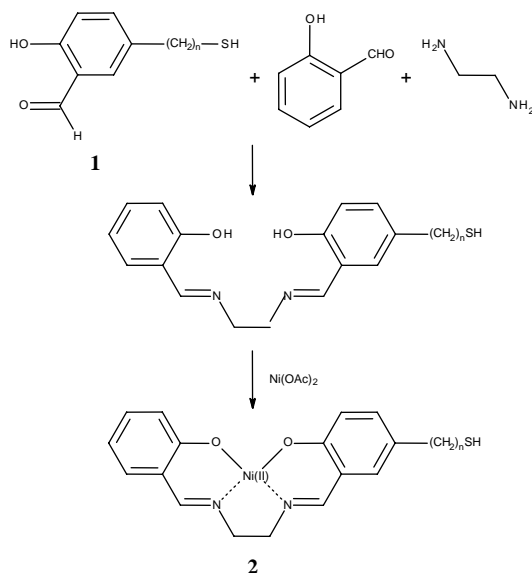


AN INITIAL STUDY OF COATING NICKEL SALEN ON GOLD ELECTRODE VIA SELF-ASSEMBLY

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Metal Schiff base complexes such as cobalt(II) salophen and oxovanadium(IV) salen have been used to prepare modified carbon paste electrodes for the electrochemical detection of various important compounds by catalytic oxidation or reduction (1). It has also been reported that nickel(II) salen can undergo anodic polymerization on different electrodes for the catalytic reduction of organic halides (2). For these studies, the catalysts are only physically embedded or adsorbed on the electrode surface, which could limit the sensitivity and robustness of the electrochemical sensors.

In this paper, the alkanethiol-modified salicylaldehyde (**1**, $n=6$ or 8) was prepared (3) for the synthesis of a novel nickel(II) salen with a side alkanethiol chain (**2**, Scheme 1), which was subsequently used to coat gold (Au) electrode via self-assembly, a well known chemisorption process. The surface-modified gold electrode was examined by cyclic voltammetry. The corresponding electrochemical properties were characterized by both oxidation and reduction.



Scheme 1. Synthesis of alkanethiol-modified nickel(II) salen.

Fig. 1 depicts the cyclic voltammograms (CV) of **2** ($n=8$) self-assembled on gold electrode surface in DMF recorded at a scan rate of 100 mV s^{-1} between $+0.25 \text{ V}$ and $+1.25 \text{ V}$ vs. SCE. The first anodic scan for the adsorbed nickel(II) salen gives an oxidation peak at $+0.90 \text{ V}$, which quickly decreases and disappears with the following scans. This irreversible wave can be assigned to the oxidation of nickel(II) to nickel(III) salen, which may undergo intramolecular electron-transfer reaction to generate a polymerized film (2). Due to the formation of a more conjugated structure, the immobilized polymer film shows a redox couple at approximately -0.50 V when scanned in the negative direction (Fig. 2). The new cyclic voltammetric peaks seem to be reversible and appear at potentials much more positive than those for the reduction of nickel(II) to nickel(I) salen (-1.66 V) (4), indicating electrons can be easily transferred to the film.

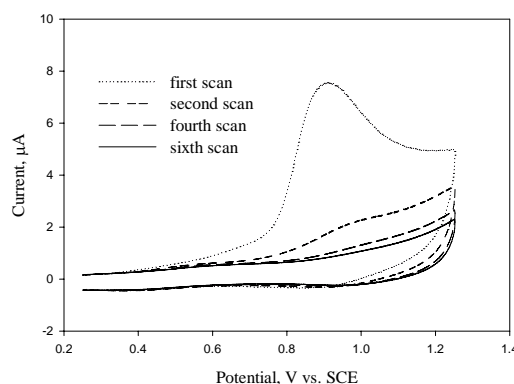


Fig. 1. CVs recorded at 100 mV s^{-1} in DMF containing 0.050 M TMABF_4 for **2** ($n=8$) adsorbed on a gold electrode (2 mm in diameter).

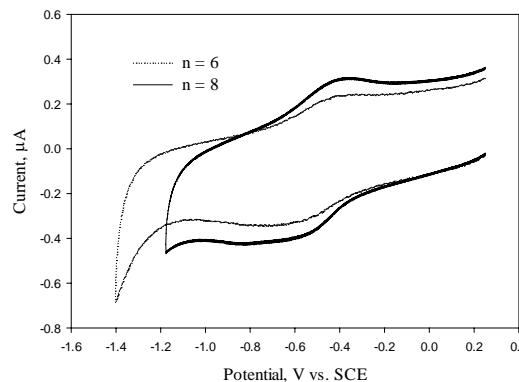


Fig. 2. CVs recorded by scanning the potential in the negative region at 100 mV s^{-1} in DMF containing 0.050 M TMABF_4 for polymerized **2** on gold electrode.

When the potential is scanned to more negative region for the catalyst-modified gold electrode, no distinctive redox waves are observed for the reduction of nickel(II)-nickel(I) salen couple. This electrochemical behavior is similar to that of polymer-bound nickel salen on glassy carbon electrode (2b), at least to some extent. A large cathodic peak shows up at approximately -2.0 V , corresponding to desorption of the polymer film from electrode surface. CVs also illustrate that the diffusion of ferrocene to gold electrode surface can be efficiently blocked by the catalyst film (Fig. 3). The alkanethiol chain length ($n=6$ or 8) does not significantly affect the electrochemical properties of the surface-modified electrode, which is reasonably stable in acidic media.

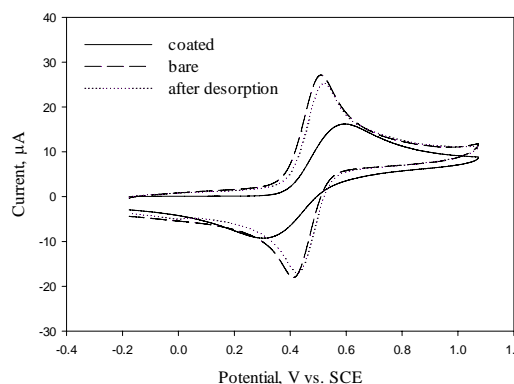


Fig. 3. CVs of 2.4 mM of ferrocene recorded for various Au electrodes.

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