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Micheal P Moloney, Nicolas Massoni, Hans-Conrad Zur Loye, Shani Egodawatte, Agnes Grandjean. Silver modified SBA-15 for Iodine entrapment. *Journal of Inorganic and Organometallic Polymers and Materials*, 2020, 30 (7), pp.2756-2763. 10.1007/s10904-020-01447-3 . cea-03564253

HAL Id: cea-03564253

<https://cea.hal.science/cea-03564253>

Submitted on 10 Feb 2022

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Silver modified SBA-15 for Iodine entrapment

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KEYWORDS Solvent free, SBA-15, Silver nanoparticles, Iodine Extraction

ABSTRACT: A green solvent-free approach was used to produce grey colored Ag/AgNO₃ functionalized SBA-15. This easy to handle powder was then used to extract molecular Iodine from cyclohexane by simple addition and filtration. The resulting yellow powder was examined by UV-Vis, FT-IR, XRD, TGA and SEM/TEM. It was found that nanosized AgI particles were now present on/in the porous silica support. Despite numerous washing steps with a range of solvents (ranging from cyclohexane to water) no leaching was observed. The sorbent proved highly efficient extracting 0.46 moles of I₂ for every mole of silver, almost 1:1 Ag:I. Finally, TGA demonstrated an increased melting point for AgI indicating a degree of protection from the silica support. This is important when considering transformation into the final waste form.

Although produced in relatively small quantities by the nuclear industry, the extraction and storage of radioactive iodine is important due to its biological sensitivity and long half-life (10⁷ years).^{1,2} Separately, the upswing in shale gas production has added new interest to this topic as shale gas produced water can have high iodide concentrations, (54mg/L).^{3,4,5,6} Although not radioactive or inherently toxic

these iodides can interact with other products during the drinking water treatment processes to create harmful by products.⁷ The idea of a silver functionalized supports for iodine extraction is hardly new,^{8,9,10} Ag-zeolites are typically used in nuclear industry,^{1,11,12,13,14} whereas, as radiation is not a concern, in drinking water management Ag functionalized polymers can be used.^{3,15,16} Here we expand on

this work and simplify it by removing the need for solvents or stabilising ligands making this approach greener. Taking a process reported by Tang et al. porous SBA-15 and AgNO₃ are mixed, crushed and heated together.¹⁷ This simple mixing approach can be easily transposed to other mesoporous support than SBA15. This allows the AgNO₃ to decompose and for nanosized metallic Ag⁰ particles to be formed in and on the silica structure. This material can then be placed directly into an I₂ solution where it extracts iodine at a ratio of 0.45 I₂ to 1 Ag over 30 minutes. This is almost 1:1 (Ag to I) making it quite efficient *vis a vis* silver use. The silica offers a certain degree of thermal protection to the AgI raising its decomposition temperature; this is important in the nuclear industry when considering this and other materials for long term storage.¹⁸ Here, the unfunctionalized SBA-15, the silver modified Ag@SBA-15 and the I₂ modified AgI@SBA-15 were examined by UV-Vis, FT-IR, XRD, TGA, SEM and TEM. AgI@SBA-15 samples were washed with cyclohexane x2, ethanol x2, acetone x2 and finally water x2. No Ag or AgI particles were detected in the washing. Elemental analysis of the functionalized silica's allowed us to determine the total Ag or AgI particle concentrations. Changes in the surface area and porosity of the samples were examined by N₂ adsorption. The I₂ extraction kinetics and capacity was measured indirectly using UV-Vis. Elemental Analysis (EA) of the silver content of Ag@SBA-15 corresponds well to the initial reactant concentration. 50 mg of AgNO₃ were added to 500 mg of SBA-15 to create Ag@SBA-15. This results in a calculated Ag content m/m of 5.8 %. EA (20% error)

showed a silver content of 6.4% (weight %). FT-IR of all samples (Ag@SBA-15 and AgI@SBA-15) (SI) showed the typical signals associated with SiO₂.²⁰ Beyond slight shifts in the frequency of the various Si-O-Si stretches little difference was seen between the samples. These shifts may be a result of the heating process used to incorporate silver into the silica pores. A slight additional frequency change is again seen after addition of I₂. However, this is also seen when I₂ was added to unmodified SBA-15 indicating it is independent of AgI formation.

