

**ACS PETROLEUM RESEARCH FUND
PERSONNEL STATEMENT**

PRF # 51559-UNI10

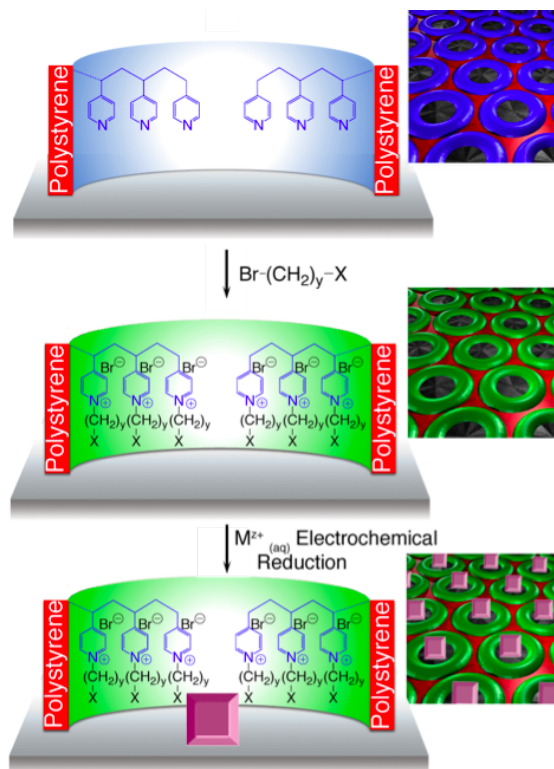
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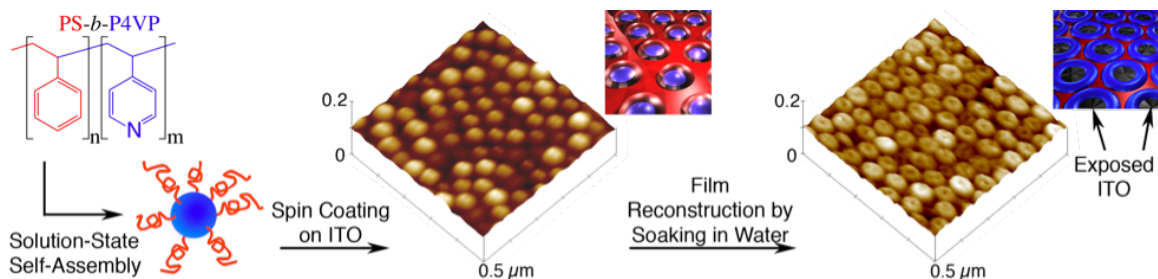
GRANTEE INSTITUTION: Western Washington University

PRINCIPAL INVESTIGATOR: David Rider

The annual energy demand of the US could be supplied by covering 2% of its landmass with current photovoltaic technology.¹ The main obstacle in this approach however is the manufacturing cost of silicon solar cell modules. New photovoltaic technology based on organic and inorganic semiconductors is an attractive alternative due to significantly reduced fabrication costs.² A recent evaluation of several inorganic semiconductors has identified cuprous oxide (Cu_2O) as a possible candidate for contributing to future solar energy infrastructure.³ Accordingly, we have investigated a new route to arrays of morphologically controlled Cu_2O nanoparticles for solar energy technology. The route employs self-assembling polyvinylpyridine (PVP) block copolymers as a template capable of (i) chemical functionalization and (ii) directing the location, size and structure of Cu_2O (Scheme 1).



Scheme 1. Chemical functionalization of self-assembled PS-*b*-P4VP films with habit modifiers [e.g. $\text{Br}-(\text{CH}_2)_y\text{-X}$] for the templated electrochemical growth of shape-tunable semiconductor nanocrystals.



Scheme 2. Preparation of PS-*b*-P4VP film and its reconstruction into a nanostructured template for electrochemical deposition.

The precursor template films are formed by spin coating micellar solutions of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) onto an electrode (Scheme 2). An array of nanoscaled domains lined with P4VP chains is formed when the template is exposed aqueous or methanolic solution (atop in Scheme 1). For chemical functionalization, we have confirmed a quaternization reaction of pyridine groups with methanolic alkylhalide. These self-assembled nanodomains represent a well-defined array of electrochemical nanoreactors suitable for controlled electrodeposition as the P4VP linings contain built-in chemical functionality that can be exploited to control the nanoparticle morphology during electrodeposition (middle and bottom in Scheme 1).

