One stone, two birds: silica nanospheres significantly increase photocatalytic activity and colloidal stability of photocatalysts

To cite this article: Kowsalya D Rasamani et al 2018 Nano Futures 2 015003

View the article online for updates and enhancements.
One stone, two birds: silica nanospheres significantly increase photocatalytic activity and colloidal stability of photocatalysts

Kowsalya D Rasamani, Jonathan J Foley IV and Yugang Sun

Abstract

Silver-doped silver chloride \([\text{AgCl}\{\text{Ag}\}]\) nanoparticles represent a unique class of visible-light-driven photocatalysts, in which the silver dopants introduce electron-abundant mid-gap energy levels to lower the bandgap of AgCl. However, free-standing AgCl(Ag) nanoparticles, particularly those with small sizes and large surface areas, exhibit low colloidal stability and low compositional stability upon exposure to light irradiation, leading to easy aggregation and conversion to metallic silver and thus a loss of photocatalytic activity. These problems could be eliminated by attaching the small AgCl(Ag) nanoparticles to the surfaces of spherical dielectric silica particles with submicrometer sizes. The high optical transparency in the visible spectral region (400–800 nm), colloidal stability, and chemical/electronic inertness displayed by the silica spheres make them ideal for supporting photocatalysts and significantly improving their stability. The spherical morphology of the dielectric silica particles can support light scattering resonances to generate significantly enhanced electric fields near the silica particle surfaces, on which the optical absorption cross-section of the AgCl(Ag) nanoparticles is dramatically increased to promote their photocatalytic activity. The hybrid silica/AgCl(Ag) structures exhibit superior photocatalytic activity and stability, suitable for supporting photocatalysis sustainably; for instance, their efficiency in the photocatalytic decomposition of methylene blue decreases by only ~9% even after ten cycles of operation.

1. Introduction

Photocatalysis is an important strategy for utilizing solar energy for chemical transformations, including synthesis of valuable fine chemicals [1–7], pollutant decomposition for environmental remediation [8–12], and water splitting for hydrogen production [13–15]. Intensive efforts have been devoted to enhancing the optical absorption of photocatalysts in a broad spectral range through either narrowing the bandgap of light-absorbing semiconductors or sensitizing wide-gap semiconductors with light-absorbing components [16–20]. For example, binary (AgX) and ternary silver halides (AgXY), a class of semiconductors with both direct and indirect bandgaps, usually exhibit weak optical absorption in the visible region [21, 22]. Partial reduction of silver halides can convert silver ions to metallic silver (Ag\(^0\)), resulting in the formation of Ag-doped AgX [AgX(Ag)]. Ag\(^0\) enables strong absorption of visible light in AgX(Ag) due to the addition of extra energy states between the conduction band and valence band of AgX or possible strong optical absorption of metallic Ag nanodomains originating from their surface plasmon resonances, making AgX(Ag) composite materials promising visible-light photocatalysts [23–27]. AgCl nanoparticles containing Ag\(^0\), which are hundreds of nanometers and even micrometers in size, have been extensively studied and applied in photocatalytic water splitting [24, 28], CO\(_2\) reduction [29, 30], and removal of toxic heavy metal ions [31, 32], organic pollutants and dyes [25, 33, 34]. In addition, the existence of metallic Ag in AgCl can increase the chemical stability of AgCl since the high density of electrons in Ag could alleviate the photoreduction of AgCl during photocatalysis [25, 35–37]. Despite these advantages of AgCl(Ag) composite materials for photocatalysis, AgCl(Ag) nanoparticles with
small sizes (i.e., < 100 nm) have barely been studied because of their low colloidal and chemical stability. AgCl(Ag) nanoparticles < 100 nm in size tend to aggregate and be reduced to Ag nanoparticles upon photo-illumination, leading to a significant decrease in photocatalytic activity. AgCl(Ag) nanoparticles are often loaded on stable colloidal supports with large sizes—for example, graphene oxide [38, 39], SiO2 [40], TiO2 [41], C, N4 [42] and WO3 [43]—to mitigate their instability.

In general, reducing particle size increases the available surface area of the photocatalysts, benefiting photocatalytic activity [44, 45]. However, small nanoparticles usually exhibit weak optical absorption cross-sections due to the small volume of the materials [46, 47]. Here, we report a composite containing AgCl(Ag) nanocubes (NCs) with sizes of ~60 nm attached to the surfaces of optically transparent, dielectric silica (SiO2) nanospheres (NSs) with hundreds of nanometers in size, which serves as an efficient photocatalyst with dramatically improved efficiency and stability compared to free-standing AgCl(Ag) colloidal dispersions.

