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Zirconia-silica based mesoporous desulfurization adsorbents

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HIGHLIGHTS

- Mesoporous silicate sorbent materials templated by long-chain primary alkylamine.
- Excellent saturation adsorption capacity (39.4 mgS/g) and silver efficiency (1.21 molS/molAg).
- 86% of initial capacity towards model fuel maintained after solvent regeneration.
- Spectroscopic studies indicate that both S–M binding and π complexation are occurring.

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ABSTRACT

We report a series of mesoporous silicate sorbent materials templated by long-chain primary alkylamines that display record level of desulfurization of the jet fuel JP-8. Pure silica frameworks and those with a Si:Zr synthesis molar ratio ranging from 44:1 to 11:1 were investigated. The optimum sorbent was identified as dodecylamine-templated silica-zirconia synthesized from a gel with Si:Zr molar ratio of 15:1. With an optimized silver loading of 11 wt.%, a saturation adsorption capacity of 39.4 mgS g⁻¹ and a silver efficiency of 1.21 molS mol Ag⁻¹ were observed for JP-8. This sorbent displayed exceptional regenerability, maintaining 86% of its initial capacity in model fuel after solvent regeneration with diethyl ether. Low-cost, portable and reusable sorbents for the desulfurization of JP-8 jet fuel are needed to make solid oxide fuel cells (SOFCs) a reality for military power needs. SOFCs require ultra-low sulfur content fuel, which traditional desulfurization methods cannot achieve.

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1. Introduction

The development of auxiliary power units (APUs) is a high priority for the Department of Defense [1]. Silent watch missions require prolonged energy use in combat vehicles. SOFCs offer an alternative to traditional generators, as they use substantially less fuel and are significantly quieter [2,3]. JP-8 fuel is an ideal hydrogen feedstock for these SOFCs as it is already available on-site and has a high energy density [4]. The native organosulfur compounds present in JP-8, however, poison components of the SOFCs, reducing their lifetime [1]. In addition, the combustion of high sulfur content fuels leads to the production of SO_x pollutants. These pollutants are

linked to various adverse health effects including asthma and contribute to environmental issues including acid rain [5,6].

Currently, fossil fuels are desulfurized through hydrodesulfurization (HDS), which is a high temperature, high pressure process that must be performed at a refinery and requires hydrogen. HDS is effective for lighter fossil fuels that contain more thiols and thiophenes, but heavier fuels containing methylated benzothiophenes and dibenzothiophenes cannot be desulfurized to a low level by this process [7–9]. Additionally, the HDS process non-selectively hydrogenates the fuel, which lowers its overall energy density, and has poor hydrogen economy.

On-site desulfurization of JP-8 is highly desirable and has given rise to the study of adsorptive desulfurization. This method involves the creation of sorbents that can quickly remove organosulfur compounds (ideally to a sub ppm_wS level) under ambient conditions without the need for co-catalysts such as hydrogen gas, while being reusable and affordable to produce [10,11]. Of

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particular interest in this regard is high surface area open-frameworks. A myriad of such frameworks have been explored, including silicates and mixed metal silicates. Zirconia-containing mesoporous frameworks have been explored for both catalytic and adsorptive desulfurization [12–16]. Kwon and coworkers showed 20% greater sulfur adsorption for a mesoporous silica/zirconia material compared to the pure silica version, even though the latter had a higher surface area. The Si/Zr material was successfully solvent-regenerated to 78.6% with methyl isobutyl ketone [12]. Kumar and coworkers demonstrated that zirconia based materials with a range of surface area ($16.8\text{--}322.0\text{ m}^2\text{ g}^{-1}$) are good sorbents for dibenzothiophene (DBT), removing up to 9.9 mgS g^{-1} from model fuel, and the adsorption is exothermic in nature [13]. Copper supported on zirconia has been shown to be effective in the adsorption of thiophene from n-octane [14]. Larrubia and coworkers were able to show through FT-IR studies that benzothiophene (BT), DBT and dimethyldibenzothiophene (DMDBT) adsorb onto zirconia through Lewis-type acid–base interactions [16]. BT, DBT and DMDBT behave as Lewis bases with the lone pair of the sulfur interacting with the Lewis acid sites on the surface of the zirconia.

