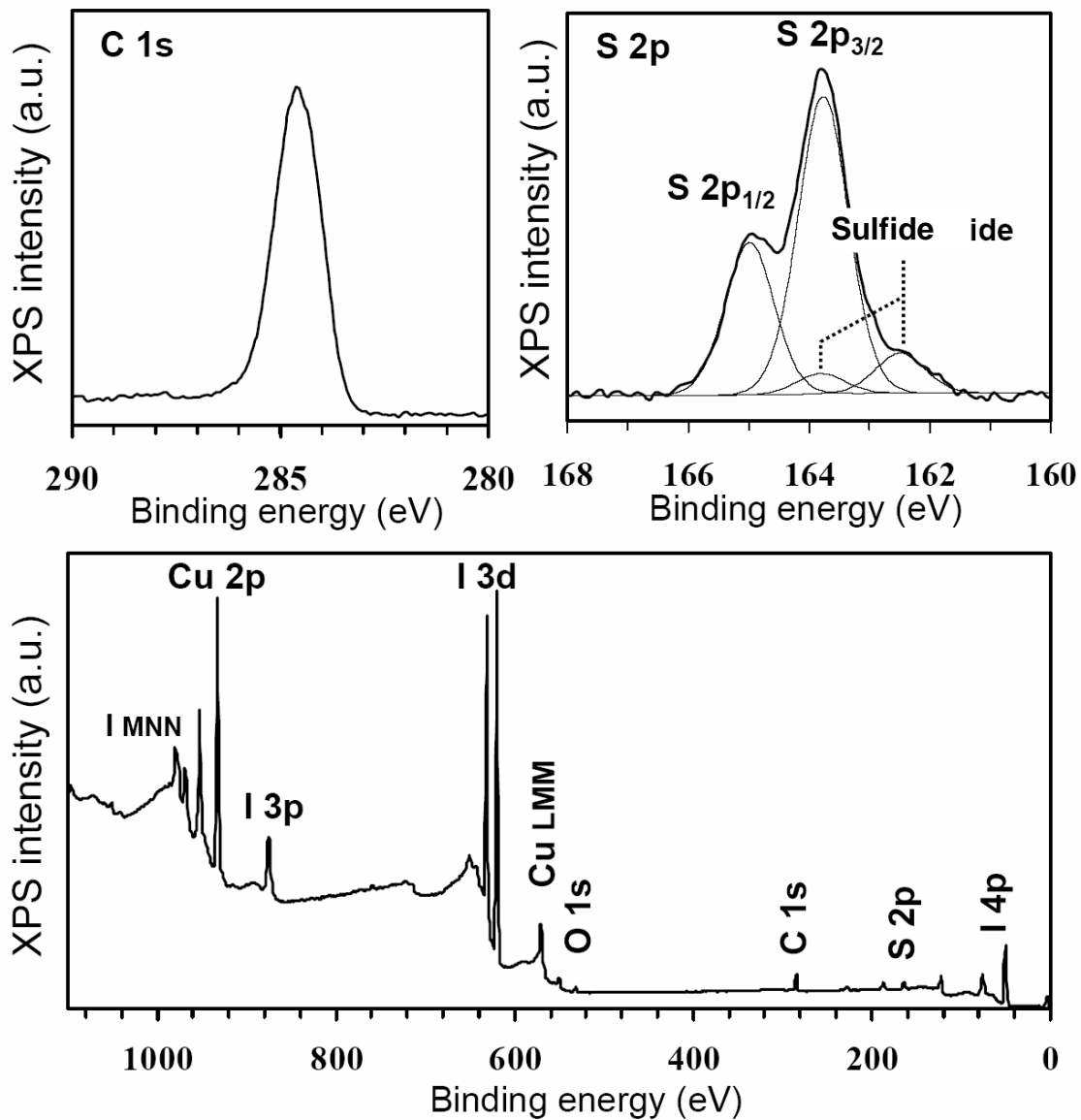
avoid photoluminescence from CuI, the polythiophene film produced on Cu was analyzed with two different excitations,  $\lambda = 435 \pm 1.5$  nm and  $455 \pm 1.5$  nm. Both PL emission spectra are identical, confirming the emission is from polythiophene, not from CuI.

