

Deposition Mechanism of Nickel-Phosphorus Electroless Plating on Hydrogen-Bonded Molecular Assemblages Studied by X-ray Photoelectron Spectroscopy

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Amphoteric azopyridine carboxylic acids bearing a pyridyl group as a hydrogen acceptor and a carboxy group as a hydrogen donor at the respective molecular terminals can form fibrous hydrogen-bonded molecular assemblages with a submicron diameter.¹ We have recently reported that the fibrous molecular assemblages are available to a template-directed synthesis to prepare nickel-phosphorus (Ni-P) and copper nanotubes through electroless plating as illustrated in Figure 1.²⁻⁴ Azopyridine carboxylate anions dissolved in an alkaline aqueous solution are transformed to azopyridine carboxylic acids in neutralization by acidic substance, which form continuous hydrogen bonds between the hydrogen donor and acceptor, to give fibrous molecular assemblages of hydrogen-bonded polymers. Immersion of the fibrous molecular assemblages as templates in a PdCl₂ aqueous solution and in a Ni-P plating bath containing H₂PO₂⁻ as reductant, followed by removal of the organic template with an alkaline aqueous solution, result in formation of Ni-P nanotubes.

In this report, we described studies by X-ray photoelectron spectroscopy to comprehend deposition mechanisms of Ni-P electroless plating on hydrogen-bonded fibrous molecular assemblages formed from 6-(2-propyl-4-(4-pyridylazo)phenoxy)hexanoic acid.

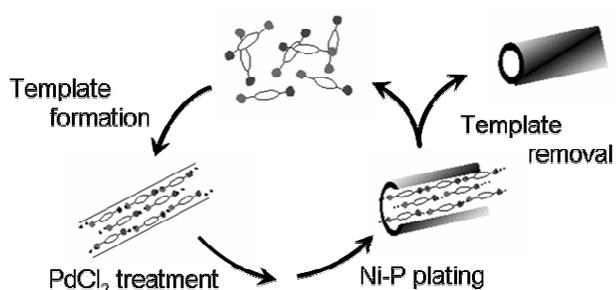


Fig. 1. Schematic illustration of a template-directed synthesis of Ni-P nanotubes involving template formation, PdCl₂ treatment, Ni-P plating and template removal.

To measure XPS spectra, we prepared three kinds of fibrous molecular assemblages after (I) template formation, (II) PdCl₂ treatment, and (III) NaH₂PO₂ treatment. Figure 2 indicates N(1s), Pd(3d) and Cl(2p) XPS spectra of each sample in left, middle and right columns, respectively, with a result for Na₂PdCl₄ as a

reference sample showed in marks (IV).

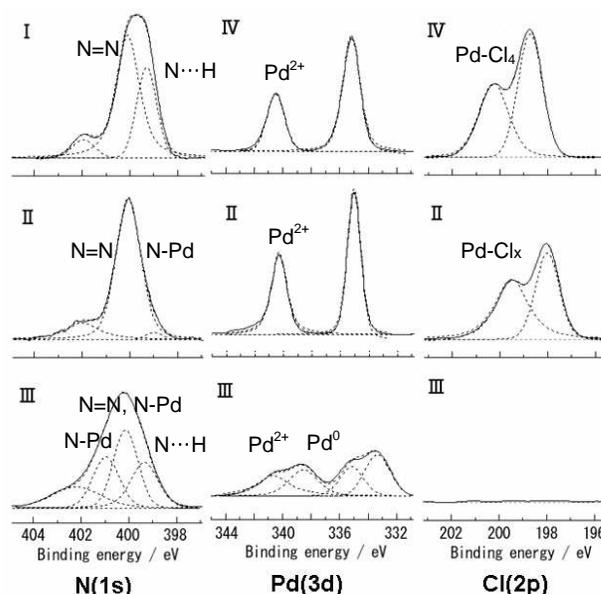


Fig. 2. N(1s) (left column), Pd(3d) (middle column) and Cl(2p) (right column) XPS spectra of fibrous molecular assemblages after (I) template formation, (II) PdCl₂ treatment, and (III) Na₂HPO₂ treatment and of (IV) Na₂PdCl₄ as reference.

An N(1s) XPS spectral profile of the sample after (I) template formation could be fitted to two major components with a peak binding energy of 399.3 and 400.1 eV, which were attributable to nitrogen atoms of a hydrogen bond (N...H) and a diazo bond (N=N). After (II) PdCl₂ treatment, the N(1s) peak at 399.3 eV was reduced and, alternatively, Pd(3d_{5/2}) and Pd(3d_{3/2}) peaks at 340.3 and 335.1 eV corresponding to Pd²⁺ appeared. In addition, a Pd-Cl bond with a low energy shift from 198.7 eV to 198.0 eV was observed for a reference sample of Na₂PdCl₄ in the Cl(2p_{3/2}) XPS spectrum. These results suggested that PdCl₄²⁻ ion in a PdCl₂ aqueous solution was reacted with a pyridyl group of the azopyridine carboxylic acids and PdCl_x species was coordinated on the pyridyl group. A coordination bond of Pd-N might be overlapped with the diazo bond at 400.1 eV in the N(1s) XPS spectrum. After (III) NaH₂PO₂ treatment, Cl(1s) peaks disappeared, and new Pd(3d) peaks at 399.3 and 338.5 eV attributable to metal palladium appeared.

From the XPS studies, we found out that Pd²⁺ ions were adsorbed through coordination bonds, subsequently reduced to Pd⁰ working as plating catalyst by reductant of H₂PO₂⁻ ions in the Ni-P plating bath. As a result, uniform electroless deposition will take place on a surface of the fibrous molecular assemblages because a molecular long axis of the component molecules aligns in parallel to a long axis of the template fiber.¹

- 1) Aoki, K. et al. *J. Am. Chem. Soc.* **2000**, *122*, 10997.
- 2) Nakagawa, M. et al. *JPO3533402*, registered in **2004**.
- 3) Ishii, D. et al. *Trans. Mater. Res. Soc. Jpn.* **2002**, *27*, 517.
- 4) Ishii, D. et al. *Trans. Mater. Res. Soc. Jpn.* **2003**, *28*, 577.