Herein we describe a series of zirconium doped, silver loaded mesoporous silica materials synthesized with varying surfactant chain length and zirconia content. Both model fuel and actual JP-8 were studied to ascertain an optimal sorbent for the desulfurization of JP-8 fuel.

2. Experimental

2.1. Materials

All chemicals were used as received without further purification. Tetraethylorthosilicate (TEOS), dodecylamine (DDA), hexadecylamine (HDA), benzothiophene (BT), and dibenzothiophene (DBT) were all obtained from Acros Organics. Naphthalene (NA) was obtained from Fisher Scientific. 70% zirconium n-propoxide in isopropanol was obtained from Alfa Aesar. 200 proof ethanol was obtained from Decon Laboratories, Inc. Silver nitrate was obtained through MP Biomedicals, decane from TCI and 4,6-dimethyldibenzothiophene (DMDBT) from Frontier Scientific.

2.2. Synthesis of DDA based frameworks

In a typical synthesis, 1.36 g of DDA was dissolved in 7.14 g of ethanol with magnetic stirring, then 11.14 g of water was added to the solution and stirring continued for at least 5 min. A second solution of 4.16 g TEOS and the desired amount of zirconium n-propoxide in 70% isopropanol was mixed and added in a quick dropwise fashion to the first solution, over about 30 s. Stirring was continued for 1 h followed by static room temperature aging overnight. The solid was filtered and rinsed with doubly deionized water and ethanol, then refluxed for 1 h in approximately 100 g of 200 proof ethanol, followed by filtration and ethanol rinsing. The solid was then calcined at $450\text{ }^{\circ}\text{C}$ for 7 h with a $1\text{ }^{\circ}\text{C min}^{-1}$ ramp rate.

2.3. Synthesis of HDA based frameworks

The synthesis of HDA based frameworks is a modified version of that published by Tuel and coworkers [17]. In a typical synthesis 1.45 g of HDA was dissolved in 6.01 g of ethanol with magnetic stirring, then 11.13 g of water was added to the solution and stirring continued for at least 5 min. A second solution of 4.16 g TEOS and the desired amount of zirconium n-propoxide in 70% isopropanol was mixed and added in a quick dropwise fashion to the first

solution, over about 30 s. Stirring was continued for 30 min followed by static room temperature aging overnight. The solid underwent the same filtration, reflux, and calcination procedures as the DDA materials.

2.4. Silver loading

The desired amount of silver was loaded onto the frameworks via wet impregnation: silver nitrate was dissolved in a water/ethanol solution and then added dropwise to the framework until moist. The framework was then dried at $110\text{ }^{\circ}\text{C}$ under vacuum. This process was repeated until all the silver solution was loaded onto the framework.

2.5. Characterization

Powder X-ray Diffraction (PXRD) was performed on a Rigaku MiniFlex + X-ray diffractometer with Cu K α radiation. Samples were analyzed from 1.5° to 10° (2θ) with a step size of 0.01° and scan rate of 1° per minute. BET surface area of the samples was measured by physical adsorption of N_2 at 77 K using a Micromeritics physisorption analyzer (TriStar II 3020 v1.03). Adsorption/desorption isotherm measurements were collected in the relative pressure range (P/P_0) from 0.01 to 1.00. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) data were collected with a FEI Quanta 3D Dualbeam microscope. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were obtained by using a Varian Cary 5000 UV–Vis–NIR spectrophotometer (Harrick Praying Mantis diffuse reflectance cell attachment, Teflon standard). Infrared spectra were recorded using a Perkin–Elmer Spectrum-One FT-IR. Transmission electron microscopy (TEM) was collected using a JEOL 2100F microscope operated at 200 kV. Samples were prepared for TEM by sonication in acetone for 3 min prior to dispersal on a TEM grid covered in holey carbon film.