**Figure S-1.** Photoluminescence spectra of polythiophene thin films produced on SiO<sub>2</sub> and Au.

Excitation = 435 nm



**Figure S-2.** High-resolution C1s and S2p region spectra and survey spectrum of photochemically produced polythiophene on Cu



**Figure S-3.** XPS spectra of photochemically produced polythiophene on Au. (a) Survey spectrum, (b) C1s region, (c) S 2p region, and (d) I 3d<sub>5/2</sub> region.

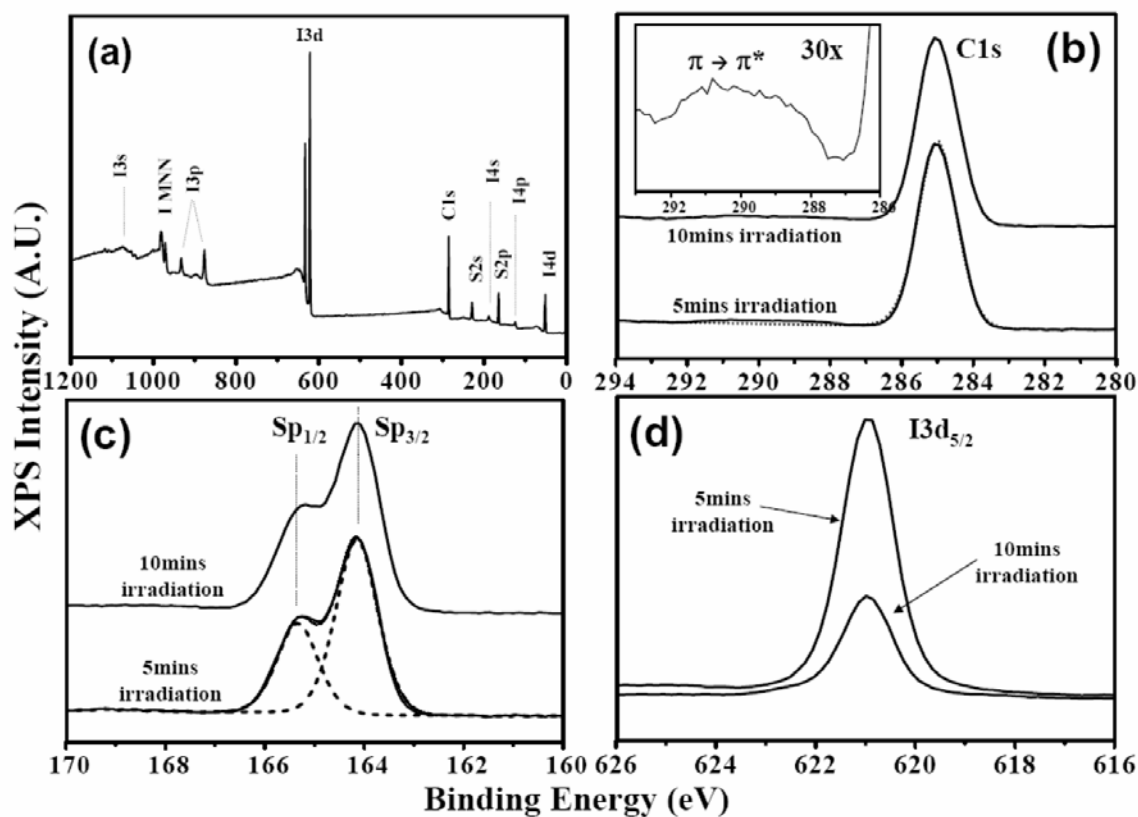


Figure S-3 shows XPS analysis results of the photochemically produced polythiophene on Au. The efficacy of the Ar environment in preventing photooxidation of radicals and products can be verified with the absence of detectable oxygen peak in the survey spectrum and the oxygenated carbon species in the C1s region. Note that the Au substrate peak is not detected indicating the polymer film is covering the entire substrate. The iodine peak intensity decreases (Figure S-3d) as UV irradiation time increases while the carbon and sulfur peak intensities (Figures S-3b and 3c) are not changing. The high-resolution spectra of the carbon 1s region and the sulfur 2p region show that the thiophene ring structure is intact. In addition, there is a  $\pi \rightarrow \pi^*$  shake-up transition peak at 288 ~ 292 eV characteristic of conjugated polymers.