

SULFUR-CONTAINING ORGANIC MOLECULES THAT HAVE BEEN COMPLEXED WITH METALS

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ABSTRACT

A possible new approach that is more favourable to the environment is the coupling of carbon dioxide with epoxides, which results in the synthesis of COCs and APCs. The purpose of this research is to provide a comprehensive review of metal complexes with sulfur-containing ligands as homogeneous catalytic systems that are able to effectively drive this transition while also offering a concise explanation of the most significant results that were discovered. The essential role that sulphur plays as the hemilabile ligand and the influence that it has on the catalytic activity are also brought to light here. This work presents a novel, equipment-free, generic approach for the identification of sulfur-containing compounds by using the ability of sulfur-containing compounds to delay the photoreduction kinetics of gold ions to gold nanoparticles. The technique has been developed as part of this investigation. The method comprises monitoring the amount of time that passes between the addition of the target analyte and the emergence of a red colour in the sample that is being tested. The presence of this colour in the sample is an indication that gold nanoparticles have been created. Because it just requires two solutions (a buffer solution and a gold solution), a source of ultraviolet or visible light, and a timer, the process may be carried out with a minimal amount of effort and in a simple manner. Because it reacts to such a wide variety of sulfur-containing compounds, the method has been applied to the determination of a variety of sulfur-containing compounds in a variety of samples, including natural waters and wastewater, biological fluids, and prescription drugs. These compounds include dithiocarbamate and organophosphorous pesticides, biothiols, pharmaceutically active compounds, and sulphides. The method has a number of analytical figures of merit, some of which include acceptable repeatability (ranging from 4.8 to 9.8%), decent recoveries (ranging from 93 to 109%), and high sensitivity (quantitation limits at the low M values). The method is simple enough that a user with no special training may execute it, flexible enough to be used for both quantitative and semiquantitative analysis outside of a laboratory context, and economical. All of these benefits come together to make the method attractive.

Keywords: *homogeneous catalysis; sulfur; carbon dioxide; epoxides; cyclic carbonates; polycarbonates*

INTRODUCTION

Because the course of a specific reaction may be precisely adjusted by the rational design of the catalyst architecture, homogeneous catalysis is a discipline of chemistry that is expanding at a fast rate. This is one of the reasons why. In point of fact, the mechanisms that drive the activity and selectivity are well understood, which enables a substantial improvement in overall performance in contrast to heterogeneous catalysis. The

use of soluble transition-metal complexes in catalysis, in particular, has created possibilities for fine-tuning product features that were previously inconceivable. This is accomplished by careful manipulation of the electronic and steric properties of the auxiliary ligand. Because of this one fundamental concept, ingenious stereoselective procedures spanning all kinds of chemical synthesis have been devised as a result (for example, oxidations, cross-coupling reactions, polymerisations, and so on). In a similar vein, the need for chemical processes that are less harmful to the environment has, over the course of the last two decades, led to an increase in the utilisation of renewable feedstocks. Carbon dioxide utilisation, also known as CDU, has emerged as an important tool for the transition to a carbon-neutral society because of its capacity to complete an anthropogenic carbon cycle without the net creation of glasshouse gases via the use of renewable energy. This makes carbon dioxide utilisation a significant instrument for the transition. In addition, when compared to other C1 feedstocks, such as phosgene and carbon monoxide, carbon dioxide clearly exhibits advantages in terms of toxicity, flammability, and the capacity for storage, which makes the implementation of industrial processes based on this molecule particularly practical. A great deal of interest has been generated in cyclic organic carbonates (COCs) and aliphatic polycarbonates (APCs) as a result of their adaptability as well as the ease with which they may be synthesised, commencing with the same amount of CO₂. When CO₂ is coupled with an epoxide, the formation of a cyclic or polymeric product is determined by a number of parameters, the most important of which are the kind of substrate, the reaction circumstances, and the catalytic system. Despite the efforts that have been put into developing efficient metal-free catalysts, the majority of active systems still depend on the combination of a metal complex that has been activated by a suitable nucleophile. These nucleophiles are often delivered in the form of an ammonium or phosphonium salt. The metal-epoxide coordination step, the ring-opening of the activated epoxide by nucleophilic attack, and the carbon dioxide (CO₂) insertion step are the essential stages of the reaction process. Path A results in the development of the COC by an intramolecular ring-closing reaction, while Path B results in the formation of the APC through the alternating insertion of epoxide and CO₂ in the process. As a consequence of the fact that a third route, route C, makes it possible to insert two epoxides one after the other, the final polymer typically contains polyether linkages as well. Because the course of a specific reaction may be precisely adjusted by the rational design of the catalyst architecture, homogeneous catalysis is a discipline of chemistry that is expanding at a fast rate. This is one of the reasons why. In point of fact, the mechanisms that drive the activity and selectivity are well understood, which enables a substantial improvement in overall performance in contrast to heterogeneous catalysis. The use of soluble transition-metal complexes in catalysis, in particular, has created possibilities for fine-tuning product features that were previously inconceivable. This is accomplished by careful manipulation of the electronic and steric properties of the auxiliary ligand. This basic concept has led to the discovery of a wide variety of ingenious stereoselective processes that span all kinds of chemical synthesis (including oxidations, cross-coupling reactions, polymerisations, and so on).