2. Experimental

2.1. Synthesis and surface functionalization of SiO2 NSs

SiO2 NSs with a mean diameter of 285 nm were synthesized through a Stöber sol–gel method reported previously [48]. Briefly, 1.7 ml of tetraethyl orthosilicate (TEOS, 98%, Acros Organics) was added dropwise to a mixture containing 18.12 ml of ethanol (190 proof, Pharmco-Aaper), 3.21 ml of deionized water, and 1.96 ml of ammonium hydroxide (20%–30%, Fisher Scientific). The solution was continuously stirred at 600 revolutions per minute (rpm) for 2 h at room temperature, leading to a controlled hydrolysis of the TEOS and the formation of SiO2 NSs. The obtained colloidal SiO2 NSs were washed with ethanol several times, collected by centrifugation at 6000 rpm, and dried at 60 °C in an oven for 4 h. The surfaces of the as-synthesized SiO2 NSs were modified to exhibit a surface —NH2 group by employing the procedure described in a previous report [48]. In brief, 1 ml of (3-amino propyl)triethoxysilane (APTES, 98%, Alfa Aesar) was added to a 100 ml ethanol dispersion of 0.2 g SiO2 NSs maintained at 60 °C under constant stirring at 800 rpm for 4 h. The APTES-functionalized SiO2 (APTES-SiO2) NSs were washed multiple times with ethanol to remove excessive APTES, re-dispersed in 100 ml deionized water, and stored in the dark at room temperature for further use.

2.2. Synthesis of Ag-doped AgCl NCs

AgCl NCs with a mean edge length of 60 nm were synthesized using the procedure reported in our previous work with appropriate modifications [49]. In a typical synthesis, 0.35 mmol of NaCl (Fisher Scientific) and 2.5 g of poly (vinylpyrrolidone) (PVP, molecular weight ∼55,000, Sigma Aldrich) were dissolved in 12 ml ethylene glycol (Fisher Scientific) at a temperature of 60 °C with magnetic stirring of 1100 rpm under a N2 atmosphere. After the complete dissolution of the PVP, the stir rate was maintained at 800 rpm and the temperature was kept at 60 °C. To this solution, 1 ml of freshly prepared AgNO3 solution (0.34 M in ethylene glycol, Acros Organics) was injected rapidly. The reaction mixture was allowed to stir at 800 rpm for an additional 20 min in the dark. The as-synthesized, pristine AgCl NCs were washed several times with ethanol to remove ethylene glycol and excess PVP, and were then re-dispersed in ethanol. The ethanol dispersion of AgCl NCs was illuminated with a lamp (350–750 nm, xenon light source, 100 W MAX-330, Asahi Spectra, Japan) at an intensity of 4 mW cm⁻² for 2 h to partially convert AgCl to metallic Ag through the photoreduction of AgCl. The resulting composite AgCl(Ag) NCs were washed and re-dispersed in water and the stock dispersion was stored in the dark for further use.

2.3. Formation of SiO2/AgCl(Ag) heterostructures

For the formation of SiO2/AgCl(Ag) heterostructures, a 2 ml dispersion of AgCl(Ag) NCs was added dropwise to a 5 ml aqueous dispersion of 2 mg ml⁻¹ APTES-SiO2 NSs at a magnetic stirring of 600 rpm for 2 h. This mixing process enabled the attachment of the AgCl(Ag) NCs with negative surface charges to the positively charged APTES-SiO2 NSs through electrostatic attraction. The obtained heterostructures of SiO2/AgCl(Ag) were collected by centrifugation at 10,000 rpm and re-dispersed in 5 ml deionized water (solution A). Similarly, an equivalent volume of the AgCl(Ag) stock dispersion was diluted to 5 ml deionized water (solution B) and stored in the dark as a reference for photocatalytic evaluation.

