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Facile assembly of polyoxometalate-polyelectrolyte films on nano-MO_2 (M = Sn, Ti) for optical applications

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Abstract

The polyoxometalate $[PMo_{12}O_{40}]^{3-}$ (POM) has been deposited onto high surface area nano-SnO_2 using a polycation. The POM surface coverage recorded was approximately 17 times higher than that achieved on planar substrates using the same method, reducing considerably the time needed to assemble conducting films suitable for optical applications such as electrochromism. The immobilisation of the analogous tungstate $[PW_{12}O_{40}]^{3-}$ onto a nano-TiO_2 semiconductor electrode demonstrates the versatility of this approach, and underscores potential applications using a large combination of polyoxomolybdates or polyoxotungstates with various metal oxide films.

1. Introduction

Polyoxometalates comprise a wide class of molecular metal oxide clusters suitable for diverse applications spanning photochemistry, electrochemistry, catalysis, and sensing.[1] The majority of POMs are anionic, rendering them highly soluble in either water or organic solvents, depending on the counterion employed. Relatively ordered POM films can be created through layer-by-layer (LBL) assembly consisting of alternating polyelectrolyte and POM layers. This involves alternately dip-coating an electrode material into solutions of anionic POM and various cationic species, rinsing between each cycle, to build up multilayer structures. This method is straightforward, removes the need for complex covalent modification of the POM, is robust, and is widely applicable to a host of POM-based systems.[2]

However, there are several disadvantages to the electrostatic multilayer LBL approach. First, each cycle deposits approximately a monolayer of POM and thick (of the order of 100-200 nm) films require multiple deposition cycles which is a slow process, e.g., a 16-bilayer film requires 32 dip steps and would only be *ca*. 100 nm thick.[3] Second, we have shown previously that the rate of charge transport through thicker films consisting of the polyoxometalate α-$[S_2Mo_{18}O_{62}]^{4-}$ and a polycationic Ru(II) metallopolymer is slow due to mass transfer limitations, making thicker films less useful in photoelectrocatalytic applications (time to electrolyse whole film 2 - 50 s).[4] In principle, low film conductivity can generally be addressed by either (a) increasing the supporting electrolyte concentration or (b) by incorporating conducting materials into the film - this has successfully been used in electrocatalytic applications using, for example, multi-walled carbon nanotubes.[5] However, for applications involving an optical component (photocatalysis, photoelectrochemistry, colorimetric sensing, electrochromic displays, photochromism) the addition of particulate or coloured materials into a film can, while rendering the film conducting, also significantly change its optical properties. In addition, high electrolyte concentrations can disrupt the electrostatic interactions which drive the formation of the film.[6] The ideal POM based film would therefore be facile to assemble, be optically transparent, and be amenable to fast potential switching.

Fluorine-doped tin oxide (FTO) has found widespread use as a transparent, planar conducting substrate in photovoltaics and photoelectrochemistry. However, monolithic, planar materials are a poor choice for catalysis and light harvesting due to their inherently low surface areas. Nanoparticle films immobilised on FTO have been used extensively over the past decades to increase surface loading of the material of interest, in effect making a transparent, high surface area electrode; in particular TiO_2 has been used to great effect in dye-sensitized solar cells.[7] While TiO_2 makes an excellent electrode material for immobilising electrocatalyst molecules, its