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## ELECTROCHEMICAL CODEPOSITION OF CERAMIC NANOCOMPOSITE FILMS

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### ABSTRACT

A novel method for deposition of ceramic nanocomposite films has been developed. This approach allows controlling the exact composition of the deposit, e.g., Cu-TiO<sub>2</sub>, Au-SiO<sub>2</sub> and should enable the formation of a wide variety of coatings such as graded films, catalysts etc, in a straightforward approach.

Sol-gel films are traditionally deposited via spin-coating, dip-coating or spraying. We describe a single step electrochemical deposition method for the preparation of ceramic nanocomposite films in which micro and nanoparticles are embedded. It is based on the electro-assisted deposition of sol-gel thin films. According to this methodology, applying either negative or positive potentials to a conducting substrate alters the pH at the electrode surface, which catalyses the polymerisation of sol-gel monomers, leading to the deposition of the appropriate oxide films.

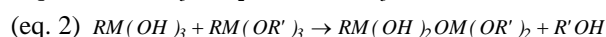
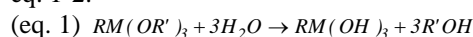
We have applied this method for preparing thin films of metal ceramic materials, such as copper-titania and copper-silica and the introduction of different nanoparticles into sol-gel coatings. Organic nanoparticles have also been incorporated in the course of the electrodeposition.

### 1. INTRODUCTION

Electrodeposition of ceramic films employing electrochemical methods is a fast evolving field [1-6]. The methods for electrodeposition may be divided into two: electrophoretic and electrolytic deposition. Electrolytic deposition can be driven using cathodic currents by either reducing the metal ions, which causes their deposition, e.g., Cu<sub>2</sub>O, or by driving a proton-dependent reducing process, leading to an increase of the pH on the electrode surface and the subsequent metal hydroxide deposition. Alternatively, the deposition of metal oxides and hydroxides can be driven by anodic currents as a result of oxidizing the metal ions, thus increasing their oxidation state, which usually results in lower solubility of their hydroxide salts, such as in Fe(OH)<sub>3</sub> deposition.

Ormocers (ORganically MODified CERamics) are metal oxides that are formed at room temperature and comprise organic moieties. They are formed as a result of the

hydrolysis and condensation of functionalized trialkoxymetals, e.g., alkyl-trimethoxysilanes, as shown in eq. 1-2:



There are enormous advantages to using sol-gel technologies for preparing thin films as the non-hydrolyzable group, R, can be used to tune the chemical and physical properties of the coating.

The electro-assisted deposition of ormocers has recently been reported by us [7-10]. This approach takes the advantage of enhancing the hydrolysis and condensation (both processes are acid and base catalyzed) of the sol-gel process by altering the pH at the surface as a result of applying a potential.

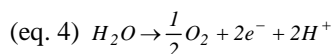
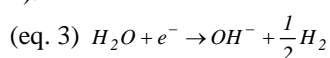
The deposition of ceramic nanocomposite materials is of utmost importance in different fields spanning from supercapacitors to anticorrosion films and from coatings of medical implants to advanced lubricant materials [11-14]. We report here the formation of ceramic nanocomposite materials by our electrochemical codeposition method. We have succeeded to electrochemically codeposit different sol-gel materials, such as organic derivatives of silica and zirconia and metallic and inorganic micro and nanoparticles and conducting and non-conducting polymers.

### 2. EXPERIMENTAL

Electrochemical codeposition was carried out in a conventional three-electrode cell equipped with a working electrode, reference electrode and a counter electrode. The working electrode on which the nanocomposite thin film was deposited was made of different materials, including thin gold film, 316L stainless steel and indium tin oxide (ITO). The deposition solution consisted of a sol-gel monomer, e.g., tetramethoxysilane, ethanol, 0.1 M HCl aqueous solution and an electrolyte (0.1 M LiClO<sub>4</sub> or tetrabutylammonium tetrafluoro borate). The electrode was attached to a home-made lifter that allowed the controlled withdrawal of the electrode from the deposition solution. A constant potential for a given time was applied to the working electrode using a potentiostat after which the electrode was withdrawn from the solution and dried at room temperature for 24 hr before use.

### 3. RESULTS AND DISCUSSION

Deposition of sol-gel materials involves hydrolysis of the monomers and condensation (eq. 1-2). Both these reactions are acid and base catalyzed, which means that the rate of deposition can be significantly enhanced by altering the pH. The latter can easily be controlled in the vicinity of an electrode by applying a potential or current that causes the reduction or oxidation of protic solvents, such as water and alcohols. Negative potentials or cathodic currents increase the pH due to solvent reduction and generating a strong base (eq. 3), whereas positive potentials or anodic currents decrease the potentials as a result of solvent oxidation and generation of protons (eq. 4).



