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

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Abstract
Novel nanohybrid materials were prepared by covalent grafting of a polyphenolic polymer [Humic Acid Like Polycondensate (HALP)] on SiO2 nanoparticles. Four nanohybrids 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 nanohybrids 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 l moles of DPPH radicals per gram of HALP, while [A90]-HALP and [A300]-HALP NPs can scavenge 514 and 832 l moles of DPPH radicals per gram of HALP, respectively. The colloidal SiO2[S300]-HALP can scavenge fewer DPPH radicals (252 l moles) 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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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. Fe3+/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 Polycendesants [HALP] can by produced via oxidative co-polymerization of simple polyphenolics e.g. Gallic and Protocatechuic acid [18,19] under O2 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 matric or particle e.g. such as SiO2, 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 SiO2 improves their radical-stabilization [20] and interfacial chemistry [21] properties. In this context, it has been demonstrated recently that grafting of gallic acid on SiO2 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 SiO2–HALP nanohybrids that combine the advantages of well-defined/metal-free HALPs and their grafting on SiO2. As we show herein, the SiO2–HALP material is the first example of nanomaterial consisting of an antioxidant polymer covalently grafted on SiO2 nanoparticles. It is demonstrated herein that we can tune the hydrogen-atom-transfer efficiency by controlling the surface-density of the SiO2 nanoparticles.

Well characterized HALP was used [18], that can be used as a model to estimate quantitatively the antioxidant capacity of the derived SiO2–HALP nanohybrids. To explore the interfacial physiochemical properties of the SiO2–HALP nanohybrids we have used four different types of commercially available SiO2 nanoparticles with different particle sizes, Specific Surface Area and porosity. The successful attachment of HALP on the SiO2 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 & SiO2 NPs

3,4,5-Trihydroxybenzoic (gallic) acid, 3-Aminopropyl-triethoxysilane (APTES, >98%), N-3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) [puri à 98%], and ultrapure methanol [puriss, absolute, over molecular sieve (H2O < 0.01%), >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 SiO2 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 m2/g, was used. Herein, these particles are codenamed as SiO2[OX50], SiO2[A90], and SiO2[A300], for SSA: 50, 90 and 300 m2/g, respectively. The colloidal silica is labeled as SiO2[S300]. All SiO2 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 O2, 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 IHS 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 4000g/15 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 SiO2–HALP NPs

According to Deligiannakis et al. [7,20], the preparation protocol for the SiO2–HALP NPs consisted of two main steps. First, aminopropyl-SiO2 (APTES-SiO2) was prepared by reacting 5 g of dry SiO2 with 5 ml of aminopropyl-triethoxysilane 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-SiO2, herein named SiO2–NH2 for brevity. Covalent immobilization of HALP on the formed aminopropyl- SiO2 has been
achieved by the method of Koopal et al. [21,25] by formation of amide bonds between the amine groups of aminopropyl-SiO₂ and the carboxyl group of HALP activated by EDC coupler. One gram of amino-functionalized APTES-SiO₂ was suspended in 50 ml of toluene, and then HALP and EDC were added in the suspension. For all materials, a [HALP:EDC] mass ratio (3:1) was used, for example, 300 mg of HALP and 100 mg of EDC per gram of SiO₂-NH₂. The mixture was refluxed for 12 h at 80 °C. The solid was centrifuged and rinsed three times with toluene, three times with methanol and three times with acetone and dried at 80 °C for 12 h. This method was successfully applied previously on SiO₂ as well as for grafting of GA on SiO₂ NPs via the carboxylate groups [7]. Here the protocol did not involve washing in aqueous solution in the final step, to avoid formation of stable phenolic radicals on the SiO₂–HALP NPs. The same protocol was used for the synthesis of colloidal SiO₂-S300–HALP.

2.4. Particle characterization

The nitrogen adsorption–desorption isotherms were measured at 77 K on a Sorptomatic 1990, thermo Finnigan porosimeter. Specific surface area (SSA) of hybrid SiO₂–HALP NPs was determined with the BET method by taking care that the pertinent consistency criteria are met [26]. Samples used for the surface analysis were outgassed at 423 K for 20 h under high vacuum (10⁻⁵ mbar) before measurement. Non-linear Density Function Theory (NLDFT) pore size distribution calculations were performed using the commercial software AS1Win from Quantachrome Instruments. The calculation method used, was N₂ at 77 K on silica, cylindrical pores, NLDFT adsorption–branch kernel model.

