

Silsesquioxane organofunctionalized with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole: Preparation and subsequent reaction with silver and potassium hexacyanoferrate(III) for detection of L-cysteine



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ABSTRACT

The octakis(3-chloropropyl)octasilsesquioxane (SS) was organofunctionalized with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald). The functionalized silsesquioxane with Purpald (SP) was characterized by Fourier transform infrared spectroscopy (FT-IR), and nuclear magnetic resonance (NMR). After functionalized, silsesquioxane can interact with silver nitrate and subsequently with potassium hexacyanoferrate (III) (AgHSP). The novel hybrid composite formed (AgHSP) was characterized by Fourier transform infrared spectra, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). AgHSP was electrochemically characterized by cyclic voltammetry (CV) using graphite paste electrode. The AgHSP incorporated into a graphite paste electrode (20% w/w) was tested for detection of L-cysteine. The modified electrode showed a linear response from 9.0×10^{-5} to 5.0×10^{-3} mol L⁻¹ with the corresponding equation $Y(A) = 0.01315 + 1.865 [L\text{-cysteine}]$, and a correlation coefficient of $r^2 = 0.9995$. The method showed a detection limit of 1.76×10^{-4} mol L⁻¹ with a relative standard deviation of $\pm 2\%$ ($n = 3$) and amperometric sensitivity of 1.865 A/mol L⁻¹.

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1. Introduction

Polyhedral oligomeric silsesquioxanes (POSSs) are among the most promising and rapidly emerging materials in the field of nanoscience. The term polyhedral derives from the precise geometry of the POSS cage, which strongly resembles a polyhedron. The term "silsesqui" refers to the ratio of the silicon and oxygen atoms, i.e., Si:O = 1:1.5 [1–3]. In the cubic silsesquioxane, the number of silicon atoms (8) on each POSS molecule ($(\text{SiO}_{3/2})_8\text{R}_7\text{X}$), is not the only parameter characterizing the different POSS compounds. R generally indicates a chemically stable substituent organic group such as methyl, phenyl or vinyl. These organic groups may act as compatibilizers and solubilizers of the POSS molecules with organic media, while X is a highly reactive substituent group, such as Cl, NH₂, OH or OR, and when R = X, a potential precursor in the formation of new hybrid materials for chemical modification or polymer grafting. Thus, for polymeric systems with different R and X, a wide variety of chemical compounds can be obtained [4–6]. Generally,

octafunctional cubic cages are called "T8", while Q8 refers to analogues of the T8, but with the addition of the OSiMe₂ spacer group at each corner [7]. POSSs are known as hybrid organic–inorganic nanocomposites – the inorganic core provides stability to the molecule and organic arms can establish its specific properties [7–11]. In particular, due to the highly symmetrical three-dimensional nature of their nucleus, POSSs are good precursors for the production of hybrid organic–inorganic materials [6,12] and these nanomaterials have recently shown great or advantageous functional properties for a wide range of technological applications, such as dendritic precursors [13–16], polymer precursors [17,18], as precursors for developing liquid crystals [19,20], homogeneous and heterogeneous catalysis [21,22], electroactive films [23], additives [24,25], antibacterial [26], and also used in thin films and coatings for various applications, including nanocomposites [10,11,27]. Thus, silsesquioxanes containing the chlorine element at their ends, such as octakis(3-chloropropyl)octasilsesquioxane, can be easily modified by the organic/inorganic process. Depending on the peripheral groups, a new material with different properties and applications [13] can be obtained. Thus, the chemistry of organofunctionalized silsesquioxanes has emerged as a fascinating new field of modern nanotechnology [28,29].

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Some studies were recently published by the Do Carmo research group on the role of chemically modified silsesquioxanes, which act as electron mediators or electrochemical sensors [30–34].

A synergistic effect of these structures was observed after the specific chemical modification of these nanostructured materials. The large surface area, the presence of metallic sites and the synergistic effect provided by the peripheral cube groups make these materials potential candidates to be used as catalysts and electrocatalysts and chemical and electrochemical sensors. The electroanalytical field has few studies about modified silsesquioxanes as substrates, acting as electron mediators or electrochemical sensors.

In this paper we report on the preparation and characterization and thermal behavior of polyhedral oligosilsesquioxane with Purpald® (SP). Additionally, based on our interest in developing modified electroactive hybrid composites for electroanalytical purposes, an electroanalytical application of this material is proposed. The functionalized polyhedral oligosilsesquioxane with the Purpald® (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole), (SP), and respective interactions with Ag^+ and potassium ferrocyanide (III) follow two stages. At the first stage the SP adsorbs Ag^+ and at the second stage the composite formed (AgSP) reacts with hexacyanoferrate (III) forming a new composite (AgHSP). The preliminary characterization and voltammetric studies on these materials and their use for sulfite determinations have not been published yet [35]. Purpald® (Fig. 1(B)) is a chromogenic agent that is commonly used in the determination of aldehyde. Purpald® has S–C–N linkages and displays potential ligands for metal complexes that may also be biologically active just like some other amine- and thione-substituted triazoles [36]. Thus, the interest in using this ligand is due to the fact that it has NH_2 sites conducive to organofunctionalization with octakis(3-chloropropyl)octasilsesquioxane, as well as S groups that are

excellent active sites for the adsorption of metal ions. Thus S will be used to chelate the Ag^+ ions.

