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Recognition-Directed Orthogonal Self-Assembly of Polymers and Nanoparticles on Patterned Surfaces

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Engineered microscopic surface structures for chemical, analytical, and diagnostic applications are of interest in many areas of science and technology,[1] including the fabrication of microelectrodes,[2a] biochips,[2b,c] and microfluidic devices.[2d] The use of supramolecular interactions, including hydrogen bonding, metal coordination, and electrostatics, to direct the immobilization of functional building blocks has been of growing interest due to their attractive characteristic features: high specificity, controlled affinity, and reversibility.[3] These specific and highly controllable interactions can be manipulated independently and simultaneously,[4] providing orthogonal self-assembly.[5] This concept, integrated with various microlithographical techniques, provides rapid and site-selective adsorption of molecules and mesoscopic objects at predefined regions, a key step in many surface-related applications. Several recent studies reported the fabrication of two-component micropatterned polymer films or colloid arrays relying on electrostatic interactions or DNA hybridization.[6] Surface modification using synthetic recognition elements to direct multiple building blocks in a self-sorting, one-step fashion, however, has yet to be established.

We have exploited the use of noncovalent interactions, including multipoint hydrogen bonding,[7a−c] electrostatics,[7d,e] metal coordination,[7f,g] and hydrophobic interactions,[7g] to direct the assembly of nanoparticles,[7a,d−g] polymers,[7a−c,f] proteins[7e] and to modify surfaces,[7c] with the purpose to create functional or bioactive materials.[7] To combine these interactions and supramolecular building blocks in a self-sorting fashion provides access to a simple, rapid fabrication process capable of providing complex patterning. Herein, we report the patterning of silica substrates with thymine (**Thy-PS**) and positively charged *N*-methylpyridinium (**PVMP**) containing polymers using photolithography (Figure 1A) and the subsequent orthogonal modification of these surfaces using diaminopyridine-functionalized polystyrene (**DAP-PS**) and carboxylate-derivatized CdSe/ZnS core−shell nanoparticles[8] (**COO-NP**) through diamidopyridine−thymine three-point hydrogen bonding and pyridinium−carboxylate electrostatic interactions, respectively (Figure 1B). This recognition-induced orthogonal self-assembly provides high specificity and selectivity in both sequential and one-step functionalization of surfaces.

Clean silicon wafers were spin-coated with **PVMP** to create a positively charged polymer film (Figure 1A), which was stabilized by photocrosslinking,[9] and then a **Thy-PS** overlayer was spin-coated. The chips were exposed to UV light under a photoresist mask, followed by rinsing with chloroform. The resulting surface patterns were stable upon treatment of chloroform, ethanol, THF, or water, enabling the subsequent adsorption processes.

Once the surface was patterned with **Thy-PS** (squares) and **PVMP** (lines), the orthogonality was demonstrated by specific deposition of fluorescent materials. **DAP-PS** was tagged with flavin that has strong fluorescence at 537 nm,[7b] while **COO-NP** (∼5 nm) features an emission maximum at 592 nm (Figure 2A). The

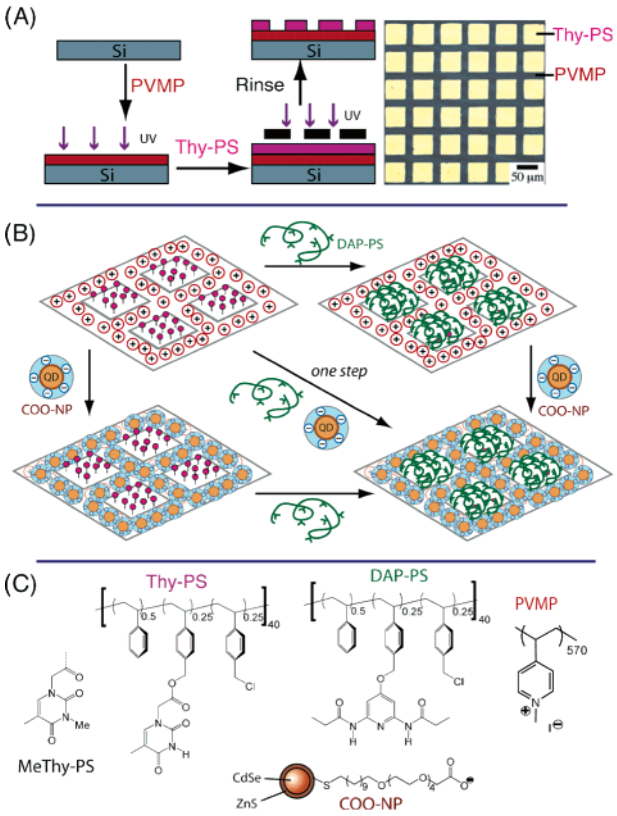

Figure 1. Schematic illustration of the fabrication process. (A) Formation of the patterned **PVMP**/**Thy-PS** surface and optical micrograph of the resulting pattern. (B) One-step and sequential orthogonal functionalization by **DAP-PS** and **COO-NP** through **PS-Thy**:**PS-DAP** recognition and **PVMP**:**COO-NP** electrostatic interactions. (C) Chemical structures of the materials, including control polymer **MeThy-PS**.