SILVER COMPLEXES OF SPECIFIC ENVIRONMENTAL MERCAPTANS

If you can think of a mercaptan, there is a good chance that there is a reference to the silver derivative of that mercaptan somewhere in the scientific literature. This is because mercaptans frequently form silver complexes. The shocking aspect of the situation is how little we know about many of these compounds, particularly mercaptans found in the environment. To the best of our knowledge, silver complexes of N-acetyl cysteine or 3-mercaptopyruvic acid have never been characterised, and up until very recently, crystalline versions of any of the other known complexes had never been formed. presents a concise summary of the known properties of silver thiolates that are produced from ambient mercaptans, as well as a list of references that discuss these

compounds. The categorisation of the table is determined by the additional functionality of the ligand, which may include amino acids, carboxylic acids, or neutral compounds. The most notable characteristic of all of the mercaptans mentioned in from an ecological point of view is the presence of hydrophilic groups in all of the ligands, with the exception of mercaptomethane, when the sulphur is connected to silver. Mercaptomethane is the only exception to this rule. This results in a notable solubility in water; however, this solubility is pH sensitive due to the fact that amine and carboxyl groups may or may not be charged. As a consequence, we can only assume that the majority of these silver complexes will be dissolved at the micromole level at pH values that are slightly above or slightly below 7. Even at very low concentrations, the complexes show signs of becoming considerably aggregated into larger structures. Even at 50 mM concentration (pH 7), for example, D-penicillaminato-silver proton NMR spectra revealed broad signals, which are signs of aggregation. These signals were the same as those detected at higher levels. Now we will have a quick discussion on the many different classes of chemicals.

ENVIRONMENTAL FATE OF SILVER

When subjected to conditions that are high in sulphur, Ag(I) found in silver thiolates will, in the end, transform into Ag₂S. The organic fragment might be oxidatively destroyed (likely by radical processes with dioxygen), leaving Ag₂S as the most stable residual species, or it could be liberated as the mercaptan upon reactivity of the silver thiolate aggregate with hydrosulfide ion. Both of these outcomes would result in Ag₂S being the most stable residual species. The conceptual outline of a possible framework for the environmental cycling of Ag(I) is shown in Figure 6. In order to facilitate comprehension, the plan has been arbitrarily separated into inorganic and organic pathways; nevertheless, in practise, these pathways will be entangled with one another. In addition to this, the strategy is not all-encompassing. Its purpose is to stimulate people's thought processes and provide a framework for more investigation. Consider, as an example, the kinetics of the transfer of Ag(I). How does the rate change depending on things like the particle size, the particle density, and the particle composition? Is it feasible to investigate this topic using simpler model systems in order to get a deeper understanding of the environmental process at play here?