The organic loading in hybrid SiO₂ NPs was estimated by thermogravimetric (TGA) analysis performed using a Schimadzu DTG-60 analyzer. Infrared spectra (FTIR) were recorded in KBr pellets on a Spectrum GX Perkin–Elmer FT-IR spectrophotometer. Absorbance measurements were recorded on a Perkin Elmer, USA, lambda 35, UV spectrophotometer at 515 nm and 1 s interval using DPPH radical–method [7,8,11] which offers a suitable basis for evaluation of the Radical Scavenging Capacity (RSC) of SiO₂ functionalized NPs [7]. Stock suspensions of SiO₂–HALP NPs were prepared by dispersing 5 mg of such NPs in 5 ml methanol and sonicating in a low-power (80 W) ultrasonic bath-sonicator (Pranson 2000) for 20 min.

2.4.1. EPR spectroscopy

Electronic paramagnetic resonance (EPR) spectra were recorded with a Bruker ER200D spectrometer at 77 K (in liquid-N₂), equipped with an Agilent 5310A frequency counter. Adequate signal-to-noise was obtained after 5–10 scans. Spin quantitation was done using DPPH as spin standard [27]. Error bars in radical concentrations were estimated based on 4 repetitions for each sample.

Herein, EPR spectroscopy was used as a state-of the art tool with a double purpose:

(i) To determine the maximum concentration of radical-forming phenolic moieties of each hybrid SiO₂ NP. Maximum radical concentration was achieved via oxidation of HALP by O₂ in aqueous solution at alkaline pH [20,28,29].

(ii) To monitor the radical reactions, for example, between DPPH and SiO₂–HALP NPs.

For each SiO₂–NP, the reaction mixture consisted of SiO₂–HALP nanoparticle suspension in methanol plus DPPH inside the EPR tube (Willmad Glass Suprasil, 5.5 mm outer diameter). To monitor the DPPH radical scavenging, we quenched the reaction at selected times from 0 to 60 min, by rapid freezing (within 10 s) the sample at 77 K. The EPR signals for DPPH: SiO₂–HALP were recorded at non-saturating microwave power 0.125 mW with a modulation amplitude of 4 Gpp [20].

2.5. Evaluation of Hydrogen Atom Transfer (HAT) for SiO₂–HALP NPs by the DPPH method

The antioxidant activity of SiO₂–HALP NPs was determined using the well-established DPPH radical scavenging method [7,8,11]. A light-protected methanolic solution of DPPH radical was prepared daily. In each kinetic experiment, small volumes of DPPH* from stock (30 × 10⁻⁶ mol/L in MetOH) was added in situ in a stirred 1 cm quartz cuvette (Hellma suprasil quartzglass, 100-QS) containing 3 ml of SiO₂–HALP NPs suspended in methanol. DPPH* in methanol is characterized by a peak at 515 nm which is usually used for quantitation of the remaining DPPH radicals in solution. Absorbance kinetic measurements started immediately after DPPH* addition, and all experiments were performed at least in duplicate. For comparison, similar kinetic experiments were performed for DPPH* interacting with colloidal silica and pure HALP. In all cases parallel EPR and UV–Vis experiments were run to ensure that the kinetic decay of the DPPH* absorbance at 515 nm – measured by UV–Vis spectroscopy—is exclusively due to DPPH radical scavenging –monitored by EPR.

In accordance to Deligiannakis et al. [7] the non-functionalized SiO₂ NPs have a negligible effect on the concentration of DPPH radicals.

3. Results and discussion

3.1. Characterization of SiO₂–HALP NPs

In Fig. 1 pictures of SiO₂[A300] NPs are presented before (a) and after (b) the surface functionalization with HALP. After functionalization with HALP, the color of NPs was converted from pristine-white (Fig. 1a) to deep-brown (Fig. 1b), due to coverage of the NP surface by HALP. In methanolic solution, these particles resulted in a stable brown suspension (Fig. 1c). This corresponds to a featureless UV–Vis spectrum (Fig. S1 in Supporting Information) that is typical for humic substances and HALP [19].