deposition was accomplished by dipping the patterned surfaces into PS or NP containing solutions for 5 min, followed by solvent washing and air-drying. Specific three-point hydrogen bonding directs flavin-labeled **DAP-PS** to the **Thy-PS** squares (Figure 2B), while negatively charged **COO-NP** is selectively adsorbed onto positively charged **PVMP** lines (Figure 2C). To demonstrate the specificity of **DAP**−**Thy** interaction, N-methylated thymine polystyrene (**MeThy-PS**) was utilized, as the methyl group has been shown to block the H-bonding site.[7c] Microscopy indicated essentially no adsorption of **DAP-PS** after identical treatment (see Supporting Information), demonstrating that specific recognition is responsible for the PS adsorption. As a further control, at pH 4, little adsorption of NPs was observed, indicating that electrostatic interaction is the main driving force for the NP deposition (see Supporting Information). Two-component site-selective deposition was achieved by sequential exposition of the patterned surface to NP and polymer-containing solutions, regardless of the order

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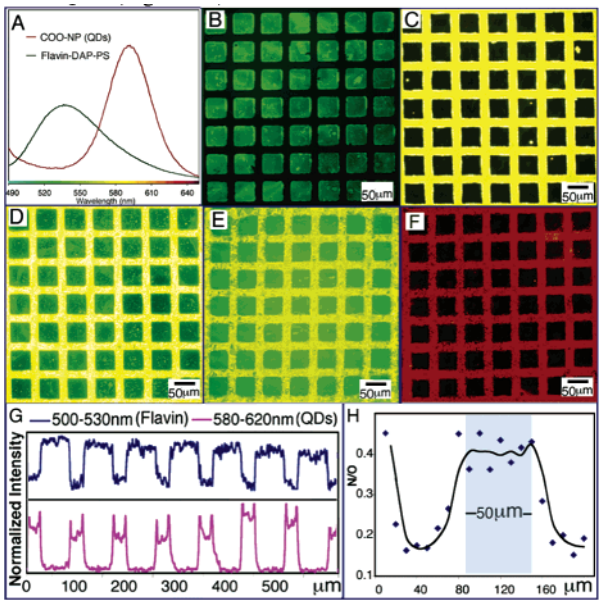

Figure 2. (A) Fluorescence emission of **DAP-PS** and **COO-NP**. Fluorescence microscopy of modified surfaces by (B) **DAP-PS**, (C) **COO-NP**, and two components in (D) multistep and (E) one-step fashion. (F) Micrograph of the two-component modified surface at higher exciting wavelength (>480 nm) showing specificity of **COO-NP**. (G) Confocal fluorescence intensity profiles of modified surface with two different emission wavelength channels of 500−530 and 580−620 nm, respectively. (H) The representative distribution of nitrogen/oxygen atomic concentration ratio analyzed by XPS.

(Figure 2D). Significantly, this orthogonal modification can be accomplished *in one step* by applying the mixture of **DAP-PS** and **COO-NP** to the patterns. Both components selectively self-assembled into the complementary domains (Figure 2E). In both cases, when a higher exciting wavelength (>480 nm) was employed, at which flavin has little or no absorption, only **COO-NP**-modified lines were observed due to the broad adsorption band of QDs (Figure 2F).

The selectivity and specificity of the deposition process were verified by both confocal fluorescence microscopy and X-ray photoelectron spectroscopy (XPS). Two emission channels were employed to follow the distribution of the two fluorescent materials, respectively: flavin (500−530 nm) and QDs (580−620 nm). Figure 2G shows the normalized fluorescence intensity profiles from the two channels. Across the same analyzed area, the flavin-fluorescence domains (50 μm wide) are exactly complementary to the QDs-fluorescence domains (25 μm wide), demonstrating the high selectivity of two components toward the specific prepatterned regions on the surface. In addition, XPS was utilized to probe the elemental distribution across the patterns. As shown in Figure 1C, a large number of nitrogen atoms are present in the grafted functionalities of PS, while the TEG ligands of NP feature high levels of oxygen. A representative profile of the nitrogen/oxygen concentration ratio (N/O) across the surface (Figure 2H) clearly demonstrates selectivity in the adsorption process.

In summary, we demonstrated here a proof-of-concept system using supramolecular orthogonal self-assembly of polymers and NPs for surface modification. This methodology demonstrates the self-sorting characteristics of supramolecular assemblies, concomitantly providing a powerful tool for practical, rapid, and multicomponent fabrication in a single-step fashion. This method provides a significant expansion of the binary capabilities of purely electrostatic deposition. The extension of this process to the creation of complex 3-D functional materials is under investigation.

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Supporting Information Available: Detailed experimental procedures and control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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