Solid UV-Vis measurements of Ag@SBA-15 and AgI@SBA-15 are shown in **Figure 1**. The presence of nano size Ag in the Ag@SBA-15 samples is confirmed by the presence of silver plasmon bands at 455 nm.^{21,22} After the addition of I₂ the Ag peak is replaced by a strong well-structured e peak at 424 nm.^{23,24,25} The position, strength and shape of the peak(s) indicates that monodisperse AgI nanocrystals has now been formed.

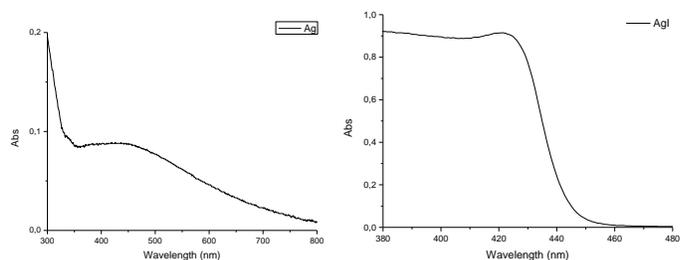


Figure 1: UV-Vis of Ag@SBA-15 (left) and AgI@SBA-15 (right). Ag plasmon band around (left) is completely replaced by AgI exciton peak.

XRD (**Figure 2 and Figure 2 in SI**) confirms the presence of cubic silver (PDF00-001-0503 Fm3m), as well as

the continued presence of silver nitrate (PDF04-011-0004) in Ag@SBA-15 batches. The presence of AgNO₃ does not seem to be a problem as after I₂ extraction XRD shows only AgI (a mixture of β, and γ)^{26,27} reflections indicating that all detected Ag and AgNO₃ has been converted to AgI.

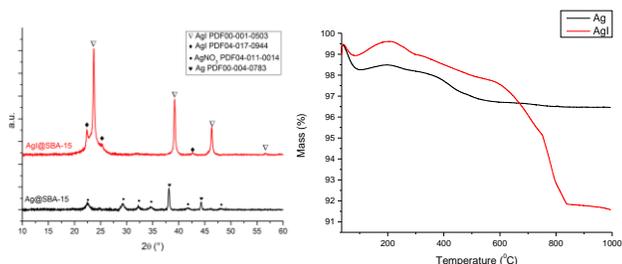


Figure 2: Left; XRD of Ag@SBA-15 (black) and AgI@SBA-15 (red). Note the presence of both Ag and AgNO₃ in the Ag@SBA-15 samples. Only AgI is detected after I₂ addition. Right; TGA of Ag@SBA-15 (black) and AgI@SBA-15 (red). Mass increase at 200 °C is ascribed to Ag₂O formation. However it starts to decompose almost immediately after formation. Mass loss beginning at 380 °C in the Ag@SBA-15 samples is believed to be AgNO₃ decomposition. Mass loss beginning at 600 °C in the AgI@SBA-15 samples is believed to be AgI decomposition.

TGA of the Ag@SBA-15 shows a dehydration step between 30-100 °C, followed by Ag₂O formation from 100 - 205 °C. This is in turn followed by its gradual decomposition of Ag₂O. The final mass loss step, beginning at around 380 °C and finishing at 450 °C corresponds to the decomposition of AgNO₃ (Figure 2).¹⁷

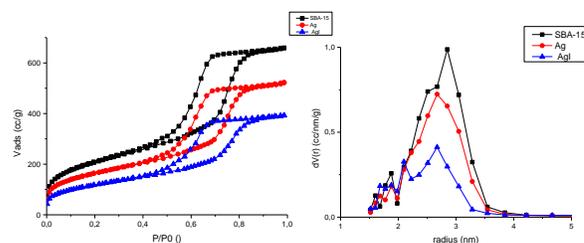


Figure 3: Nitrogen sorption isotherm of SBA-15, (black), Ag@SBA-15, (red) and AgI@SBA-15, (blue).