Hence, we have used initially this approach for the electrochemical deposition of different sol-gel films based on silica, zirconia and titania [8-10].

Recently, we have focused on the electrochemical codeposition of nanocomposites based on sol-gel films and different additives.

Four different systems have been employed by us: metal ions, which were electrochemically reduced in the course of the polymerization, nanoparticles, which were incorporated into the sol-gel matrix, polymers being codeposited with the sol-gel and conducting polymers that were electropolymerized simultaneously with the sol-gel.

Prior to deposition the potential was scanned in order to determine the optimal potential for the reduction or oxidation of the solvent, and at the same time, to avoid massive evolution of hydrogen (at negative potentials) or oxygen (at positive potentials). Figure 1 shows the cyclic voltammetry recorded with a stainless steel 316L (SS) electrode in 0.1 M HCl solution and a silane monomer, i.e., phenyltrimethoxysilane (PhTMOS). It can be seen that the cathodic current begins to increase at ca. -0.5 V vs. Ag/AgBr. This current is due to water reduction (eq. 3) and plays a major role in the enhancement of the condensation and deposition of the sol-gel.

This approach has been further extended to the electrochemical codeposition of sol-gel and other substances, such as metals, nanoparticles and polymers.

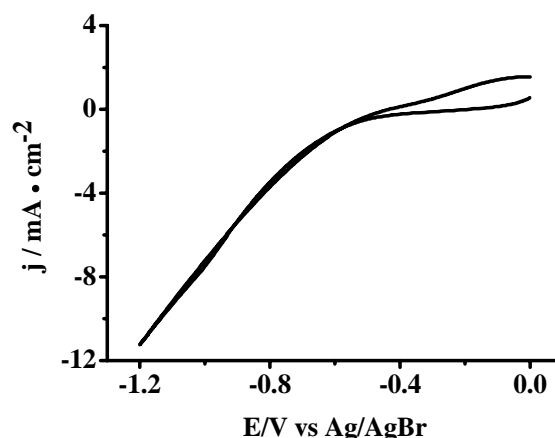
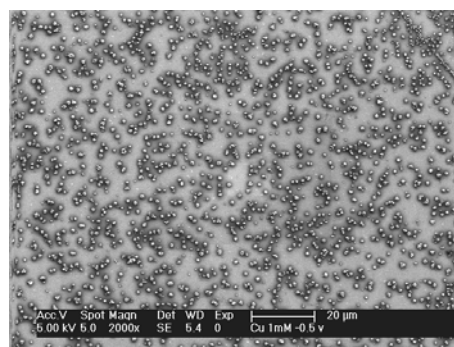


Figure 1: Cyclic voltammetry of a stainless steel 316L electrode recorded in 0.1 M HCl solution, 65% (v/v) of ethanol and 10% (v/v) PhTMOS.

#### 3.1. Electrochemical codeposition of sol-gel and copper

Adding electro-reducible metal ions, e.g.,  $\text{Cu}^{2+}$ , to the

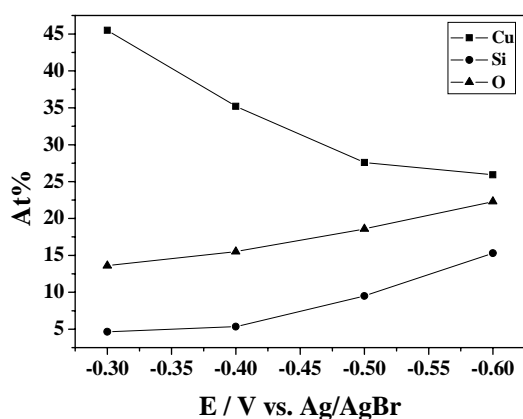


deposition solution allows codepositing the sol-gel and the metal that is electrochemically reduced.

Figure 2: SEM image of  $\text{Cu/SiO}_2$  electrodeposited film (1 mM  $\text{CuCl}_2$ ) after applying negative potential of -0.5 V on an ITO substrate for 10 min.

Figure 2 shows SEM image of film that was deposited upon applying negative potential in the presence of cupric ions. EDX analysis confirmed that the deposits are made of copper and the area between the deposits contains mostly silica. Moreover, we found that the applied potential strongly affected the morphology and grain size of the deposited copper. As the applied potential was more negative, the average size of the grains decreased and their density increased.

