

Interfacial Hydrogen Atom Transfer by nanohybrids based on Humic Acid Like Polycondensates



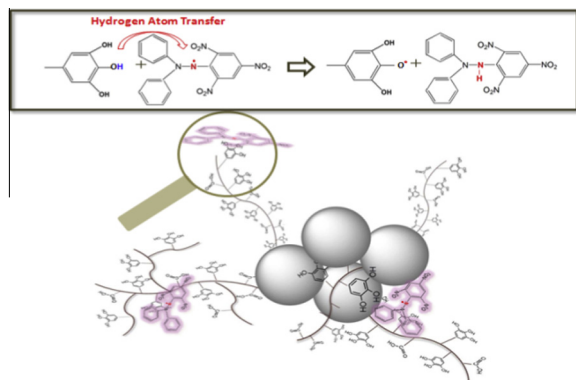
Eleni Bletsa^a, Panagiota Stathi^b, Konstantinos Dimos^c, Maria Louloudi^b, Yiannis Deligiannakis^{a,*}

^a Department of Physics, University of Ioannina, GR-45110 Ioannina, Greece

^b Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece

^c Department of Materials Science & Engineering, University of Ioannina, GR-45110 Ioannina, Greece

GRAPHICAL ABSTRACT



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ABSTRACT

Novel nano hybrid materials were prepared by covalent grafting of a polyphenolic polymer [Humic Acid Like Polycondensate (HALP)] on SiO₂ nanoparticles. Four nano hybrids were so-produced, using four different types of SiO₂ i.e. three Aerosil flame-made nanoparticles with nominal specific surface area of 50, 90 and 300 m²/g, herein codenamed OX50, A90, A300 respectively, plus a colloidal SiO₂[S300] with SSA = 300 m²/g. The antioxidant activity of the SiO₂-HALP nano hybrids was evaluated by assessing their kinetics for Hydrogen Atom Transfer [HAT] to DPPH radicals. When normalized per same HALP concentration, bigger NPs SiO₂[OX50]-HALP NPs can scavenge 280 μmoles of DPPH radicals per gram of HALP, while [A90]-HALP and [A300]-HALP NPs can scavenge 514 and 832 μmoles of DPPH radicals per gram of HALP, respectively. The colloidal SiO₂[S300]-HALP can scavenge fewer DPPH radicals (252 μmoles) per gram of HALP. Based on detailed kinetic data it is shown that (i) surface grafted HALPs perform 300% better HAT than non-grafted HALP in solution. (ii) By controlling the particle type and grafting-loading, we can control/optimize the HAT performance: when grafted on the appropriate SiO₂ surface the HALP macromolecules are able to quench up to 0.8 mmoles of DPPH-radical per gram of HALP.

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* Corresponding author.

E-mail address: ideligia@cc.uoi.gr (Y. Deligiannakis).

1. Introduction

Antioxidants are one of the principal components in human health protection from oxidative stress [1,2], protection of food quality [3,4] as well as in preventing molecular deterioration in materials industry [5]. Typically, antioxidants act against reactive radical species [6,7].

The free radicals are generated by various metabolic processes and environmental stress [8].

The complex implications of free radical reactions in biology and medicine are well known [6,9,10]. The relationship between free radicals and antioxidants are widely discussed in the clinical and nutritional literature [1]. Antioxidants are used to delay the oxidation processes [11] by preventing the formation/or action of free radicals.

In natural systems, there are numerous antioxidant molecules [8]. Among them, polyphenols play a key role as antioxidants due to their OH substituents in their aromatic structure, which enables them to scavenge free radicals [12–14]. The number and positions of ring-OH groups determines the antioxidant capacity of polyphenols [7,15].

Natural Humic acids (HA) consist mainly of polyphenolic compounds (R–OH), as well as carboxylic (R–COOH), carbonyl (C=O) and quinoid [16]. HAs are well known for their antioxidant properties thanks to their polyphenolic compounds [17]. Practically this means that each HA macromolecule contain multiple antioxidant R-OH sites, a property entailing them very attractive from the environmental and technological point of view. However, use of natural HAs in antioxidants' technology e.g. for example to protect materials, polymers, etc. from oxidative deterioration, is hampered by two main factors (i) the non-controlled structure of natural-HAs, (ii) the ubiquitous presence of redox-active metals e.g. $\text{Fe}^{3+/2+}$ [16,17] in their structure. Both these factors can be circumvented using well-defined HA structures produced synthetically with no-use of metal catalysts [18,19]. Our group has demonstrated that Humic Acid Like Polycondensates [HALP] can be produced *via* oxidative co-polymerization of simple polyphenolics e.g. Gallic and Protocatechuic acid [18,19] under O_2 with no use of a metal of inorganic catalyst [18,19].