2.4. Evaluation of photocatalytic activity

Photocatalytic degradation of methylene blue (MB) was used as the model reaction to evaluate the photocatalytic activity of the synthesized AgCl(Ag) samples. In a typical evaluation, 2 ml of 10 mg ml⁻¹ aqueous MB solution was added to 2 ml of solution A or solution B, followed by stirring in the dark for 30 min. This process led to the adsorption/desorption equilibrium of MB molecules on the surfaces of the AgCl(Ag) NCs. The mixture was then illuminated with visible light (400–750 nm, employed with a long-pass optical filter to cut off light with a wavelength of <400 nm) at an intensity of 16 mW cm⁻² for ∼30 min while magnetic stirring of 600 rpm
was maintained. This setup allowed us to study the rate of MB degradation and the stability of free-standing AgCl(Ag) NCs and SiO$_x$/AgCl(Ag) heterostructures in photocatalysis. Experiments with a N$_2$ atmosphere were performed similarly. In these cases, the reaction dispersion was purged with N$_2$ gas for 1 h in the dark followed by employing a N$_2$ blanket above the solution throughout the entire experiment. Photocatalytic MB degradation in the inert atmosphere was carried out under photo-illumination of 20 min. The same reaction dispersion was then purged with O$_2$ for 30 min. With the O$_2$ flow maintained above the solution, photocatalytic degradation of

**Figure 1.** (a) SEM image and (b) optical absorption spectrum of the AgCl(Ag) NCs. The insets in (b) are photographs of the ethanolic dispersions of AgCl(Ag) NCs and their parent AgCl NCs. (c) Decrease of MB with time in the course of photocatalytic reactions using AgCl(Ag) NCs as photocatalyst. The AgCl(Ag) photocatalyst was recovered for three times of the photocatalytic reaction, highlighting the significant reduction of photocatalytic activity in the third cycle of reaction.
MB was then continued under photo-illumination. The kinetic rate constants of MB degradation under different reaction atmospheres were calculated by considering the respective concentrations of MB at the start of photo-illumination. Experiments were also conducted in sunlight to evaluate the practical promise of the SiO\textsubscript{X}/AgCl\textsubscript{Ag} photocatalyst. In a typical experiment, a 20 ml aqueous dispersion containing 5 mg ml\textsuperscript{-1} MB and a 5 ml stock dispersion of the photocatalyst was placed in sunlight for 30 min.

2.5. Material characterization

Scanning electron microscopy (SEM) images of the AgCl NCs, AgCl\textsubscript{Ag} NCs and SiO\textsubscript{X} NSs were obtained using a scanning electron microscope (FEI Quanta FEG 450) operated at 30 kV. The images were taken with a secondary-electron imaging mode. Diffuse reflectance spectra (DRS) for the aqueous dispersions of SiO\textsubscript{X} NSs, AgCl\textsubscript{Ag} NCs, and SiO\textsubscript{X}/AgCl\textsubscript{Ag} heterostructures were obtained using a UV–vis spectrophotometer (Thermo Scientific, Evolution 220) with an optical integration sphere.

3. Results and discussion

AgCl NCs were synthesized through a precipitation reaction between Ag\textsuperscript{+} and Cl\textsuperscript{-} ions in viscous ethylene glycol in the presence of PVP at 60 °C (figure S1(a) is available online at stacks.iop.org/NANOF/2/015003/mmedia). PVP served as a surfactant to stabilize the as-grown AgCl NCs in the reaction solution. Rapid injection of AgNO\textsubscript{3} solution triggered the fast nucleation of AgCl, leading to the formation of a high concentration of AgCl nuclei and thus AgCl NCs with small sizes: an average edge length of 60 nm and a narrow size distribution of ±4.8\%. The PVP-stabilized AgCl NCs exhibited a negatively charged surface with a zeta potential of −31.2 ± 8.8 mV when dispersed in water. Energy-dispersive x-ray (EDX) spectroscopy of the AgCl NCs revealed a 1:1 atomic ratio between the Ag and Cl (figure S1(b)). Irradiating an ethanol dispersion of the AgCl NCs with a xenon light source led to partial conversion of AgCl to Ag\textsubscript{0} (figure 1(a)), forming composite AgCl\textsubscript{Ag} nanoparticles and inducing a color change (inset, figure 1(b)). SEM images of the AgCl\textsubscript{Ag} nanoparticles clearly show that the cubic morphology was maintained during irradiation (inset, figures 1(a) and S1(a)). EDX
spectroscopic characterization indicated the conversion of ∼16% AgCl to Ag₀ (figure S2(a)). The AgCl(Ag) NCs dispersed in water still exhibited an average particle edge length of ∼60 nm and a negative surface charge with a zeta potential of $-13.3 \pm 6.7$ mV (figure S2(b)).