Is it possible for Ag(I) to exist in a metastable complexed state that has exchange kinetics that are sufficiently slow to be physiologically active? How could various silver thiolates' rates of interaction with cells or organisms be affected by sorbtion on colloids? Although several biological studies have offered hints at potential answers to these issues, it will continue to be a primary focus of future research to gather accurate data on the kinetics and metabolic pathways followed by the great majority of species. Our plan calls for Ag₂S(s) to serve as the ultimate destination for Ag(I). But must we necessarily proceed in this manner? When does Ag(I) get remobilized from Ag₂S(s), and under what conditions? What kind of threat, if any, would these high amounts of Ag(I) present? These kinds of worries demand for further investigation. According to the results of a laboratory study, organic Ag(I) thiolates gradually degrade over time, particularly when exposed to light, and produce Ag₂S(s). There are no descriptions that can be found that specify what happened to the organic component, however it is most probable that it was decomposed by oxidation. We have shown that the atom of sulphur may be converted into a sulfonate by the use of strong oxidants. In this state, the silver ion is connected to an oxygen, making it much more kinetically labile. Do enzymes involved in oxidation have the capability of doing the same thing? It's possible that evolution has reached the conclusion that any remobilization of Ag(I) is so minor that it's OK to neglect Ag₂S(s) or a silver metallothionein complex. However, it is wise to check nature's verdict.

OBJECT

1. The research an increasingly environmentally friendly option is coupling carbon dioxide with epoxides.
2. The research Sulfur's impact on catalytic activity as a key hemilabile ligand

RESEARCH METHODOLOGY

In this paper, we provide a novel method to sensing based on nanotechnology that, for the very first time, makes advantage of the kinetics of the photochemical reduction of gold ions to gold nanoparticles. The method depends on using a simple clock and the naked eye as detectors to record the time lag in the photoinduced creation of gold nanoparticles in the presence of sulfur-containing compounds. This time lag may be used to determine whether or not the procedure was successful. The photoreduction kinetics of gold ions were shown to be retarded by a wide range of organic and inorganic compounds having different sulphur moieties. These compounds include thiols, thioesters, disulfides, thiophosphates, metal-sulfur links, and inorganic sulphur. Additionally, the photoreduction kinetics of gold ions were found to be slowed by inorganic sulphur. We demonstrated the applicability of this concept by applying it to the analysis of sulfur-containing substances and demonstrating that it can be used in a variety of sensing applications without the need of any specialised apparatus.

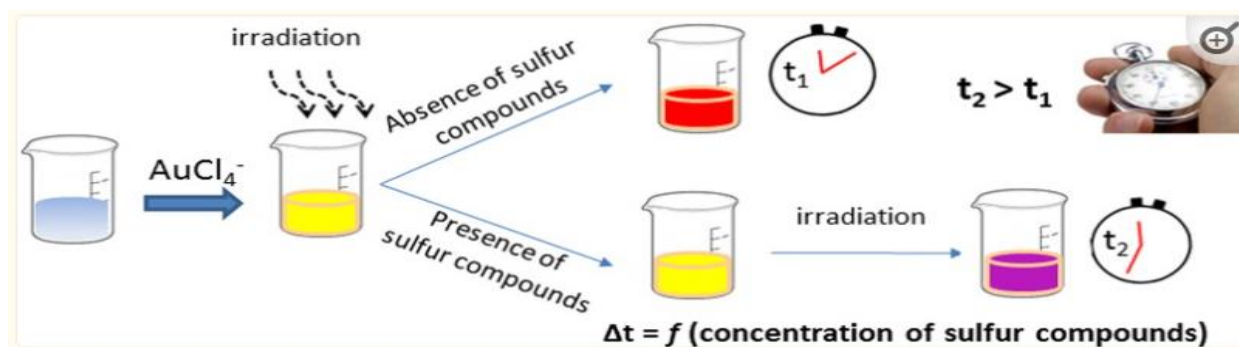


Figure 1 Graphical Representation of The General Experimental Procedure for The Time-Based Assay of Sulfur-Containing Compounds.