![Fig. 1.](image-url) (a) Untreated and (b) functionalized SiO₂[A300]–HALP NPs. (c) Suspension SiO₂[A300]–HALP NPs in methanol (500 mg/L).
3.1.1. Pore and surface characterization

The specific surface area of SiO$_2$ NPs and colloidal SiO$_2$, before and after functionalization, was estimated by the BET method (Fig. 2) [26]. Nitrogen adsorption–desorption isotherms and the corresponding NLDFT-derived pore size distributions for all samples are shown in Fig. 2. The SSA for the non-functionalized SiO$_2$ was calculated to be 62, 102 and 300 m$^2$/g for pristine SiO$_2$[O50], SiO$_2$[A90] and SiO$_2$[A300] NPs, respectively and 297 m$^2$/g for SiO$_2$[S300]. On the other hand, the HALP-modified particles possess lower SSA i.e. 48, 84, 172, and 157 m$^2$/g respectively, see Table 1. The lower SSA values indicate a characteristic blockage of the internal pores of the SiO$_2$ voids by HALP. From

Fig. 2. Nitrogen adsorption–desorption isotherms and corresponding NLDFT pore size distributions as insets of SiO$_2$ NPs and colloidal SiO$_2$[A300] before (a, c, e, g) and after functionalization with HALP (b, d, f, h).
Table 1 it is characteristic that the smaller particles [higher SSA] had undergone more severe SSA-decrease. Analysis of the pore size, Fig. 2, shows that functionalization affects the small-pore-size voids (2–4 Å) of the hybrid materials, which are blocked after functionalization, while the higher-pore-size voids (15–40 Å) are less affected.

Thus, the BET data reveal that the HALP macromolecules upon grafting may result to a significant degree of pore-filling/pore-blockage. As we show hereafter, this has also a measurable effect on the radical-scavenging performance of the present nanohybrids.

The amount of HALP loading on SiO2 NPs, determined by TGA, is listed in Table 2. The data in Table 2 show that in SiO2[OX50]-HALP NPs loading is by 30% lower than for the SiO2[OX50]-HALP NPs.

Taking into account the BET data, the decreasing loading in high-SSA particles, see Table 2, can be attributed to the blockage effect of the internal surface area by the HALP macromolecules which occupy a significant volume-fraction of SiO2 nanovoids in the smaller particles. Here it is of pertinence to notice that, when gallic acid molecules – that are significantly smaller that HALP macromolecules- were grafted on similar OX50, A90 or A300 NPs [7] such a pore-‘blockage’ effect was not observed.

The higher loading observed for the colloidal SiO2[S300]-HALP vs. the nanoparticulate SiO2[A300]-HALP NPs can be explained taking into account the pore size distribution from Table 1 and Fig. 2: in colloidal SiO2[S300] the pores have significantly higher diameter i.e. d = 11–18 Å, vs. 3–5 Å in SiO2[A300] NPs. Thus the HALP macromolecules are able to be grafted at the interior of the voids in SiO2[S300] while they cannot access the interior of the narrow voids in SiO2[A300] NPs.

**Grafted HALP surface density estimation:** Based on the HALP-loading data in Table 2, a simple calculation of the surface density of grafted HALP can be done e.g. assuming an average molecular weight of 1500–2000 for HALP [18]. Accordingly, a 15% w/w loading for SiO2[OX50]-HALP NPs corresponds to 15 to 20 HALP molecules grafted per \(100 \times 10^2\) nm \(^2\), that is, 15 to 20 HALP molecules on a \(10 \times 10\) nm \(^2\) square. Assuming a surface density of 2.8 OH per nm \(^2\) for Aerosil SiO2 [23] the \(10 \times 10\) nm \(^2\) contains on average 280 OH groups, that bind 15–20 HALPs. Since each HALP can be linked via the 3 ethoxy groups of APTES, this shows that the 15–20 HALPs engage a maximum 45–60 OH sites or 25–30% of the available OH groups in SiO2[OX50]. In the case of SiO2[A300]-HALP NPs with a 9%w:w loading, taking into account the SSA = 300 m\(^2\)/g we estimate ~3% of surficial OH to be engaged in HALP binding. This estimate provides a significant information, that is, in SiO2[A300]-HALP the macromolecules are 10-fold more dispersed per same surface than in SiO2[OX50]-HALP NPs. A schematic representation is shown in Fig. 3 which exemplifies in pictorial manner that in the A300, the surface sites are less-favorable, thermodynamically, for HALP binding that on the less aggregated OX50. This trend is also valid for the intermediate-SSA particles A90.
The radicals are stabilized on phenolic-ring oxygens of the phenolic molecule [29,30]. Spin counting, see Table 3, shows that (i) in all types of Aerosil-based nanohybrids, the same number of radicals are formed per same number of HALPs. In other words, after grafting the surface-available HALPs behave in the same way in OX50, A90 and A300. In all cases, the Aerosil nanohybrids after the functionalization treatment retain at least 50% of their radical forming activity. (ii) Strikingly S300 shows a lower radical forming capacity per HALP (1.1 μmole per gram of HALP) i.e. despite its higher HALP loading (16.7%). In accordance with the BET data, this can be attributed to kinetic limits i.e. due to steric hindrance of HALPs that are grafted inside the S300-SiO2 voids. This reveals that the radical formation reactions are sensitive to a complex interplay between surface-density and surface accessibility events in the nanohybrids.