The dispersion of AgCl(Ag) NCs exhibits a broad optical absorption peak in the range of 400–550 nm and a strong absorption peak at 260 nm (figure 1(b)). The strong UV absorption peak corresponds to the direct bandgap of AgCl, while the broadband absorption in the visible region is attributed to the presence of Ag₀ in AgCl. The doped Ag₀ atoms provide additional energy states that fall between the conduction band and valence band of AgCl, enabling electronic transitions with lower energies (i.e., smaller than the bandgap of AgCl). This effect leads to an increase in optical absorption of the AgCl(Ag) NCs in the visible region and thus improves their photocatalytic activity [23, 24].

The dispersion of AgCl(Ag) NCs exhibits a broad optical absorption peak in the range of 400–550 nm and a strong absorption peak at 260 nm (figure 1(b)). The strong UV absorption peak corresponds to the direct bandgap of AgCl, while the broadband absorption in the visible region is attributed to the presence of Ag₀ in AgCl. The doped Ag₀ atoms provide additional energy states that fall between the conduction band and valence band of AgCl, enabling electronic transitions with lower energies (i.e., smaller than the bandgap of AgCl). This effect leads to an increase in optical absorption of the AgCl(Ag) NCs in the visible region and thus improves their photocatalytic activity [23, 24]. The photocatalytic performance of the AgCl(Ag) NCs is evaluated with the photocatalytic degradation of MB as a model reaction. Irradiating a solution containing both MB and AgCl(Ag) NCs with visible light decreases the absorbance of MB, indicating the degradation of MB molecules over time (figures 1(c), S3(a)–(f)). The decrease in photocatalytic activity at the end of the third cycle indicates the low stability of the AgCl(Ag) NCs when they are used as free-standing particles in a colloidal solution. The significant decrease in MB degradation can be attributed to the aggregation of free-standing AgCl(Ag) NCs in the colloidal solution during photocatalysis. For each reaction cycle, the AgCl(Ag) nanoparticles are collected from the reaction solution by centrifugation and re-dispersed in deionized water by sonication for the next cycle of reaction. Even after prolonged ultrasonication, their photocatalytic activity cannot be recovered in the sequential cycles, making it evident that severe aggregation occurs during the photocatalytic reaction. The SEM images of the AgCl(Ag) nanoparticles after three photocatalytic reaction cycles confirm the nanoparticle aggregation (figure S4(a)). In addition, the AgCl(Ag) nanoparticles transform into irregular shapes, no longer exhibiting a cubic geometry. The morphological variation of the AgCl(Ag) nanoparticles implies the possible chemical conversion of AgCl to Ag₀ in the course of the photocatalytic reactions, which leads to a redistribution of mass in individual nanoparticles and thus to a reconstruction of their morphology. Statistical analysis of the
irregular AgCl(Ag) nanoparticles after three photocatalytic cycles indicates their broad size distribution with a value of 180 ± 30 nm, further confirming the severe aggregation of AgCl(Ag) NCs in the course of photocatalysis (figure S4(b)). The increase in particle size increases the diffusion length of the excited electrons to reach the particles’ surface and drive chemical reaction. As a result, fewer excited electrons can drive surface chemical reaction and more excited electrons stay in the nanoparticles and reduce Ag⁺ into metallic Ag⁰ in the AgCl lattices. The leftover holes oxidize Cl⁻ ions into Cl₂ atoms, which then produce Cl₂ [34]. Such chemical transformation of the AgCl(Ag) nanoparticles leads to significant morphological and compositional changes in the nanoparticles and thus to reduced photocatalytic activity. The corresponding EDX spectrum of the used AgCl(Ag) nanoparticles exhibits a much higher concentration of Ag compared to that of the freshly prepared AgCl(Ag) NCs, indicating that ~95% of AgCl is reduced to Ag⁰ after three cycles of photocatalytic reactions (figure S4(c)). Chemical conversion of AgCl to metallic Ag changes the surface chemistry and surface charge density of the AgCl(Ag) NCs, which are responsible for their aggregation and reduced photocatalytic activity.