DATA ANALYSIS

When compared to chemical reduction (bottom-up) methods, those that involve the formation and controlled synthesis of gold nanoparticles from aqueous gold solutions under the influence of light have several advantages. For one, (b) irradiation diffuses throughout the entire mass of the solution, so reduction occurs uniformly under controlled reaction r . UV irradiation is most commonly used because it corresponds to the absorption band of Au^{3+} (about 323 nm), while other light sources (including UV, sunshine, laser, -irradiation) have been used.

Studies have shown that when UV light is shone on AuCl_4^- , the excited Au^{3+} is immediately reduced to the more stable Au^{2+} , which then quickly disproportionate to generate Au^+ and Au^{3+} . After then, Au^+ either disproportionate slowly into Au^0 and Au^{2+} or absorbs another photon and photo reduces to Au^0 . Possibly catalyzing the disproportionation further is the formation of gold nuclei and AuNPs from Au^0 gold atoms. The presence of an additive is essential to all of these processes because it speeds up or triggers the synthesis of

AuNPs in a variety of chemical ways. Many other substances have been tried as sensitizers for the photochemical reduction of gold ions to AuNPs, including surfactants, polymers, ethylene glycol, citrate, etc.

In this study, we found that sulfur-containing compounds not only slowed the photoreduction kinetics of AuNPs creation but also affected the photochemical synthesis and development of AuNPs. Kinetics of photochemical production of AuNPs under UV light irradiation, as shown by UV-vis absorbance spectra (inset graphs) in the absence and presence of cysteine as a model sulfur-containing substance. The procedure is shown on film (at actual speed but shortened from 1:43 to 3.06 minutes) in an aqueous solution containing 50.0 M of cysteine under natural light. No AuNPs were generated during longer irradiation periods, i.e., >30 min under 40 W of irradiation at 254 nm, indicating that citrate was required to sensitize and expedite the photoreduction of gold to AuNPs. The photoreduction of citrate to acetone-1,3-dicarboxylate and free electrons, which reduce Au^{m+} ($m = 1, 2, 3$) to Au^0 , or the direct excitation of the citrate- Au^{3+} complex, which reduces Au^{3+} through electron-transfer mechanisms, could make AuNPs more photosensitive.