2.6. Model fuel and JP-8 testing

The procedure is similar to that we have previously published [18]. All model fuel tests were performed with a 50:1 fuel to sorbent weight ratio. For both model fuel and JP-8 tests, the materials were heated under vacuum at $110\text{ }^{\circ}\text{C}$ overnight. Model fuels were made with n-decane and BT, DBT, DMDBT or NA as the contaminant. All sulfur containing model fuels were $500\text{ ppm}_w\text{S}$ (11.38 mM) and the NA model fuel was 11.38 mM . Model fuel batch tests were performed over 1 h unless otherwise noted. JP-8 batch tests were performed over 24 h with approximately 40 mg of sorbent in 5 g of JP-8. The JP-8 used for all experiments had an average initial sulfur concentration of $750\text{ ppm}_w\text{S}$. Both column and 24-h batch (beaker) test experiments were analyzed for total sulfur concentration using a UV total sulfur analyzer (multi EA 3100, Analytikjena) with a detection limit of 45 ppb. A Chromtech column (4.6 mm ID, 50 mm length) was packed with the material for column tests. A Shimadzu HPLC pump was used to pump the JP-8 fuel into the column at a rate of 0.5 mL min^{-1} . Batch tests used $\sim 0.05\text{ g}$ of sorbent in $\sim 5.5\text{ g}$ of JP-8 and column experiments used $\sim 0.18\text{ g}$ of sorbent and up to 40 mL of JP-8. 50–60 mL of diethyl ether through the column was used for regeneration followed by drying the material at $110\text{ }^{\circ}\text{C}$ in a vacuum oven. Model fuel tests concentrations were determined by UV–Vis on a Hewlett–Packard Model 8452A spectrophotometer. FT-IR data was collected after exposing sorbents to $500\text{ ppm}_w\text{S}$ model fuel of DBT in n-decane for 1 h, rinsing with decane to remove any physisorbed DBT, followed by drying at $110\text{ }^{\circ}\text{C}$ under vacuum before forming KBr pellets.

Fig. 1. PXRD of unloaded materials (DDA-X denotes material made with DDA templating agent and X is the Si:Zr gel ratio. HDA-X represents a material made with HDA as the templating agent) with the difference in d_{100} spacing between the HDA and DDA based materials denoted with dashed lines.

3. Results and discussion

3.1. Characterization

Materials using both of the templating agents were synthesized. The amounts of zirconia were varied for the materials made with HDA and DDA. DDA-X denotes a material made with DDA templating agent where X is the Si:Zr mole ratio of the gel. DDA-SiO₂ contains no zirconia. HDA-15 represents a material made with HDA as the templating agent and a 15:1 Si:Zr mole ratio. Initial characterization was performed using powder X-ray Diffraction (PXRD). Fig. 1 compares the PXRDs of all the materials made. HDA, the longest surfactant consisting of a 16-carbon chain, gives rise to a material with the lowest angle (100) peak as expected. The materials templated by DDA, with a 12-carbon chain, have a (100) peak at a higher angle.

BJH calculations from the N₂ isotherms (Fig. 2) were used to calculate pore width and pore volume of DDA-15 and HDA-15. These values are shown in Table 1 along with a summary of the PXRD data. The BJH pore width of HDA-15 is 34 Å, 7 Å greater than DDA-15's pore width of 27 Å. These results correspond well to the

Table 1
Summary of PXRD findings and pore characteristics.

Material	$d_{(100)}$ (degrees 2 θ)	$d_{(100)}$ spacing (Å)	Surface area (m ² g ⁻¹)	BJH pore width (Å)	BJH pore volume (cm ³ g ⁻¹)
DDA-15	2.54	34.7	1471	27	1.35
HDA-15	2.10	42.0	1055	34	1.32

Table 2
Surface area of sorbents after calcination as measured by BET and 1-h adsorption capacities using 500 ppm_wS model fuel of DBT in n-decane.

Material	Surface area (m ² g ⁻¹)	Silver loaded surface area (m ² g ⁻¹)	Adsorption capacity (mgS g ⁻¹)
DDA-SiO ₂	1573	807	7.4
DDA-44	1513		9.2
DDA-22	1434		9.8
DDA-15	1471	843	12.3
HDA-15	1055		9.9
DDA-11	1246		10.5

Fig. 3. UV-Vis diffuse reflectance spectra of DDA-templated materials.

Fig. 2. N₂ adsorption (blue) and desorption (red) isotherms for DDA-15 (a) and HDA-15 (b). Inset shows the pore size distribution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. SEM micrographs of DDA-15 (a and b), STEM micrograph of DDA-15 (c) and SEM micrograph of HDA-15 (d).

