One-step Preparation of Vinyl-Functionalized Material Surfaces for Surface Modification

Zhaoqiang Wu, Jun Du, Xiaoli Liu and Hong Chen*

College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Soochow 215123, China Fax: +86 512 65880567; Tel: +86 512 65880827; E-mail: chenh@suda.edu.cn; wzgwhu@suda.edu.cn

Introduction: Control of surface properties is of great importance in materials science, chemistry and biotechnology. Therefore, simple methods of surface modification for the introduction of a variety of desired properties have attracted increasing attention for materials science and biomedical applications.² However, the lack in general of reactive functional groups on material surfaces makes the modification of these materials difficult. Dopamine can undergo self-polymerization to produce an adherent polydopamine layer on many different substrates. Taking advantage of this unique property, different molecules like growth factors and other biomolecules have been immobilized on surfaces to achieve many different properties.³ Inspired by this, we developed a facile and general method for surface modification by combining the advantages of dopamine and conventional radical polymerization. First, a dopamine derivative, dopamine methacrylamide, a molecule with adhesive properties that mimic those of mussels, was subjected to oxidative polymerization in a basic aqueous medium to coat the substrate. Carbon-carbon double bonds were thus formed on the surface and could subsequently copolymerize with different monomers by radical polymerization. Using this method different materials can be functionalized leading to surfaces with a variety of properties.

Methods: Dopamine methacrylamide (DAMA) was prepared according to the method previously reported.⁴ Polyvinylchloride (PVC) film and gold-coated silicon wafers were used as model substrates. Vinyl-functionalized Surfaces were prepared by dipcoating method. Poly(N-vinylpyrrolidone) (PVP)-Grafted Surfaces was prepared by radical copolymerization on vinylfunctionalized surfaces. Double bond surface functionalization and subsequent polymer grafting were verified X-ray photoelectron spectroscopy (XPS) measurements. The quantities of adsorbed fibrinogen were determined by surface plasmon resonance (SPR) measurement.

Results: The scheme of surface modification process is shown in Figure 1. In this method, DAMA molecules are attached to the materials by immersion in an alkaline solution for a given period.



Figure 1. The scheme of surface modification process.

carbon-carbon double bonds introduced enable copolymerization with other functional monomers thus giving surfaces with the desired properties. The XPS data for PDAMAfunctionalized PVC surface and PVP-grafted PVC surfaces are showed in Figure 2. For a PVC-PDAMA surface, the appearance of nitrogen at 400 eV in the XPS spectra confirmed that DAMA was covalently attached to the PVC surface. After the graft polymerization of NVP, the characteristic signals attributed to carbon C1s, nitrogen N1s, and oxygen O1s became much stronger, indicating that a thin layer of PVP was grafted on the surface.

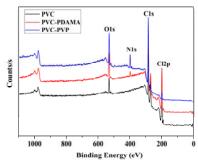


Figure 2. XPS spectra of the PVC substrate before and after PVP modification.

The above-described method based on DAMA/DA treatment was used to modify the gold surface of SPR chips. The levels of Fg adsorption on unmodified and PVP-grafted SPR chips were 0.59 μg/cm² and 0.086 μg/cm², respectively; i.e., PVP grafting reduced Fg adsorption by 85% compared with unmodified chips (Figure 3). The present data suggest that this method has strong potential for surface modification of sensor chips.

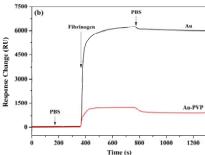


Figure 3. Fibrinogen adsorption (1 mg/mL) on the SPR sensor chips before and after PVP modification.

Conclusions: The one-step incorporation of carbon-carbon double bonds into various substrate surfaces using dopamine methacrylamide offers the advantages of introducing different properties to a solid surface by choosing various double-bond containing monomers by conventional radical polymerization. The materials thus modified may find potential applications in different areas, in particular bioengineering.

References:

- [1] Kang SM and et al. Adv Funct Mater. 2012; 22(14): 2949-2955.
- [2] Gooding JJ and et al. Chem Soc Rev, 2011, 40(5): 2704-2718.
- [3] Ye Q and et al. Chem Soc Rev, 2011, 40(7): 4244-4258.
- [4] Fan X and et al. J Am Chem Soc, 2005, 127(45): 15843-15847.

Acknowledgments: Work supported by the National Natural Science Foundation of China (21174098 and 21334004).