The idea is that AgHSP can provide a good electron transfer between the substrate (i.e., enzyme) and the electrode. Additionally, the presence of silsesquioxane, which is an electron acceptor [22], can provide a stabilizing microenvironment around the substrate. After rigorous voltammetric studies, the composite was tested for the electrocatalytic determination of L-cysteine.

2. Experimental

2.1. Reagents and solutions

All reagents and solvents were of analytical grade (Alpha Aesar, Sigma, Merck or Aldrich) and were used as purchased. All solutions and supporting electrolytes were prepared using Milli-Q water. The 0.1 mol L^{-1} NaOH solution was used to adjust the different pHs.

2.2. Synthesis of octakis(3-chloropropyl)octasilsesquioxane (S)

A procedure described in the literature was followed for the synthesis of octakis(3-chloropropyl)octasilsesquioxane (S) (Fig. 1) [37].

800 ml of methanol, 27 ml of hydrochloric acid (HCl) and 43 mL of 3-chloropropyltriethoxysilane were added into a 1000 mL round-bottom flask. The system was kept under constant stirring at room temperature for 6 weeks. The solid phase was separated by filtration in a sintered plate funnel, yielding a white solid, octakis(3-chloropropyl)octasilsesquioxane (S), which was then oven dried at 120°C for 4 h. Fig. 1(A) illustrates a representative scheme of this synthesis.

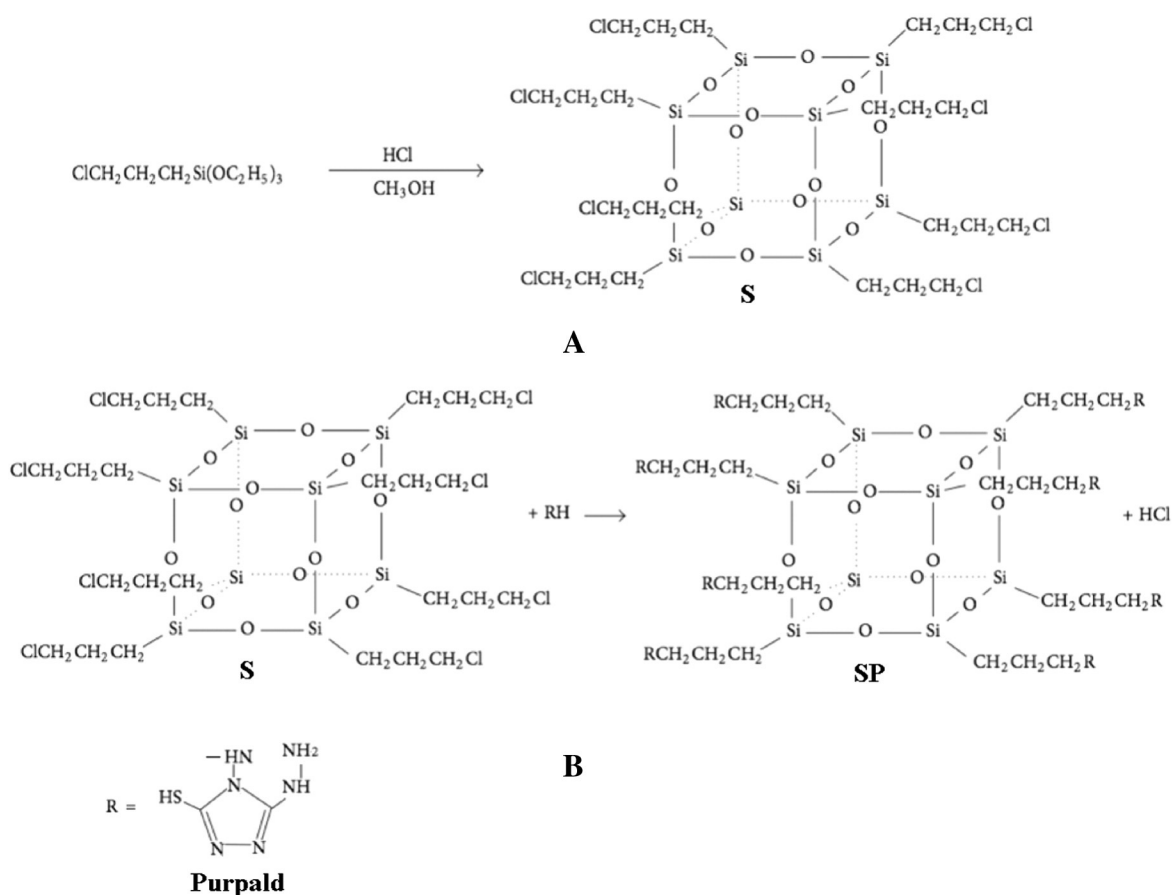


Fig. 1. (A) Schematic representation of the preparation of octakis(3-chloropropyl)octasilsesquioxane (S) [38]. (B) Organofunctionalization of octakis(3-chloropropyl)octasilsesquioxane (S) with the modifying agent Purpald®.

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