3.3. Antioxidant activity

3.3.1. UV–Vis EPR spectroscopy

The 1,1-diphenyl-2-picrylhydrazyl free radical (DPPH) shows a characteristic UV–Vis spectrum with a maximum of absorbance at 515 nm in methanol [8,10,11,31,32]. It is known that, the addition of an antioxidant on this solution results on a decrease of absorbance of the DPPH radical [12]. The diminution of the UV–Vis spectrum of DPPH radical, upon interaction with the SiO2[A90]-HALP in Fig. 6A, parallels the decay of the DPPH-radical (monitored by EPR, Fig. 6B). This DPPH-radical decay is due to Hydrogen Atom Transfer, where one H is transferred from the OH-groups of HALP to one DPPH-radical (monitored by EPR, Fig. 6B). This DPPH-radical decay is due to Hydrogen Atom Transfer, where one H is transferred from the OH-groups of HALP to one DPPH-radical (monitored by EPR, Fig. 6B). The DPPH-radical decay is due to Hydrogen Atom Transfer, where one H is transferred from the OH-groups of HALP to one DPPH-radical (monitored by EPR, Fig. 6B).

The present data show that the SiO2–HALP nanohybrids are also able to perform Hydrogen-Atom-Transfer to DPPH radicals. The kinetics of this phenomenon are presented in the following, tracing the kinetics of the 515 nm absorbance of DPPH.

3.3.2. Kinetics

In Fig. 7a, we present the kinetics of 515 nm absorbance decay for DPPH radical interacting with SiO2[A90]-HALP NPs vs. time. The SiO2–HALP suspension in methanol, gives a characteristic stable brown opaque color and this absorbance has been subtracted from the kinetic data (Fig. S1-SI). The kinetics in Fig. 7a show a fast initial decrease of the DPPH radical absorbance attributed to the H-Atom Transfer [HAT] reactions for reaction times below 2 min [7], followed by a slow subsequent of DPPH radical. As detailed in [7] the fast phase reaction, equation (1), corresponds to the HAT from one OH of the phenolic molecule to one DPPH-radical.

\[
\text{ArOH} + \text{DPPH}^+ \rightarrow \text{ArO}^- + \text{DPPH}^{-} + \text{H}
\]  

(1)

Accordingly, a short-lived semiquinone ArO radical is formed which reacts rapidly with a second DPPH-radical to produce a non-radical product (quinone).

\[
\text{ArO}^- + \text{DPPH}^+ \rightarrow -\text{ArO-quinone}
\]  

(2)
Thus the stoichiometry ratio for reactions (1) and (2) corresponds to $n_{\text{fast}} = 2$, e.g., two DPPH radicals are quenched per each ArOH molecule.

The slow decay phase, observed for $t > 2$ min can be attributed to secondary slow reactions particle–particle/radical–radical couplings that are not relevant to the HAT phenomenon [7,8,10,11,13] thus the slow phase is not further discussed in the present work.