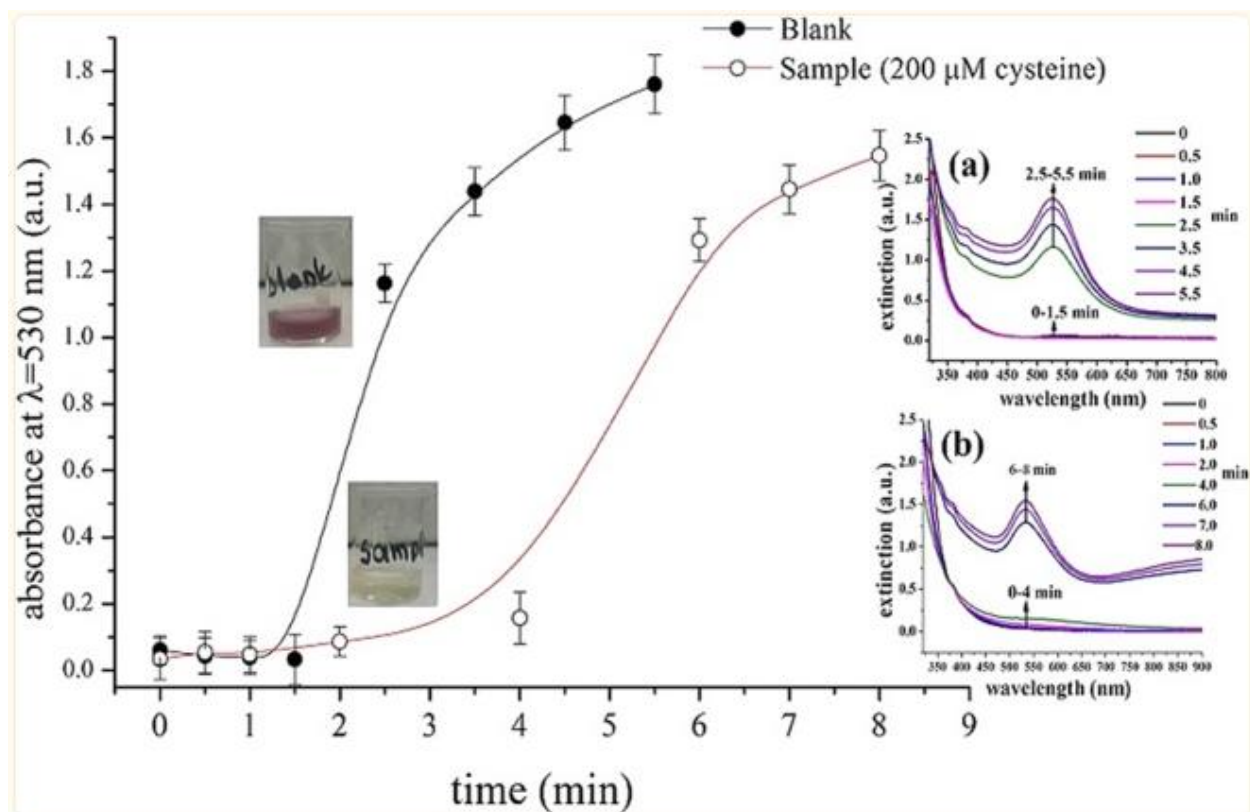


Figure 2 Kinetics Of Aunps Photochemical Formation In The Absence And Presence Of 200.0 Mm Cysteine. Inset Graphs Show The Respective UV-Vis Spectra At Different Time Intervals (A) UV-Vis Spectra Of Aunps Formation In The Absence Of Cysteine And (B) UV-Vis Spectra In The Presence Of 200.0 Mm Cysteine. Experimental Conditions: Ph 4 (Citrate Citric Acid Buffer, 8.0 Mm), $\Lambda = 254$ Nm, And 40 W.

OPTIMIZATION OF GOLD PHOTOREDUCTION

The production and development of AuNPs by photochemistry in gold chloride solutions is a kinetic event that persists after irradiation has been turned off. The creation and development of AuNPs may continue for many hours after the irradiation is turned off, depending on the experimental circumstances (intensity of UV

irradiation, concentration of gold ions, presence of additives, etc.). Our time-based assay is unaffected by this occurrence since the analytical signal is the duration of time needed for a colored solution to arise; once this occurs, the synthesis of AuNPs is no longer being tracked. However, we employed solution absorbance to acquire (absorbance) values at a constant time in order to adjust the assay's experimental conditions. Therefore, the first factor examined was incubation time (after the cessation of UV irradiation). After exposing the solutions to UV light (254 nm, 40 W) for 1.5 minutes and incubating them in the dark at room temperature for varying amounts of time, we evaluated the absorbance of the blank and sample solutions at 525 nm.

Based on the kinetic curves, we found that irradiating the samples for 1.5 minutes did not significantly raise the absorbance values of either the sample or the blank solutions, but irradiating them for longer resulted in a sudden increase in the absorbance of the blank. Light, which can cause photoreduction of AuCl₄⁻, was also avoided by keeping the samples in the dark.– The results show that after 5 minutes of incubation at room temperature (25 °C), the net analytical signal (i.e., absorbance intensity of the sample minus absorbance intensity of the blank solution) increases initially, but sharply drops with time. Since AuNPs form more quickly in the blank sample during the first 4 min of incubation, and more slowly in the presence of cysteine, the difference in the net absorbance value peaks at 5 min and then decreases over the remaining incubation time. Similar studies conducted at 4 °C slowed the reaction rate and caused the absorbance signal to peak after 12 minutes of incubation. According to these results, the rate of gold photoreduction also depends on ambient temperature. In light of these results, all absorbance readings were taken under the same conditions: 1.5 minutes of exposure to UV radiation (40 W, 254 nm), followed by 5 minutes of incubation at room temperature in a darkened environment, away from any external light.