Figure 3 displays the atomic percent of the elements, i.e., Cu, Si and O in the film (from the EDX analysis) as a function of the applied potential. It can be seen that as the applied potential was more negative, the amount of the deposited copper decreased and, at the same time, the content of silicon and oxygen increased respectively. Shifting the potential to negative values should increase the heterogeneous kinetics of both the reduction of  $\text{Cu}^{2+}$  and that of  $\text{H}^+$ . However, since  $E^0$  of cupric ions is more positive than that of protons, it is likely that the reduction of  $\text{Cu}^{2+}$  will become diffusion-controlled and therefore



potential independent.

Figure 3: Atomic percent of copper, silicon and oxygen in the deposited films as a function of the applied potential. The concentration of  $\text{Cu}^{2+}$  in the deposition solution was 1 mM and time of deposition was 10 min.

### 3.2. Electrochemical codeposition of sol-gel and nanoparticles

Metallic as well as inorganic and organic nanoparticles can also be codeposited with the sol-gel. Figure 4 shows a cross-section of a coating formed upon adding onto a tetramethoxysilane solution hollow silica nanoparticles containing a fluorescent dye. It can be seen that the layer is made of a dense phase embedded with nanoparticles. Fluorescent optical microscopy indicates that the fluorescence of the dye is kept upon electrochemical codeposition (not show).

Au nanoparticles stabilized by different trimethoxysilane derivatives, which were prepared following the literature [15-17] have been also codeposited onto a variety of surfaces including stainless steel and gold. The different parameters, which affect the density of nanoparticles within the film, have been studied. In general, the most important parameters are the potential of deposition and concentration ratio between the nanoparticles and the sol-gel monomers.

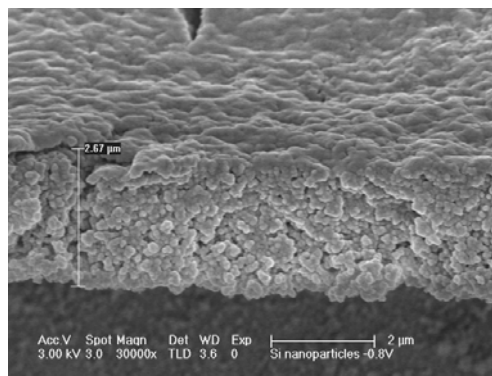


Figure 4: Electrochemically deposited films made of silica nanoparticles containing a fluorescent dye and tetramethoxysilane. The film was obtained as a result of applying -0.8 V to an indium tin oxide electrode for 10 min.

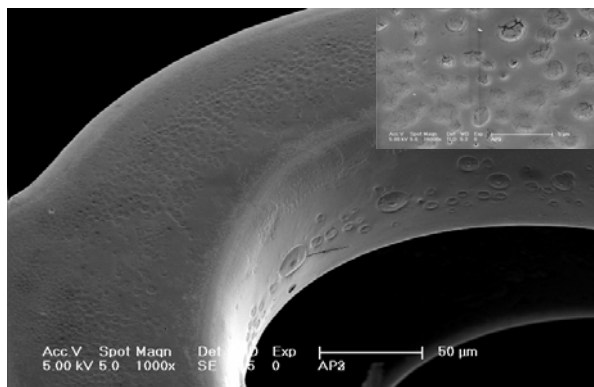
### 3.3. Electrochemical codeposition of sol-gel and non-conducting polymers

The incorporation of different substances in the course of the electrochemical codeposition of sol-gel is quite generic and requires only the interaction between the substance and the sol-gel monomers. Hence, for example, it is possible to codeposit different polymers, such as polyethyleneoxide and its derivatives. Moreover, one of the significant advantages of electrochemical coating is the ability to coat complex geometries including medical devices.

Figure 5 shows SEM image of a stent coated with an aminopropyltriethoxysilane based coating, which was electrochemically deposited in the presence of pluronic 127 (a block copolymer based on polyethylene oxide and polypropylene oxide). Although the two components were completely dissolved in the deposition solution, the two distinct phases, so-called two-phase structure of the film, can be clearly observed in the higher magnified image (Figure 5, inset). In this case, the codeposited polymer segregates presumably due to better intramolecular interactions and therefore two phases are formed. There are other cases in which segregation is not observed and a homogeneous phase is formed.