Hybrid materials consisting of an organic functionality grafted on the surface of an inorganic matrix or particle e.g. such as SiO_2 , offer added-value scaffolds since they can -by design- combine the function/characteristics of the organic with those of the inorganic support. When nanoparticles are used as solid supports, the organic-nanoparticle material consists a nanohybrid. Recently, we have shown that grafting of simple polyphenols e.g. gallic acid [20] or natural HAs [21] on SiO_2 improves their radical-stabilization [20] and interfacial chemistry [21] properties. In this context, it has been demonstrated recently that grafting of gallic acid on SiO_2 nanoparticles [7] results in a hybrid material that is very efficiently as Hydrogen Atom Transfer agent [7]. The benefits of grafting a phenolic antioxidant molecule on a polymer-matrix have also been exemplified [22].

Thus, in the present work we introduce a novel type of SiO_2 -HALP nanohybrids that combine the advantages of well-defined/metal-free HALPs and their grafting on SiO_2 . As we show herein, the SiO_2 -HALP material is the first example of nano-material consisting of an antioxidant polymer covalently grafted on SiO_2 nanoparticles. It is demonstrated herein that we can tune the hydrogen-atom-transfer efficiency by controlling the surface-density of the SiO_2 nanoparticles.

Well characterized HALP was used [18], that can be used as a model to estimate *quantitatively* the antioxidant capacity of the derived SiO_2 -HALP nanohybrids. To explore the interfacial physicochemical properties of the SiO_2 -HALP nanohybrids we have used four different types of commercially available SiO_2 nanoparticles

with different particle sizes, Specific Surface Area and porosity. The successful attachment of HALP on the SiO_2 matrix was verified by TGA, EPR and FTIR spectroscopy. Their antioxidant Hydrogen Atom Transfer capacity was quantified vs. HALP in solution by detailed kinetic study, using the well-known DPPH' (2,2-diphenyl-1-picrylhydrazyl radical) scavenging method [7,8,10–12,14], using UV-vis and EPR spectroscopy.

2. Materials and methods

2.1. Chemicals & SiO_2 NPs

3,4,5-Trihydroxybenzoic (gallic) acid, 3-Aminopropyl-triethoxyxilane (APTES, >98%), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) [purum >98%], and ultrapure methanol [puriss, absolute, over molecular sieve ($\text{H}_2\text{O} \leq 0.01\%$), $\geq 99.5\%$ (GC)] were obtained from Sigma-Aldrich. 3,4-Dihydroxybenzoic (protocatechuic) acid was obtained from Merck. DPPH was obtained from Sigma-Aldrich and used within 1 month of its purchase. Three well-characterized commercially available, hydrophilic fumed SiO_2 nanoparticles with different specific surface area [Aerosil 90 and Aerosil 300 and less-aggregated Aerosil OX50] were used as received. For comparison, colloidal silica obtained from Fluka with specific surface area $320 \text{ m}^2/\text{g}$, was used. Herein, these particles are codenamed as SiO_2 [OX50], SiO_2 [A90], and SiO_2 [A300], for SSA: 50, 90 and $300 \text{ m}^2/\text{g}$, respectively). The colloidal silica is labeled as SiO_2 [S300]. All SiO_2 materials used, had an average OH surface density of 2.6–2.8 OH/nm [23].

2.2. Synthesis of HALP

HALP was produced by the oxidative polymerization of Gallic acid (3,4,5-trihydroxybenzoic acid) and Protocatechuic acid (3,4-dihydroxybenzoic acid), with no use of a catalytic material, according to Giannakopoulos et al. [18]. The obtained free-of-metals HALP was fully characterized as detailed by Giannakopoulos et al. [18]. The polymerization was carried out in aqueous solution under ambient O_2 , at controlled pH 10.5. In brief, 1:1 mol solution 31.47 g of gallic acid (GA) and 28.53 g of protocatechuic acid (PA), were suspended in 3 L of milli-Q water. The mixture was continuously stirred for 12 h at 26°C in a closed glass jar, under controlled air bubbling. Then the pH was adjusted at pH 10.5 with NaOH and the mixture was further bubbled with a continuous flow of natural air under stirring for up to 10 days. During that period the -initially transparent reaction mixture- turned to green and then to a dark-brown/black color. Finally, the standard IHSS procedure for HA isolation was applied [24]. In brief, the pH was adjusted to >1 with HCl and the solution was allowed to precipitate for 72 h. Then, the precipitate obtained after centrifugation at $4000\text{g}/15 \text{ min}$, was washed with Milli-Q water to remove monomer residues and Cl^- , freeze-dried at 66°C with a CHRIST-ALPHA 1-2LD freeze drier, and stocked until further use.

2.3. Preparation of SiO_2 -HALP NPs

According to Deligiannakis et al. [7,20], the preparation protocol for the SiO_2 -HALP NPs consisted of two main steps. First, aminopropyl- SiO_2 (APTES- SiO_2) was prepared by reacting 5 g of dry SiO_2 with 5 ml of aminopropyl-triethoxy-silane in 50 ml of toluene. The suspension was refluxed for 24 h at 80°C , rinsed several times with toluene, ethanol and acetone and dried for 12 h at 80°C in a Buchi rotating furnace-drier. The obtained NPs were aminopropyl- SiO_2 , herein named SiO_2 - NH_2 for brevity. Covalent immobilization of HALP on the formed aminopropyl- SiO_2 has been

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