TGA of the AgI@SBA-15 sample is quite similar to the pure Ag sample at lower temperatures with the dehydration, Ag₂O formation/decomposition steps visible. No AgNO₃ decomposition step is visible indicating its absence. A large mass step loss slowly begins around 450 °C before increasing at 600 °C with a final steep inflection point at around 700 °C. These losses are not present in the Ag@SBA-15 TGA curves. The total mass lost (~ 6%) at this temperature corresponds to I₂ content as observed by EA (4.8%). Nitrogen sorption isotherms (Figure 3 and Table 1) showed that the unfunctionalized calcinated SBA-15 has a surface area of 735 m²/g. This drops to 582 m²/g batches once functionalized with silver. The surface area is further reduced to 369 m²/g after I₂ extraction. These reductions in surface area are accompanied by decreases in the pore volume; from 0.98 cm³/g for SBA-15 to 0.78 (0.495) cm³/g for the Ag and AgI modified samples respectively.

Table 1: N₂ sorption data corresponding to figure 3.

| | Surface Area (m ² /g) | Pore Vol. (cm ³ /g) | Pore Radius (nm) |
|-------------------|-------------------------------------|-----------------------------------|---------------------|
| SBA-15 | 729 | 0.981 | 2.85 |
| Ag@SBA-15 | 582 | 0.784 | 2.67 |
| AgI@SBA-15 | 369 | 0.495 | 2.66 |

These decreases indicate that at least some of the silver and consequently the AgI is located inside, or on, the pores of the SBA-15. TEM shows the SBA-15 pores to be around 6 nm in diameter in good agreement with the nitrogen sorption isotherm result. Silver particles (1-3 nm) can be seen freely dispersed inside the pores, however, a large population are either along or on the pore walls. SEM-FEG (Figure 4) shows a dispersion of what EDX (Figure 3 and 4 SI) confirmed was silver throughout the silica. These artefacts are quite large and may represent a macro silver population or large aggregates of individual silver nanoparticles. As UV-Vis (Figure 1) shows only a single silver plasmon band we believe it is the latter. These spots become smaller and more numerous and more disperse after I₂ addition indicating the latter. This again supports the disaggregation of aggregates of individual Ag nanoparticles as AgI is formed. EDX of these bright spots confirms the presence of Ag and I (Figure 3 and 4 in SI). The AgI (semiconductor) is now seen as 3 nm white spheres inside the silica pores. This is good agreement with the position and sharpness of the exciton peak seen in Figure 1. Silica pores also appear to have narrower to 3 nm.

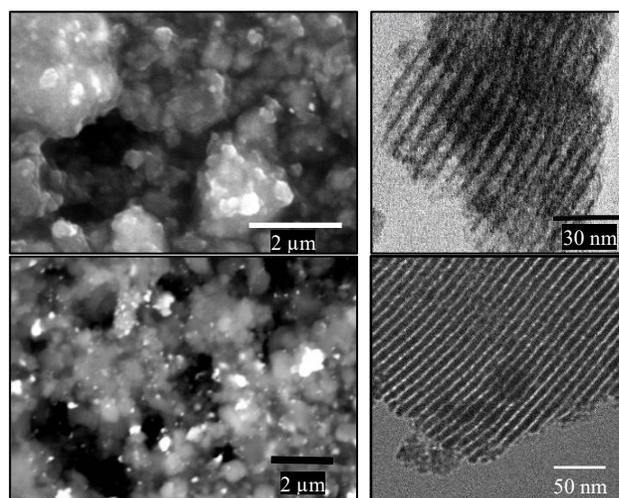


Figure 4: SEM (left) and TEM (right) images Ag@SBA-15 (top) and AgI@SBA-15 (bottom). Silver nanoparticles appear as 3 nm black dots in/on silica pores and pore walls. AgI semiconductor QDs are seen as white dots lined up within the pore network.