In order to ensure colloidal stability and improve photocatalytic activity, the AgCl(Ag) NCs are loaded onto the surface of colloidal SiO₂ NSs (figures S5(a) and S5(b)) that are stable in aqueous dispersions. The SiO₂ NSs synthesized through the modified Sölber process are modified with APTES to expose positively charged surfaces with a zeta potential of 20 ± 6.3 mV. The APTES-SiO₂ NSs become favorable for electrostatically attracting the negatively charged AgCl(Ag) NCs and binding them together, forming composite SiO₂/AgCl(Ag) heterostructures (figure 2(a)). The high colloidal stability of the SiO₂ NSs can efficiently prevent the aggregation of the AgCl(Ag) NCs fixed onto the SiO₂ surface. In addition, SiO₂ NSs can support resonant light scattering modes that produce enhanced electrical fields near their surfaces, on which nanocrystals can exhibit increased absorption cross-sections [48, 50, 51]. As a result, the SiO₂/AgCl(Ag) heterostructures display enhanced optical absorption throughout both the UV and visible regions in the measurements compared to the same amount of free-standing AgCl(Ag) NCs. By normalizing against the absorption spectrum of free-standing AgCl(Ag) NCs (green curve, figure 2(b)), the absorption spectrum of SiO₂/AgCl(Ag) (blue curve, figure 2(b)) is converted to the optical enhancement spectrum (red curve, figure 2(b)), which highlights how much the optical absorption of the AgCl(Ag) NCs is enhanced as a function of wavelength upon their attachment onto the SiO₂ NS surface. Interestingly, the enhancement spectrum exhibits four peaks at ~290 nm, 340 nm, 425 nm, and 715 nm with enhancement factors of 2.8, 4.9, 5.7, and 12.8 times, respectively (red curve, figure 2(b)). The positions of these peaks are consistent with the scattering resonance bands of the SiO₂ NSs [33, 34]. The optical absorption is enhanced more significantly in the visible region, making SiO₂/AgCl(Ag) heterostructures efficient photocatalysts for visible-light-driven chemical conversion. Moreover, the chemical inertness of the SiO₂ NSs eliminates any possible charge trapping or charge transfer at the SiO₂/AgCl(Ag) interface, causing the photoexcited charges in the AgCl(Ag) NCs to directly drive chemical conversion on the surfaces of the NCs.

The SiO₂/AgCl(Ag) heterostructures exhibit superior stability and activity for the photocatalytic degradation of MB when they are used for many cycles of photocatalytic reaction. The time-dependent variations of the MB absorption spectra recorded from all the photocatalytic reactions indicate only a slight decrease in the photocatalytic activity of the SiO₂/AgCl(Ag) heterostructures even after ten cycles of reactions (figures S6(a)–(j)). According to the Beer–Lambert law, the concentration (C) of MB monomers at any time can be calculated through normalization of the absorbance at 667 nm against the concentration (C₀) measured right before the photocatalytic reaction. The ratio C/C₀ represents the percentage of MB monomers that are not decomposed at a specific time (t). The decrease of C/C₀ as a function of t does not show significant differences for the ten sequential reactions using the same batch of SiO₂/AgCl(Ag) as photocatalyst (figure 3(a)), highlighting the superior stability of SiO₂/AgCl(Ag). Moreover, ln(C/C₀) exhibits a linear dependence on t, indicating that the decomposition of MB molecules follows pseudo-first-order reaction kinetics [25]:

$$\frac{-dC}{dt} = kC,$$

where k represents the reaction rate constant (figure S6(k)). The percentage of MB degradation remains larger than 90% even for the tenth cycle of reaction (figure 3(b)). The slight decrease in decomposition efficiency might be due to the loss of SiO₂/AgCl(Ag) photocatalyst in the process of material collection for new reactions. SEM images of the SiO₂/AgCl(Ag) photocatalyst after ten cycles of reaction show a morphology and dispersity similar to those of a freshly prepared sample (figure 3(c) versus figure 2(a)), again confirming that AgCl(Ag) NCs become more stable on SiO₂ NSs. EDX analysis reveals that only 11% of AgCl is reduced to Ag⁰ (figure S7), indicating the chemical stability of the AgCl(Ag) NCs on the SiO₂ NSs. In contrast to the aggregation of free-standing AgCl(Ag) NCs, that of AgCl(Ag) NCs loaded onto SiO₂ NSs can be prevented. The absence of nanoparticle aggregation maintains the short diffusion length of the excited electrons reaching the nanoparticles’ surface to efficiently drive surface chemical reaction. Since more excited electrons can reach the nanoparticles’ surface, fewer electrons stay in the AgCl lattice to reduce Ag⁺ into metallic Ag⁰, resulting in morphological and compositional stability.