PXRD data (Table 1), which includes the wall thickness in the value. The pore widths are also similar to those seen for other silica based materials templated with HDA and DDA [19–21]. A comparison of the pore size distribution (insets of Fig. 2) shows that HDA-15 has broader distribution compared to DDA-15.

Table 2 summarizes the BET surface area results. The surface area of the DDA based sorbents are higher than that of HDA, and the pure silica version has the highest of the DDA materials. The surface area trend agrees with that seen by Tuel and coworkers [16]. Their silica/zirconia frameworks with HDA as the surfactant displayed a higher surface area for a Si:Zr gel ratio of 15:1 than 25:1. DDA-15 impregnated with 11 wt.% Ag has a surface area of $843 \text{ m}^2 \text{ g}^{-1}$, demonstrating that the material retains its very high surface area after silver impregnation, and retains more of its surface area than DDA-SiO₂ (Table 2).

The diffuse reflectance UV–Vis data for DDA-SiO₂ and DDA-15 show that the silver species present are primarily Ag⁺, as evidenced by the large band just above 200 nm (Fig. 3). A small amount of Ag^{δ+} corresponds to the smaller band just above 300 nm [22,23]. There is no appreciable difference in silver species based on the presence of zirconia, as the spectra are identical for both DDA-SiO₂ and DDA-15.

SEM images show that DDA-15 is bulk powder, but with a highly textured morphology (Fig. 4). The powder contains fine particles ranging in diameter from hundreds of nanometers to several microns. Both templating agents, HDA and DDA, result in similar powder morphologies. Fig. 5 provides a closer SEM look at the morphology of DDA-15 and demonstrates that there are no changes to the bulk characteristics after silver loading.

TEM of DDA-15 (Fig. 6) does not reveal any ordered array to the packing of the pores like those seen in MCM-41. This result agrees with the PXRD, which would have shown (110) and (200) peaks if the pores were in an ordered hexagonal array. Fig. 6 also shows

DDA-15 after being loaded with 11 wt.% Ag. The silver looks relatively well dispersed, with silver nanoparticles about 10 nm across equally dispersed throughout the DDA-15 particles.

3.2. Model fuel testing

The degree of silver loading was optimized using material DDA-15, as it had both high surface area and zirconia content. It was found that as the silver content increases, adsorption capacity increases up to a maximum and then a decrease is observed (Fig. 7). This peak is attributed to an increase in silver adsorption sites with loading. Silver aggregates likely start to form at higher silver concentration, which can block the channels and result in a lower adsorption capacity. This phenomenon has been observed with other silver loaded materials, where Tatarchuk and coworkers found that as silver loading increased beyond 4 wt.%, the surface area, pore volume, and silver dispersion decreased [24]. As a result, they observed lower adsorption capacities for materials loaded with more silver [24]. For DDA-15 the optimized silver loading was found to be 11 wt.% and was subsequently used for all model and JP-8 fuel tests herein for the entire series of materials.

Table 2 displays the model fuel adsorption capacities for all the frameworks loaded with 11 wt.% Ag. The adsorption capacity correlates to both zirconia content and surface area. DDA-SiO₂ has the highest surface area, yet much lower adsorption capacity than the zirconia containing frameworks. Of those containing zirconia, 15:1 is the optimum Si:Zr ratio. The capacity increases with increased zirconia but decreases at 11:1, likely due to the lower surface area of DDA-11 (Table 2).

The increased adsorption capacity for zirconia containing materials is likely linked to the increased surface acidity. Surface acidity has been linked to desulfurization adsorption capacity for zirconia, as well as alumina and mixed metal oxides [16,25–28].

Fig. 5. SEM micrograph of DDA-15 before silver loading (left) and after loading with 11 wt.% silver (right).

Fig. 6. TEM micrograph of DDA-15 (left) and Ag-DDA-15 (right).

Fig. 7. Optimization of silver loading level for DDA-15 using 1-h fuel tests of 500 ppm_wS DBT in n-decane.

Table 3

1-hour adsorption capacities of unloaded DDA based frameworks using 500 ppm_wS model fuel of DBT in n-decane.

