

Nitinol surface modification in gentle conditions by in situ generated diazonium salt

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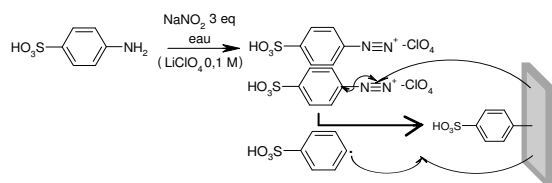


Fig. 1: Schematic representation of the work methodology

Nitinol (NiTi) is a nickel–titanium (~50/50) shape memory alloy that has become a material of great interest given its many possible applications especially in the biomedical field¹. However, one of the major problems of this alloy is its high nickel content (often more than 50%) and the cytotoxic nature of nickel(II)². Its biocompatibility properties result from the presence of a thin protective titanium dioxide surface layer which enhances corrosion resistance and prevents Ni²⁺ release¹. Therefore, in recent years, a great deal of attention has been paid to the surface modification of NiTi to impart and/or improve surface properties such as biocompatibility¹, bioactivity³ or corrosion resistance⁴.

Surface modification of metal by organics thin films is a widely studied topic. The formation of self-assembled monolayers (SAMs)⁵ and the electrochemical reduction of diazonium salts⁶ are two of the most commonly used methods to obtain such organic thin films. The covalent functionalization by grafting of diazonium has been abundantly studied in the past decades^{4,6-9}. However, purification and especially storage of diazonium salts can be problematic given the poor stability of these compounds.

Since the beginning of the past decade, a one-step procedure including in situ diazoniums generation from their amine precursor and their subsequent grafting in the same solution is actively investigated⁷. The in situ generation can be achieved by addition of either organic nitrite^{6,7} or sodium nitrite (NaNO₂) with acid⁶ as nitrosonium ion (NO⁺) precursor. This nitrosonium ion then reacts with the amine function of the precursor to form the diazonium function (i.e. diazotation reaction). The use of sodium nitrite and acid for the diazotation reaction is a versatile method that can be used in the two most commonly used solvents for this purpose i.e. water and acetonitrile (ACN)⁶. It is also an economical way to synthesize a diazonium salt from its amine precursor. The diazotation reaction is known to follow a 2 equivalent (eq.) acid/aniline ratio mechanism¹⁰. Yet, in practice, in situ generated diazonium grafting is generally described in literature with a large excess of acid (at least 8 eq.)⁸.

Biocompatibility and corrosion resistance of NiTi being due to the presence of a thin titanium dioxide layer the preservation of this layer during the modification step is critical. The use of a strongly acidic modification solution can result in the alteration and/or dissolution of this oxide layer and the loss of the NiTi biocompatibility and corrosion resistance properties. However, some authors have recently reported on the grafting of in situ generated diazonium using different aminobenzene organic acids both as precursor and as the only proton source⁹.

This work aims to graft in situ generated

diazonium salt on NiTi (figure 1). To the best of our knowledge, this modification method has never been applied to NiTi surfaces. The use of gentle conditions (i.e. aminobenzene organic acid used both as precursor and as the only proton source) for the diazonium electrografting (figure 2) allows to preserve the titanium oxide layer of NiTi (figure 3). Besides the surface state preservation, the surface modification with diazonium derived from aminobenzene organic acids such as 4-aminobenzenesulfonic acid (figure 1) leads to the covalent binding of easily chargeable chemical functions at the surface of NiTi. The presence of charged functions on surface is of great interest for post-modification steps such as the formation of layer-by-layer¹¹ (LBL) assembly of polyanions and polycations into multilayers. LBL is a very popular method for the formation of functional thin films. LBL functionalities such as drug delivery¹² are of great interest for the biomedical application of NiTi.

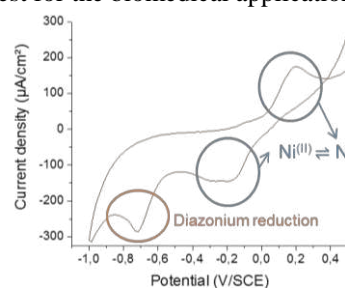


Fig. 2: Cyclic voltammogram of 5 mM sulfonic acid phenyldiazonium salt in situ generated at a NiTi electrode

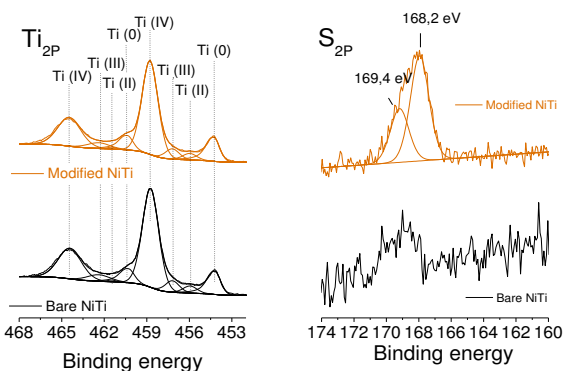


Fig. 3: XPS core-level spectrum C 1s and N 1s for bare and modified NiTi.

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