The enhanced photocatalytic activity and stability of the SiO₂/AgCl(Ag) heterostructures compared to those of the free-standing AgCl(Ag) NCs make SiO₂/AgCl(Ag) heterostructures promising as a class of practical...
photocatalysts. For example, SiO$_x$/AgCl(Ag) composite particles can be added to an aqueous solution of MB in sunlight, leading to a quick and steady decomposition of MB. As shown in figure 3(d), the optical absorbance of MB gradually and continuously decreases as a function of time until the MB molecules are completely consumed. Photographs of the reaction solution before and after the solution is illuminated for 30 min show the apparent color change from blue (corresponding to MB) to light gray (due to the scattering of SiO$_x$ NSs) (inset, figure 3(d)).

**Figure 4.** Time-dependent variation of the absorption spectrum of MB during photocatalytic degradation performed under (a) a N$_2$ atmosphere and (b) an O$_2$ atmosphere. The photocatalyst was the hybrid SiO$_x$/AgCl(Ag) particles shown in figure 2(a). (c) Reaction kinetics of the photocatalytic degradation of MB under different atmospheres derived from (a) and (b). The linear fittings indicate that the reactions follow quasi-first-order reaction kinetics with reaction rate constants of 0.014 min$^{-1}$ and 0.110 min$^{-1}$ for the N$_2$ and O$_2$ atmospheres, respectively.
The decomposition rate of MB drastically decreases when the photocatalytic experiments are carried out in an inert atmosphere (i.e., a N₂ atmosphere), before which the reaction solution is purged with N₂ bubbles for 1 h in the dark (figure 4(a)). The reaction rate constant of MB decomposition is only 0.014 min⁻¹, which is much smaller than those obtained in the ambient atmosphere (i.e., air), in the initial 20 min of measurement (figure 4(c)). The same reaction solution is then purged with O₂ bubbles for 30 min in the dark followed by a continuous flow of O₂ gas above the reaction solution to maintain the saturation of dissolved O₂ in the reaction solution. Upon exposure to visible light, the reaction of MB decomposition becomes significantly faster (figure 4(b)) and the corresponding rate constant reaches 0.110 min⁻¹ (black line). This rate constant is even higher than those obtained from the reactions under air (figure 6(k)). The strong dependence of the reaction rate on the reaction atmosphere indicates that the dissolved O₂ is actively involved in the photocatalytic process of MB degradation.

As a semiconductor, AgCl exhibits large bandgaps corresponding to the absorption of UV light (i.e., a direct bandgap of 5.15 eV or 241 nm, an indirect bandgap of 3.25 eV or 382 nm) [52]. The optical absorption of broadband visible light (>400 nm with a peak around 450 nm) in AgCl(Ag) NCs is enabled by the presence of Ag⁰, which introduces additional electron-abundant mid-gap energy states near the valence band of AgCl [23, 24]. The mid-gap states significantly lower the energy required for the photo-excitation of electrons in AgCl. This is different from optical absorption originating from the surface plasmon resonance of nanoscale Ag crystalline domains [53, 54]. Optical absorption spectra and cross-sections of the AgCl(Ag) NCs and SiO₂/AgCl(Ag) heterostructures are modeled and calculated with rigorous time-domain electrodynamic simulations. A commercial-grade simulator based on the finite-difference time-domain (FDTD) method is used to perform the calculations [55]. A uniform rectangular grid with dx = dy = dz = 5 nm is used in all simulations. The background refractive index for these calculations is set to 1.33 to simulate the optical response of the structures in water. In the calculations, the AgCl(Ag) NCs are modeled as cubes with an edge length of 60 nm and a complex, frequency-dependent dielectric function approximated by a Lorentz oscillator model [56] with the parameters chosen to closely match the experimental absorption spectrum of the synthesized AgCl(Ag) NCs dispersed in water. The particular form of this Lorentz oscillator model is given by

\[
\epsilon_{\text{AgCl(Ag)}}(\omega) = 1 + \frac{\omega^2_{p,1}}{\omega^2_{0,1} - \omega^2 - i\gamma_1\omega} + \frac{\omega^2_{p,2}}{\omega^2_{0,2} - \omega^2 - i\gamma_2\omega},
\]

where the values of the Lorentz parameters are summarized in table 1. The corresponding frequency-dependent functions (both real and imaginary parts) of these two oscillators (oscillator 1 and 2) show that there is no condition supporting surface plasmon resonance (figures S8(a)–(d)). The absence of possible surface plasmon resonance in AgCl(Ag) NCs dispersed in water.