Material	Adsorption capacity (mgS g ⁻¹)
DDA-15	1.4
DDA-SiO ₂	0.6

The majority of organosulfur compounds in jet fuel are categorized as Lewis bases, which are known to bind to Lewis acidic sites

Fig. 8. Adsorption capacity as a function of time for DDA-15 in 500 ppm_wS model fuel of DBT in n-decane as monitored by UV–Vis. Inset: magnified data for the first 3 min, showing that 70% of the adsorption capacity is reached after 22 s and maximum adsorption capacity by 180 s.

[27,28]. HDA-15 has the optimum silica to zirconia ratio. The larger pore sizes made by using HDA as the templating agent ultimately lower the surface area, which accounts for the decrease in adsorption capacity. The pores of both DDA and HDA materials are of sufficient size to accommodate the organosulfur compounds commonly found in JP-8. This is not the case for smaller pore

Fig. 9. 1-hour adsorption capacities for regeneration of DDA-15 in 500 ppm_wS model fuel of DBT in decane.

frameworks such as zeolites that cannot accommodate dibenzothiophene and its methylated derivatives [29].

To further confirm the role of zirconia in increasing adsorption capacity, DDA-15 and DDA-SiO₂ were tested without silver loading. Even though DDA-SiO₂ has about 7% more surface area than DDA-15, DDA-15 absorbed more than twice the amount of sulfur from model fuel (Table 3). This increase clearly demonstrates that the silica-zirconia surface is more active than pure silica as well as the key role of the silver loading.

It is important for a sorbent to quickly adsorb contaminants, especially for applications where it could be used in a column for on-demand, on-site desulfurization. We therefore performed adsorption kinetics studies (Fig. 8). DDA-15 reaches its equilibrium capacity in model fuel within 3 min, and is 70% saturated in only 22 s. These characteristics make it ideal for column use where fast adsorption is essential. Compared to other materials tested with model fuels under ambient conditions, this is a significant improvement. For example, previous kinetic studies of non-silver loaded frameworks such as zirconia based adsorbents reach equilibrium after 22 h, whereas carbon nanoparticles take 20 min [13,30]. Silver loaded mesoporous aluminosilicates take approximately 5 min to reach equilibrium for dibenzothiophene adsorption [31].

Regeneration and reusability is an important property for desulfurization adsorbents. Fig. 9 shows that there is an initial drop after the first regeneration, with 80% of adsorption capacity retained. The second regeneration cycle, however, displays a relatively low drop, retaining 93% of its capacity between cycles 2 and 3. We attribute this difference to an initial loss of silver during the first regeneration, with silver content stabilizing for future cycles. The rinsing with diethyl ether also likely removed physisorbed hydrocarbons, which are also adsorbed but in lower amounts than the organosulfur compounds (e.g. naphthalene [18]).

Table 4
24-hour fuel test data in JP-8 fuel.

Material	Silver content (wt.%)	Adsorption capacity (mgS g ⁻¹)	Silver efficiency (mol S mol Ag ⁻¹)
DDA-15	0	4.6	N/A
Ag-DDA-15	11	39.4	1.21
Ag-MSN	20	47.1	0.79

Fig. 10. Comparison of Ag-MSN and Ag-DDA-15 24-h adsorption capacity in JP-8 (blue) with the silver efficiency (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. JP-8 testing

Real jet fuel tests were performed using JP-8 under ambient conditions to assess the utility of the materials for this military application. 24-hour adsorption capacity studies were performed for the most optimized material, silver loaded DDA-15. The sulfur concentration reduced from 734ppm_wS to 396ppm_wS. The results are presented in Table 4 and compared to another material prepared by our lab, Ag-MSN (mesoporous silica nanoparticles): 80 nm diameter nanoparticles of MCM-41 loaded with 20 wt.% Ag [18]. Silver loaded DDA-15 has 84% the adsorption capacity towards JP-8 compared to Ag-MSN, but does so with far less silver loading. Silver is the most expensive component of both of these materials. The more efficiently that the silver is used, the more cost effective the sorbent. Ag-MSN is optimized to 20 wt.% Ag [18] compared to only 11 wt.% for DDA-15. Further, as shown in Table 4 and highlighted in Fig. 10, DDA-15 utilizes the silver sites more efficiently. Ag-MSN has a silver adsorption site efficiency of 0.79 mol S mol Ag⁻¹, whereas DDA-15 has an efficiency of 1.2 mol S mol Ag⁻¹. This increase is likely due to the DDA-15 framework itself adsorbing a high degree of sulfur compounds. As shown in Table 4, the unloaded framework adsorbs only 4.6 mgS g⁻¹.