Taking these results together, white colored calcinated SBA-15 mesoporous silica was functionalized with AgNO₃ nanoparticles through a grinding/ heating method. EA analysis of the resulting grey powder confirmed that no silver had been lost during functionalisation. UV-Vis confirmed the presence of Ag nanoparticles. Ag@SBA-15 showed a silver plasmon band at 455 nm, (Figure 1). While XRD confirmed that cubic silver had been formed it also showed that AgNO₃ was also still present, (Figure 2). This would explain the relatively low concentration of silver nanoparticles as seen in UV-Vis. TGA showed water loss below 100 °C as well as Ag oxidation at 210 °C followed by Ag₂O decomposition, all of which is recorded in the literature.¹⁷ A large mass loss for the silver modified samples is also present at around 450 °C (Figure 2). Total weight loss above 600 °C was 3.6 %. This is in very good

agreement with the total nitrate content 3.67 % as extrapolated from EA. It therefore appears that any free nitrate (liberated from the reduced silver) is also retained, possibly sorbed by the SBA-15 or used to passivate the newly formed silver surfaces. Nitrogen sorption isotherms show a decrease in surface area, pore size and pore volume of the SBA-15 after modification with silver nitrate, (**Figure 3/ Table 1**). This would seem to suggest that the silver particles are in/on or covering the pores. SEM and TEM confirmed all three, although the degree of aggregation made imaging difficult. Silver particles are visible in the pore spaces with a sizable population clearly visible along the pore walls. The average particle size appears to be around 3 nm, (**Figure 4**). However due to lack of a stabiliser the degree particle aggregation is high. Although the population is almost entirely spherical one or two truncated triangles were seen. SEM shows the presence of large 100-500 nm bright spots on the Ag@SBA-15, (**Figure 4**). EDX confirmed that this was silver. Therefore, silver structures are also present on the outside of the SiO₂. After addition of the grey Ag@SBA-15 powder to an I₂ cyclohexane solution yellow AgI@SBA-15 was formed. This is confirmed by both UV-Vis and XRD. Despite numerous washing steps using initially cyclohexane, followed by ethanol, then acetone and finally water, no leaching was observed. This combined with the highly structured UV-Vis signals (despite the absence of a surface passivating stabiliser) suggests that the AgI is well bound to the silica. That is the AgI surface is being passivated with silanol groups. Also, both UV-Vis and XRD now shows only AgI

peaks/reflections respectively. Considering that washing steps resulted in no leaching this would suggest that all Ag⁰ particles and AgNO₃ has been converted to AgI. While not surprising for the AgNO₃ (as it is a classic Ag source for AgI formation), it would seem that instead of forming Ag/AgI core shell particles all Ag particles have been converted to AgI. This is probably the result of the Kirkendall effect, allowing for diffusion of iodine throughout the silver particles, instead of simply forming an AgI shell around an Ag core.^{29,30} This makes this material highly efficient for I₂ extraction. SEM of the AgI@SBA-15 shows a dramatic change in the appearance of surface silver artefacts. The large micron sized Ag aggregates have been replaced by smaller (70-300nm) more monodisperse looking nanocrystals. This suggests that the large artefacts seen on the Ag@SBA-15 were not silver microparticles but aggregates of silver nanoparticles or perhaps physisorbed AgNO₃. Either scenario would help explain the high I₂ capacity exhibited by these materials. In the case of AgNO₃ it is a matter of chemical conversion. If the silver is present as aggregated Ag⁰ nanoparticles then the addition of the strongly nucleophilic iodine to the silver surface would aid in surface charge separation, causing the silver aggregates to disassemble thereby allowing the iodine to access all particles within the aggregate.³¹ Nitrogen sorption isotherms showed that the pore volume continued to decrease after I₂ addition indicating that AgI is also formed within the pores. TGA measurements of the AgI@SBA-15 showed an additional mass loss step at 600-820 °C. While this is assumed to be AgI decomposition the temperature is

relatively high as the literature records the melting point of AgI nanoparticles at 550 °C.³² However, according to EA the Iodine content of AgI@SBA-15 is 4.8%. This is in good agreement with these mass loss steps indicating that it is AgI decomposition with the accompanying loss of I₂. This higher melting point indicates again that the AgI is being stabilised by the silica.