### Table 1. Lorentz parameters of the two oscillators fitted from the Lorentz oscillator model.

<table>
<thead>
<tr>
<th>Lorentz parameters</th>
<th>Oscillator 1 (rad s⁻¹)</th>
<th>Oscillator 2 (rad s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_0)</td>
<td>(2.16 \times 10^{15})</td>
<td>(1.27 \times 10^{15})</td>
</tr>
<tr>
<td>(\omega_0)</td>
<td>(7.22 \times 10^{15})</td>
<td>(4.23 \times 10^{15})</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>(1.15 \times 10^{15})</td>
<td>(2.11 \times 10^{15})</td>
</tr>
</tbody>
</table>

![Figure 5. FDTD-simulated absorption cross-section of free-standing AgCl(Ag) NCs (green curve) and SiO₂-supported AgCl(Ag) NCs (blue curve). The ratio between the absorbances of these two absorption spectra represents the enhancement spectrum (red curve), showing peaks around 206 nm, 315 nm, and 675 nm.](image)

![Image](image)
resonance suggests that the absorption of visible light in AgCl(Ag) can be ascribed to the additional mid-gap states in AgCl due to the electron-abundant Ag$^0$ dopant. In the SiO$_X$/AgCl(Ag) heterostructures, the SiO$_X$ support is modeled as spheres with a refractive index ($n$) of 1.45, which matches the refractive index of fused SiO$_2$ [57]. A total-field/scattered-field formalism with a

![Figure 6](image.png)

Figure 6. Near-field intensity maps of the hybrid SiO$_2$/AgCl(Ag) plotted for incident light with wavelengths at the peak positions of the enhancement spectrum shown in figure 5: (a) 206 nm (Peak I), (b) 315 nm (Peak II) and (c) 675 nm (Peak III). These maps display a clear nodal structure in the SiO$_2$, which supports our attribution of the absorption enhancement to the near-field dielectric scattering mechanism. The color bar represents a unitless scale, $\log_{10}(E/E_0)$, where $E$ and $E_0$ represent the local electric field and the incident electric field, respectively.
broadband source spanning 200–800 nm is used to compute the absorption and scattering cross-sections of the free-standing AgCl(Ag) NCs and SiO$_2$/AgCl(Ag) heterostructures, enabling the calculation of a theoretical enhancement spectrum. The effect of SiO$_2$ supports and the resulting scattering resonances on and around the boundary of the NS responsible for the overall absorption enhancement of the photocatalysts has been further evaluated by determining the absorption and scattering behavior of incident light by a model of the photocatalyst simulated based on the FDTD method. The permittivity of AgCl(Ag) in both the composite and free-standing FDTD models is given by the Lorentz oscillator model discussed earlier (equation (2) and table 1), so these calculations are meant to selectively probe the impact of the scattering resonances of SiO$_2$ on the absorption of AgCl(Ag). In each simulation, the incident light field propagates along the y-axis and is polarized along the z-axis, though test simulations are run to confirm the relative insensitivity to polarization of the incident field.

The absorption cross-section of SiO$_2$/AgCl(Ag) is found to be greater than that of the free-standing AgCl (Ag) NCs dispersed in water (figure 5). Furthermore, the FDTD-simulated enhancement spectrum, which is obtained by normalizing the absorption cross-section of SiO$_2$/AgCl(Ag) against that of free-standing AgCl(Ag), reveals the existence of three specific peaks at wavelengths of 206 nm (Peak I), 315 nm (Peak II) and 675 nm (Peak III). These identified peaks at specific wavelengths of the enhancement spectrum are consistent with near-field scattering resonances occurring due to the presence of spherical, dielectric SiO$_2$ supports (figure 5, red open circle). The electric field intensity maps at these resonance peak positions (figures 6(a)–(c)) display nodal structures with field enhancements on and around the boundary of the SiO$_2$ NS, indicating that the increased absorption cross-section of the attached AgCl(Ag) nanoparticles is indeed due to the scattering-mediated near-field enhancement caused by the SiO$_2$ supports.