By fitting the fast kinetic phase by an exponential decay [7], (see full data set in Fig. S3 of Supporting Information) we have derived...
3.4. Reusability of the antioxidant NPs

The reusability of SiO₂[90]-HALP NPs was evaluated after their interaction with DPPH radicals as follows: 700 mg/L SiO₂[90]-HALP NPs were allowed to react with 1 mM of DPPH. After successfully scavenging of the DPPH radicals, within 30 min the particles were reused. Firstly, the NPs were washed (>3 with methanol) and re-dispersed in methanol. In the second use, the reused SiO₂[90]-HALP NPs managed to achieve 60% of DPPH radicals’ scavenged on their first reuse. Apparently, after the HAT reactions the OH groups of HALP that were transformed to quinones were not active for HAT, unless they were re-converted to OH. The mechanism of this Quinone → Phenol conversion in SiO₂-HALP nanohybrids is currently under investigation by our group.

Discussion of the Interfacial mechanism: Fig. 9, presents the number of scavenged DPPH radicals at fast phase (n_{scavenged}) normalized per same mass of HALP, according to the loading data in Table 2. A direct comparison of the kinetics of the various NPs normalized per same mass of SiO₂-HALP is presented in Fig. S4 of SI and Table S1. Fig. 9 reveals that the reference HALP can scavenge 351 µmoles of DPPH of radicals per gram while the hybrid materials follow the trend:

### Table 4

<table>
<thead>
<tr>
<th>Material</th>
<th>n_{scavenged}</th>
<th>Scavenged DPPH radicals (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂[OX50]-HALP NPs</td>
<td>8.0</td>
<td>10.0</td>
</tr>
<tr>
<td>SiO₂[A90]-HALP NPs</td>
<td>10.0</td>
<td>12.0</td>
</tr>
<tr>
<td>SiO₂[A300]-HALP NPs</td>
<td>12.0</td>
<td>20.0</td>
</tr>
<tr>
<td>SiO₂[S300]-HALP</td>
<td>5.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

These, non-obvious trends, can be understood taking into account the interplay between SiO₂ pore-size/HALP-size/HALP surface density, as discussed in paragraph Section 3.1.1: higher SSA (smaller particles) have lower surface density of HALPs (2–3 HALPs per 10 × 10 nm² in SiO₂[A300]-HALP) than lower SSA (larger NPs) (15–20 HALPs per 10 × 10 nm² in SiO₂[OX50]-HALP). However the more dispersed HALPs are more efficient DPPH scavengers. This shows that the densely-packed HALPs e.g. for example on OX-50 surface, are severely inhibited with regard to their HAT capacity to DPPH. Also, kinetic/accessibility barriers are the reason for severe inhibition of the colloidal SiO₂[S300]-HALP.

Overall, the present data show that (i) surface grafted HALPs perform 300% better HAT than pure HALP in solution. (ii) By controlling the particle type and grafting loading, we can control/optimize the HAT performance: when grafted on the SiO₂ surface, at low-enough surface density to avoid HALP-HALP aggregation-induction effects, the HALP macromolecules are able to achieve nearly 800 µmoles of DPPH-radical quenching per gram of HALP. (iii) Aerosil SiO₂ nanoparticles offer a more suitable scaffold than colloidal SiO₂.

4. Conclusions

SiO₂-HALP nanohybrids are very efficient in performing rapid Hydrogen Atom Transfer to DPPH-radicals in solution. Study of four SiO₂[HALPs] allowed a detailed understanding of the role of surface geometry, surface segregation effects on the studied HAT reactions. From the chemistry point-of-view, our data reveal the grafted HALPs retain at least 50% of their radical forming activity. When normalized per same HALP concentration, bigger SiO₂[OX50]-HALP NPs can scavenge 280 µmoles of DPPH radicals per gram of HALP, while SiO₂[A90]-HALP and SiO₂[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. Thus the present data show that surface grafted HALPs perform 300% better HAT than pure HALP in solution. This is the first example, where the ability of Humic-based nanohybrids to perform fast Hydrogen Atom Transfer [HAT] was exemplified. Moreover, this shows that detailed controlling of the particle type (SSA, porosity, pore size, aggregation state) and of the grafting-loading is required for a rational design of optimal HAT performance. Colloidal...
SiO$_2$[S300] is inferior vs. Aerosil SiO$_2$ due to steric hindrance of HALPs that are grafted inside the S300-SiO$_2$ voids.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2015.05.039.

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