Our initial investigations have focused on understanding the templated electrodeposition of Cu_2O using the unfunctionalized parent PS-*b*-P4VP template. A thermostatically controlled galvanostatic electrodeposition procedure has been developed that produces convenient access to a novel nanoring-type Cu_2O . The structure and composition of arrays of Cu_2O nanorings have been confirmed by atomic force microscopy (AFM; Figure 1 inset) and high resolution X-ray photoelectron spectroscopy (XPS; Figure 1). By curve fitting of the XPS signal, the nanorings were found to be 97% Cu(I) oxide indicating excellent stoichiometric control of the oxidation state of the copper during the electrochemical deposition procedure.

Collaborative investigations (Prof. Janelle Leger, WWU Physics) are currently ongoing to better understand the photooptical properties of these Cu_2O . As a preliminary assessment of the photovoltaic potential of

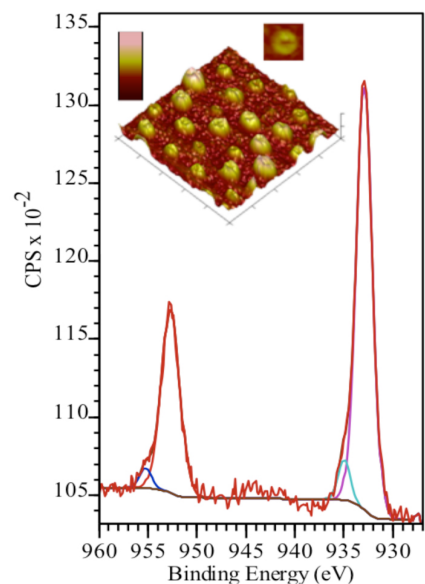


Figure 1. XPS of Cu 2p signal for templated Cu_2O . Inset: $0.5 \times 0.5 \mu\text{m}^2$ AFM image of nanoring morphology of Cu_2O (color scale = 25 nm).

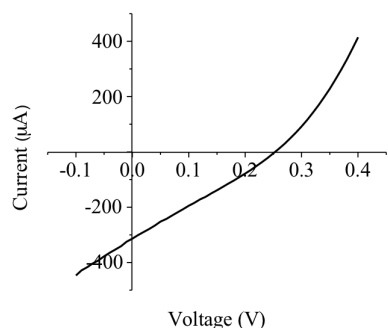


Figure 2. J - V characteristic of Al/PCBM+P3HT/ Cu_2O /ITO solar cell.

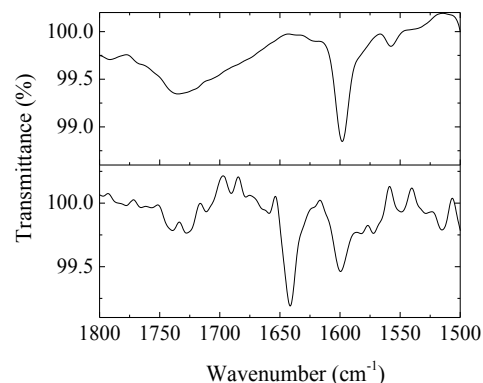


Figure 3. FTIR spectra for as-cast (top) and methyl iodide functionalized PS-*b*-P4VP film (bottom). C---N ring stretch at 1600 cm^{-1} and C---N⁺-Me ring stretch at 1640 cm^{-1} .

this material, we have introduced electrodeposited Cu_2O into a photovoltaic cells that employ a photoactive bulk heterojunction layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM). In this device architecture, electrodeposited Cu_2O acts a buffer layer for charge extraction and is anticipated to assist in the function of these devices (See Figure 2).⁴

We have recently shown that the chemical functionalization of the templates used to create the above Cu_2O proceeds by a quaternization reaction. FT-IR spectroscopy has been used to assess substitution at P4VP pyridinyl residues where the unsubstituted polymer is indicated by a C---N stretch at 1600 cm^{-1} and functionalized polymer domains are indicated by a C---N⁺-Me stretch at 1640 cm^{-1} (Figure 3). Chemical elaboration of the templates with other alkyl halides is currently underway and is the basis for our investigations into a template-specified morphology for electrodeposited Cu_2O material.

This work has provided the basis for an ongoing research program aimed at establishing fabrication routes to inexpensive and environmentally low-impact materials for enabling widespread solar energy technology. Many of these initial results have presented by the PI and student participants at local and regional meetings. Additionally, a student researcher supported by ACS PRF 51559-UNI10 has recently gone on to pursue a graduate degree in chemistry at Kent State University.

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