The experimental and theoretical results highlight that absorption of broadband visible light in SiO$_2$/AgCl(Ag) composite structures is significantly improved due to an enhanced electric field on the spherical SiO$_2$ nanoparticle surface and additional electron-abundant mid-gap energy states in AgCl. The strong light absorption efficiently excites the electrons in the newly added mid-gap levels to the AgCl conduction band followed by their transfer to surface adsorbates, i.e., O$_2$, in the ambient environment (figure 7). Combining the excited electrons with the adsorbed O$_2$ results in the formation of highly oxidative perhydroxyl radicals (HO$_2^\cdot$) [58, 59]. The HO$_2^\cdot$ radicals quickly oxidize the MB molecules, which reach the surfaces of the AgCl(Ag) NCs, to CO$_2$ and water (top process, figure 7). Holes in the mid-gap levels can also oxidize the MB molecules (bottom process, figure 7) [60, 61]. Therefore, the photo-excited electrons will accumulate in the AgCl conduction band when the reaction solution is free of O$_2$ or has a low concentration of dissolved O$_2$, leading to a possible reduction of AgCl and thus to the degradation of the photocatalytic performance of the AgCl(Ag) NCs. In this case, the photo-excited electrons cannot work in the right way to oxidize MB, resulting in a decrease in the reaction rate of MB decomposition (as shown in figure 4(c)).

4. Conclusion

Doping wide-bandgap semiconductor (AgCl) NCs with Ag$^0$ results in broadband optical absorption in the visible region since the Ag$^0$ species introduces electron-abundant mid-gap energy states in AgCl. The optical
absorption cross-section of the AgCl(Ag) NCs is further increased by loading these NCs on dielectric spherical SiO₂ particles, which produce enhanced electric fields on and around the boundary of the SiO₂ surfaces due to the resonant scattering of light. The enhanced electric fields are responsible for the enhanced optical absorption in the AgCl(Ag) NCs, making the AgCl(Ag) NCs, even those with small sizes, to photo-excite electrons with high efficiency. The excited electrons and the corresponding holes can oxidize MB molecules through the photocatalytic process. Although the small size of AgCl(Ag) NCs is beneficial for catalytic reactions, small NCs have low colloidal stability and resistance to self-reduction. For instance, the free-standing AgCl(Ag) NCs exhibit severe aggregation and reduction of 95% AgCl to metallic Ag after three cycles of photocatalytic degradation of MB in aqueous solutions. In contrast, the instability of small AgCl(Ag) NCs is significantly reduced when they are loaded onto the SiO₂ spherical particles, leading to superior efficiency and stability in the photocatalytic degradation of MB. For example, the SiO₂/AgCl(Ag) composite particles exhibit minimum variation of photocatalytic efficiency and chemical/colloidal stability after ten cycles of reactions. The results highlight, for the first time, that chemically inert and optically transparent SiO₂ spheres play critical roles in simultaneously enhancing the optical absorption and chemical/colloidal stability of small AgCl(Ag) NCs, and thus improve the photocatalytic performance of the AgCl(Ag) NCs.

Acknowledgments

Y S acknowledges the startup and OVPR seed funding from Temple University. The characterizations were performed with the use of Temple Materials Institute facilities. J J F acknowledges financial support from the Center for Research at William Paterson University.

ORCID iDs

Kowsalya D Rasamani  https://orcid.org/0000-0002-1717-1426
Yugang Sun  https://orcid.org/0000-0001-6351-6977

References

[8] Sun Y 2010 Conversion of Ag nanowires to AgCl nanowires decorated with Au nanoparticles and their photocatalytic activity J. Phys. Chem. C 114 2127–33
[27] Codrington J, Elbadagh N, Fernanado K and Foley J J IV 2017 Unique host carrier distributions from scanned mediated absorption ACS Photonics 4 552–9
[38] Codrington J, Elbadagh N, Fernanado K and Foley J J IV 2017 Unique host carrier distributions from scanned mediated absorption ACS Photonics 4 552–9
[40] Ma X, Dai Y, Yu L, Lou Z, Huang B and Whangbo M H 2014 Electron–hole pair generation of the visible-light plasmonic photocatalyst Ag@AgCl: enhanced optical transitions involving midgap defect states of Ag@C1. Phys. Chem. C 118 12133–40
[42] Numerical Solutions, Inc. (http://numerical.com/tcad-products/fdtd/)
[43] Bohren C F and Huffman D R 1998 Absorption and Scattering of Light by Small Particles (New York: Wiley)