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Hybrid layer-by-layer films based on lanthanide-bridged silicotungstates and poly(ethylenimine)

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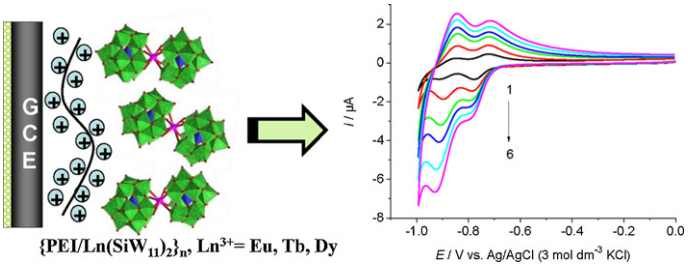
HIGHLIGHTS

- Layer-by-layer hybrid films $\{PEI/Ln(SiW_{11})_2\}_n$, Ln^{3+} = Eu, Tb, Dy were prepared.
- UV–vis was used to monitor film build-up and showed regular stepwise film growth.
- XPS confirmed successful $\{PEI/Ln(SiW_{11})_2\}_n$ film fabrication.
- The films showed two W-based reductions due to the immobilized $Ln(SiW_{11})_2$.
- Typical Eu photoluminescence was observed for $\{PEI/Eu(SiW_{11})_2\}_n$.

GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid multilayer films composed of poly(ethylenimine) and sandwich-type silicotungstates, $K_{13}[Ln(SiW_{11}O_{39})_2]$ ($Ln(SiW_{11})_2$), Ln^{3+} = Eu, Tb, Dy, were prepared on glassy carbon electrodes, quartz and glass slides using the electrostatic LbL self-assembly method. The film build up, monitored by electronic spectroscopy, showed a regular stepwise growth indicating a strong interaction between layers. The X-ray photoelectron spectroscopy measurements corroborated the successful fabrication of the hybrid films with the PEI–POMs composition and pointed out that the intrinsic charge compensation from the film components is the major contribution, although there is some extrinsic charge compensation from the counter cations from the POMs and electrolyte. All the LbL films showed W-based reduction processes due to the immobilized POMs; voltammetric responses revealed a kinetic facilitation of the first reduction process in the immobilized $Tb(SiW_{11})_2$ and $Dy(SiW_{11})_2$ polyanions relatively to the free POMs and scan rate effect showed that the tungsten reduction process for all POMs is surface-confined. The photoluminescence properties of $PEI/Eu(SiW_{11})_2$ multilayer films were investigated and showed the characteristic Eu^{3+} emission pattern.

1. Introduction

In recent years functional multilayer films incorporating various inorganic and/or organic building blocks have attracted great attention due to their potential applications in catalysis, optics, sensors and display technologies [1–3]. Layer-by-layer (LbL) self-assembly has proved to be a promising bottom-up method for the preparation of nanostructured multilayer films because it is of simple execution and versatile from the point of view of thickness and composition control and can be easily adapted to automated fabrication, which is beneficial for industrial purposes. The driving force for the multilayer build-up includes electrostatic interactions, donor/acceptor interactions, hydrogen bonding, covalent bonds or specific recognition.

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