I₂ Sorption Kinetics and capacity

The rate of I₂ extraction was measured indirectly using UV-Vis. A known mass of I₂ was dissolved in a fixed volume of cyclohexane giving a violet solution with a strong absorption peak at 522 nm. Its molar extinction coefficient (ϵ) was calculated and used to determine the amount of I₂ removed from solution after a fixed amount of Ag@SBA-15 was added. As a control the behaviour of unfunctionalized SBA-15 in this I₂ solution was also observed. It was found to sorb a very small amount of I₂ which resulted in the silica having an orange yellow hue. This is probably due to the silanol groups on the SiO₂ hydrolysis the molecular I₂. The silica would later release the iodine yellowing its container walls. This therefore is probably how the AgI is formed in the case of the Ag@SBA-15. The SBA-15 sorbed and then hydrolysed small amounts of I₂ which the Ag then converts to AgI. This process continues until all the silver has been used. Initial extraction is quite fast with 50% of total I₂ sorbed after 1 minute (Figure 5). At this stage I₂ uptake slows considerably with equilibrium been reached after 30 minutes. A Langmuir plot was used to calculate extraction capacity which was found to be 68

mg/g (corresponding to TGA and EA results); 68 mg of I₂ equals 5.4 mmoles of I⁻. (Figure 5)

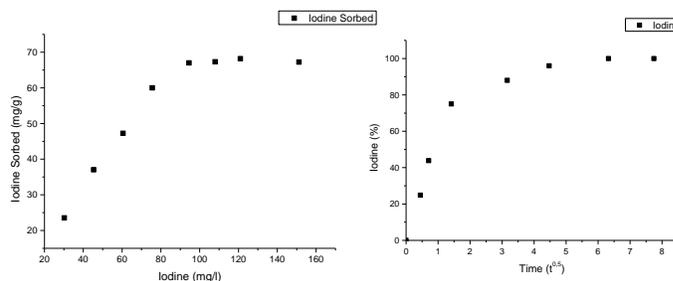


Figure 5: Left kinetics of I₂ extraction in minutes onto Ag@SBA-15. Right: Langmuir plot showing the I₂ capacity of Ag@SBA-15. Iodine (mg/L) => equilibrium concentration.

As 1g AgI@SBA-15 of contains 5.9 mmoles Ag this puts the actual yield of AgI (where Ag is the limiting factor) at 92.5%. Neither XRD nor UV-Vis detected any remaining Ag after I₂ addition allowing us to conclude that this value is within experimental error of near quantitative efficiency.

In conclusion, silver functionalized porous silica was prepared by a green solvent-free approach. XRD showed that metallic silver was present while UV-Vis and TEM showed that the silver was present as Ag⁰ nanoparticles. While the conversion of the silver precursor did not go to completion, (presence of AgNO₃) this did not affect the I₂ extraction. It was found that the conversion of Ag to AgI was almost 100 % indicating perhaps a Kirkendall effect had taken place. This type of effect is well recorded in the literature. Washing with a number of solvents ranging from cyclohexane to water resulted in no AgI leaching indicating that the particles are well bound to the silica. UV-Vis of the

AgI also indicated a well-structured and passivated surface. SEM also suggested a disaggregation effect after I₂ addition. This further influenced us to believe that any large Ag objects seen on the silica were aggregated nanoparticles and not bulk silver. The presence of unstabilised nano sized silver particles presented a large silver surface area which allowed for rapid I₂ extraction with a half-life of 1 minute, and a total conversion with a ratio Ag:I equal to 1:1. Finally, the thermal behaviour of this material with a high stability up to 600°C allows consideration to transform this kind of silica based materials into a final waste form by thermal treatment to close the porosity.

ASSOCIATED CONTENT

Supporting Information. Experimental details, FT-IR scans, XRD diffractogram and EDX spectra are available as Supporting Information should be included, ending with “This material is available free of charge via the Internet at <http://pubs.acs.org>.”

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. ‡These authors contributed equally. (match statement to author names with a symbol)

Funding Sources

Research was conducted in part by the Center for Hierarchical Waste Form Materials (CHWM), an Energy Frontier Research Center (EFRC) supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0016574. We also thank the EDDEM-CEA project for funding this work.

Notes.

ACKNOWLEDGMENT

Elemental Analysis was carried out by the Laboratoire de métallographie et d'analyse chimique, DEN/MAR/SA2I/DIR, CEA Marcoule, France.

ABBREVIATIONS

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