It is possible also to codeposit sol-gel with hydrophobic polymers from suspension. This allows creating coatings with hydrophobic sites, which can be used as a means of carrying hydrophobic drugs. Figure 6 shows an example of such coating electrocodeposited on a stent from solution containing tetramethoxysilane and SIBS (poly(styrene-*b*-isobutylene-*b*-styrene)). The latter is a triblock polymer, which is used as the drug carrier for entrapping Paclitaxel in a commercial stent. EDX analysis of the two phases found on the surface reveals an organic region of the polymer, which is poor in silicon and rich in

carbon (black curve in the EDX figure) and a sol-gel region, which contains mostly oxygen and silicon (non-



filled curved in the EDX figure).

Figure 5: SEM image of a stainless steel stent electrochemically coated with sol-gel (APTEOS) and Pluronic 127. The concentration ratio between APTEOS:Pluronic 127 was 10:1.

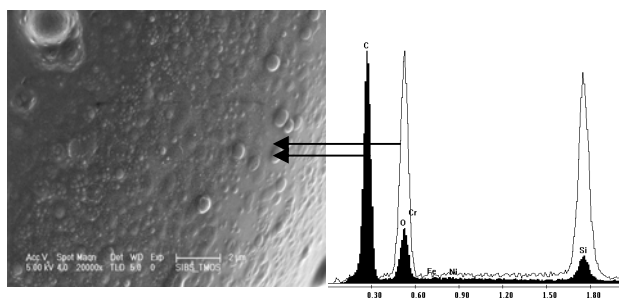


Figure 6: SEM image of electrocodeposited TMOS and a hydrophobic polymer (SIBS). EDX analysis of the coating in sol-gel (non-filled curve) and polymer (black area) sites.

### 3.4. Electrochemical codeposition of sol-gel and conducting polymers

Conducting polymers, e.g., polypyrrole, polyaniline and polythiophene, can readily be formed by anodic electropolymerization of the monomers. The polymers are electronically conducting and are envisioned as the future metals. We have succeeded to electrochemically deposit polypyrrole and sol-gel following our approach.

Specifically, polypyrrole (PPy)/sol-gel composites films were prepared by carrying out the electrochemical polymerization of pyrrole simultaneously with electrochemical deposition of triethoxysilane (TEOS) under positive potentials.

The positive potential was required to oxidize the pyrrole and at the same time it decreased the pH by generating

protons on the surface as a result of water oxidation (eq. 4).

Figure 7 shows SEM image of PPy/TEOS composite film deposited onto an ITO substrate after applying a constant positive potential.

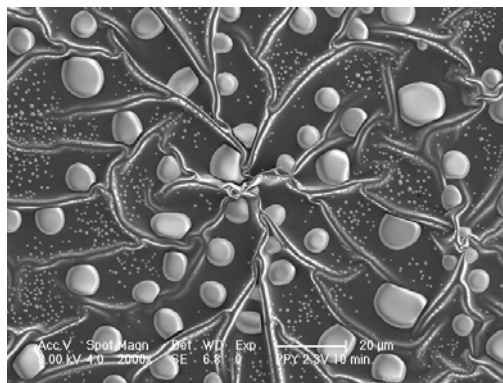


Figure 7: SEM image of an electrochemically deposited PPy/sol-gel film.

The potential affects the ratio between the electropolymerization of monomers of the conducting polymer and electrodeposition of the sol-gel as can be seen in Figure 8.

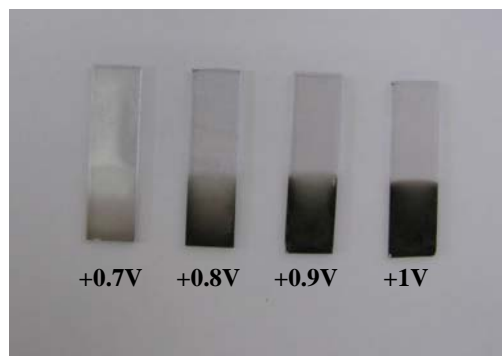


Figure 8: Photo of a series of ITO substrates on which PPy/TEOS films were deposited under different potentials (as marked in the photo).

It is evident that as the potential was more positive the film became darker indicating the higher percentage of PPy. We are currently studying the conductivity of these films.

## 4. CONCLUSIONS

We have developed a novel method for the controlled deposition of hybrid nanocomposite materials. The method is based on altering the pH by the oxidation or reduction of a protic solvent in the presence of sol-gel monomers. Codeposition occurs as a result of either

oxidizing or reducing a second substance or in case where it interacts with the sol-gel matrix. The control of the codeposition process is very high since the potential as well as the ratio between the sol-gel monomers and the other component govern the rate of deposition and the composition of the deposited film. This approach benefits from the advantages of electrodeposition and at the same time can be applied to non electroactive species.

## 5. ACKNOWLEDGMENT

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