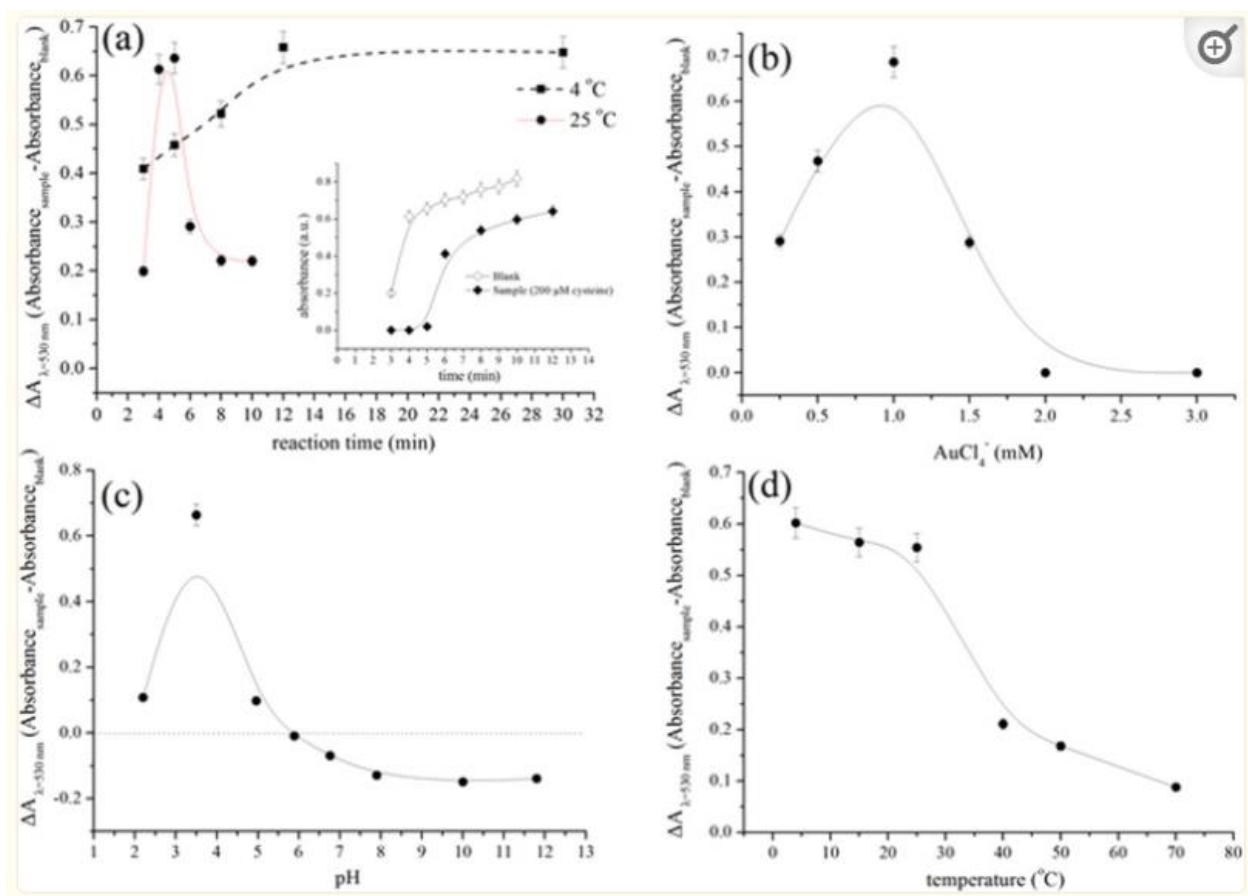


Figure 3 Optimization Of Gold Photoreduction In The Presence Of 50.0 Mm Cysteine As A Model Sulfur-Containing Compound And Citrate As Photosensitizer At $\lambda = 254$ Nm (40 W). Effects Of (A) Reaction Time In The Dark (After UV Irradiation), (B) $AuCl_4^-$ Concentration, (C) Solution Ph, And (D) Temperature On The Net Absorbance Signal Intensity (ΔA) Calculated As The Difference Between The Absorbance Signal Of The Sample And The Absorbance Signal Of The Blank At $\lambda = 530$ Nm.

