Polyoxometale-Stabilized Metal Nanoparticles: Potential Candidates for Energy Storage Applications.

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ABSTRACT: Polyoxometalates (POMs), redox active anionic metal–oxide clusters, display an extraordinary range of physicochemical properties and are some of the most promising building blocks for functional nanomaterials. The most important functionality of POMs involves their unique electrochemical behaviour.^[1] Due to the high stability of their redox states, they can participate in fast reversible multielectron-transfer reactions, making them potential candidates to achieve a high capacity for energy storage applications. Anchoring POMs on carbon materials effectively increases the number of electroactive sites for electrochemical reactions. Indeed, POM–based hybrid electrodes with a variety of nanocarbon materials have been reported.^[2-5] This combination is particularly effective for applications in hybrid supercapacitors (SCs) that combine the high power and long-term stability of SCs and the high energy density of batteries, as the carbon support contributes double-layer capacitive effects, while the POM provides faradaic charge storage.^[6] However, POMs have poor electrical conductivity, which can have a detrimental influence on specific capacitance and cycling stability.

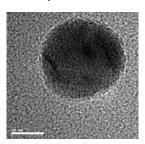


Figure 1. TEM image of POM-stabilized Silver NPs.

Nobel metal (M⁰) nanoparticles (NPs) have been widely used as conductive dopants in electrode materials for SCs due to their good conductivity and electrochemical stability.^[7,8] By combining POMs with M⁰ NPs, it is hoped to promote desirable synergistic properties and functionalities and yield composites with improved capacitive performance and cycle life. Moreover, the combination of M⁰ NPs with carbon materials enhances the electrical double layer capacitance by providing larger electrochemically active materials.^[9] POMs have been exploited for directing the synthesis of M⁰ NPs.^[10] POM–stabilized M⁰ NPs have received enormous attention because of their unique chemical and physical properties with different applications (catalysis, biosensors, biomedicine).^[11] However, their use in electrochemical energy storage remains largely unexplored. Hence, this work presents an optimized

green and reproducible protocol of synthesis to obtain M⁰ NPs stabilized with POMs, with low polydispersity and high stability. Their morphological properties are characterized using electron microscopy (**Figure 1**) and their structural and chemical properties are analysed using X-ray diffraction, X-ray photoelectron spectroscopy, IR spectroscopy and electrochemical methods. Finally, we present the incorporation of the M⁰ NPs with POMs and activated carbon to create a hybrid tricomponent composite electrode. The composite is characterized and its potential as electrode material for energy storage application is preliminary assessed.

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SmallChem2021