3.4. Mechanism studies

A variety of model fuels were studied to show the ability of DDA-15 to adsorb DMDBT and also to help elucidate the binding mechanism [32–34]. The larger adsorption capacities shown in Fig. 11 for DBT and DMDBT compared to BT are similar to the trend seen with other sorbents, and are explained by the higher electron density of the sulfur on DBT and DMDBT [18]. DMDBT has significant steric hindrance around the sulfur atom, which would explain its slightly lower capacity than the non-sterically hindered DBT. The effect of steric hindrance and the decreased capacity for the lower electron density of BT all point to sulfur being the binding site. DDA-15 does have an appreciable adsorption capacity for NA, but it is far lower than that of the sulfur containing compounds. This difference is explained by the capacity of the material to form π -bonds. It is likely that both S-M and π -bonding occur, which would account for its adsorption of the hydrocarbon-only aromatic analog NA. It would also explain the observed larger capacities towards organosulfur compounds, especially those with high electron densities around the sulfur atom.

Fig. 11. 1-hour adsorption capacities of DDA-15 in single contaminant model fuels. 4,6-dibenzothiophene (DMBT), dibenzothiophene (DBT) and benzothiophene (BT) were all 500 ppm_wS and naphthalene (NA) was used at isomolar level.

FT-IR also supports an S–M binding mechanism for DBT. A shift of unbound DBT from 734 cm^{−1} to 744 cm^{−1} for DBT bound to DDA-15 was observed after a 1-h fuel test. This shift corresponds to a perpendicular orientation of DBT to the surface of DDA-15 [35]. The combination of the model fuel studies and FT-IR show that DDA-15 is capable of both S–M and π -bonding. In addition to helping reveal the binding mode, Fig. 12 also demonstrates that diethyl ether is effective at regeneration, as no stretches from DBT are present after the framework has been rinsed with diethyl ether.

4. Conclusions

High surface area silica-zirconia frameworks templated by alkylamines are promising materials for the desulfurization of JP-8. Their high capacity coupled with a record in silver efficiency makes them an improvement upon materials previously reported. Optimization of pore size and zirconia content revealed that the

Fig. 12. FT-IR of dibenzothiophene (black), Ag-DDA-15 prior to fuel exposure (red), Ag-DDA-15 after 1 h in 500 ppm_wS model fuel of dibenzothiophene in decane (blue), and after solvent regeneration using diethyl ether (green). The stretch from unbound dibenzothiophene is marked with a dotted line at 734 cm^{−1} and bound dibenzothiophene at 744 cm^{−1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

material DDA-15 was the ideal framework. After loading with 11 wt.% Ag, the material displays a 24-h saturation adsorption capacity of 39.4 mgS g^{−1} in real JP-8 under ambient conditions. The material displays the ability to be solvent regenerated at room temperature, which is highly advantageous to thermal regeneration processes and avoids silver oxidation. Further testing reveals the capability of the material for both S–M binding and π -complexation. We are currently modifying the loading and calcination procedures for improvement on the regenerability of the material.

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List of acronyms

JP-8: Jet Propellant No. 8
 SOFCs: Solid oxide fuel cells
 APUs: Auxiliary power units
 HDS: Hydrodesulfurization
 BT: Benzothiophene
 DBT: Dibenzothiophene
 DMBT: Dimethyldibenzothiophene

TEOS: Tetraethylorthosilicate
DDA: Dodecylamine
HDA: Hexadecylamine
NA: Naphthalene
MSNs: Mesoporous silica nanoparticles
PXRD: Powder X-ray Diffraction
BET: Brunauer–Emmett–Teller

BJH: Barrett–Joyner–Halenda
SEM: Scanning electron microscopy
STEM: Scanning transmission electron microscopy
UV–Vis DRS: Ultraviolet–Visible Diffuse Reflectance Spectroscopy
UV–Vis–NIR: Ultraviolet–Visible–Near-Infrared
FT-IR: Fourier Transform-Infrared
S-M: Sulfur–Metal Bonding