We investigated the effects of $AuCl_4^-$ and citrate concentration, pH, temperature, and irradiation wavelength after reaction kinetics were optimized. Since the absorbance of the blank solution also increases dramatically at concentrations of $AuCl_4^-$ up to 1.0 mM, the net absorbance signal also increases greatly (results not shown). Possibly because more energy is needed to photoreduce the huge concentration of gold ions, absorbance drops considerably with greater gold concentrations for both the sample and the blank solutions. So, 1 mM $AuCl_4^-$ was utilized as a constant throughout all the tests.

It was discovered that the intensity of the light affected the concentration of citrate ions required to sensitize the photochemical reduction of gold ions. The longer the wavelength of the irradiating light, the less citrate was needed. Under the experimental conditions (40 W of light intensity at 254 nm, in the presence of 50.0 M of cysteine), the optimum citrate ion concentrations was 5.0 mM; at higher citrate concentrations, the net absorbance signal intensity decreased, possibly because citrate accelerated the photoreduction of gold ion solutions.

The best outcomes were observed at acidic pH values (pH 3.5) (when the pH is increased beyond the optimum (pH 3.5), the net absorbance signal intensity displays a behavior, which seems to be connected to the pKa of the dominating cysteine species. At pH 5, which is close to the isoelectric point of cysteine (i.e. 5.14), and the pKa of citric acid (i.e. 4.74), the signal drops to zero. Afterwards, the signal flips (the sample's absorbance signal strength is greater than the blank's) and steadily declines up to the value of pH 8.0, which matches with the acid dissociation constant of the sulfhydryl group (pKa2 = 8.18). When the pH is more than 8, the signal is reasonably stable. In the presence of charged species of cysteine and citrate, photoreduction of $AuCl_4^-$ ions is likely to be enhanced, most likely as a result of ligand-to-metal charge transfer reactions with the predominant gold species at these pH values (possibly $[AuCl(OH)_3]$ and $[Au(OH)_4]$). This is evidenced by the fact that the sample signal becomes higher than that of the blank at pH values above 5.

The photoreduction of $AuCl_4^-$ in the presence and absence of cysteine was likewise shown to be highly temperature dependent. The net analytical signal (A at $\lambda = 530$ nm) was lower when the samples were irradiated at temperatures above room temperature, indicating that the temperature sped up the reduction of $AuCl_4^-$ ions. We ascribed these findings to citrate, which is a powerful reducing agent of gold even at high temperatures. As a result, all the tests were conducted under ambient conditions.

We looked for the best UV (254, 312, and 365 nm) and visible light (i.e., artificial and room light) irradiation wavelengths. The photoreduction was shown to be possible at all wavelengths, including ambient light, however longer irradiation periods were needed with increasing wavelength (i.e. lower intensity). In the presence of 200.0 M cysteine and 40 W of UV irradiation at 254 nm, for instance, AuNPs formed after 6 hours at room temperature. It took more than 1 hour to get a detectable signal when the same experiment was carried out in ambient lighting conditions. In this section, we briefly recap the experimental setup and the parameters that were chosen as optimal.

CONCLUSION

Supporting metal ions in the interaction between carbon dioxide and epoxides with ligands containing sulfur has gained popularity in recent years. The inclusion of sulfur in the ligand backbone confers special features on the catalyst precursor, often increasing its activity, selectivity, and stability. Additionally, both cyclic carbonates and polycarbonates were produced with good activity and selectivity for a broad variety of substrates, indicating a great deal of room for growth. In particular, these ligands may be used with a wide range of metal centers, which improves catalytic performance and broadens the scope of the products that can be made. As a final goal, developing and synthesizing novel structural motifs with sulfur atoms in the ligand backbone is crucial for the potential development of other catalytic applications. Most of the silver in aqueous Ag(I) is in a colloidal phase with a size of 0.45 μm and a molar mass of several kilobars. Therefore, the most significant part of aqueous Ag(I) is the colloidal phase, which is likely made up of both organic and inorganic components. Understanding the behavior of Ag(I) in the very diluted condition in which it occurs in natural waters requires familiarity with the structure and chemistry of complexes of silver and sulfur, whether inorganic or organic.

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