LSPR-Induced Catalytic Enhancement Using Bimetallic Copper Fabrics Prepared by Galvanic Replacement Reactions

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A simple galvanic replacement (GR) reaction-based strategy to create copper-based bimetallic fabrics for photoreductive catalysis is reported. It is shown that a nanostructured Cu@Fabric can be easily converted into bimetallic Cu-Au@Fabric and Cu-Ag@Fabric through a spontaneous electroless process that involves simple exposure of copper fabrics to the aqueous solutions of gold and silver ions. The nanoscale hierarchical ordering of cotton fabrics combined with their high porosity and wettability make them outstanding supports for catalyst recovery and reusability. The deposition of miniscule quantities of expensive noble metals on readily available Cu not only reduces the overall catalyst cost, but also plays a major role in improving the catalyst stability and reusability over several cycles through minimizing Cu oxidation. The synergistic effects of the localized surface plasmon resonance (LSPR) properties of Cu, Au, and Ag allow these bimetallic fabrics into highly active visible light photocatalysts. Mechanistic investigation of the photocatalytic activity provides in-depth information on the electron transfer processes occurring at the catalyst/reactant interface, revealing electron transport as the rate-limiting step, which could be overcome under visible light photoillumination conditions. The outcomes enhance the understanding of template-supported bimetallic nanostructures for LSPR-induced photocatalysis applications, offering new potential to design multifunctional fabrics for various applications.

1. Introduction

Multicomponent nanomaterials, such as bimetallic structures and composites, continue to receive significant interest as they offer enhanced optical, physical, and catalytic properties compared to their individual counterparts.[1–20] In particular, nanostructures composed of two or more metals have shown great promise for applications in catalysis and sensing. To this end, a variety of solution-based synthesis routes including co-reduction,[21–23] thermal decomposition,[24,25] microwave,[26,27] galvanic replacement,[8,28–30] and seeded growth[23,31,32] have been employed to synthesize bimetallic nanomaterials.[33,34] GR reactions are not restricted to metallic systems and the concept is also extendable to inorganic[40] and organic semiconductors.[3,7,9,11,14,15] As such, this facile strategy has tremendous potential, as it is limited by no more than the requirement of a favorable difference in the reduction potentials of two reacting redox active species.

Due to the low reduction potential of the Cu(II)/0 couple when compared to noble metals, such as Au and Ag, metallic copper is a suitable candidate to prepare Cu-Au and Cu-Ag hybrids via GR reactions.[2,16] Cu nanoparticles, in particular, have been a
promising candidate for a variety of catalysis reactions due to their low-cost and high activity.\cite{5} Recent reports have shown that the localized surface plasmon resonance (LSPR) of metal nanoparticles can positively influence the catalytic activity through the production of “hot electrons.”\cite{5,41,42} Metal nanoparticles of Ag, Au, and Cu are known for their strong LSPR properties, and may therefore be suitable candidates for LSPR-induced catalytic enhancement reactions.\cite{5,34,43,45} However, the use of solvent-dispersed metal colloids as catalysts is not without challenges, including potential nanoparticle aggregation during reaction compromising the reproducibility, and difficulties associated with catalyst recovery and product purification post-reaction.\cite{46–49} Many of these shortcomings can be addressed through depositing the catalyst on the surface of nano- and microstructured templates.\cite{5,6,46–52} In doing so, the physical properties of the chosen template are important, as 3D hierarchical ordering and high solvent absorption capacity of an appropriate template may provide a further boost to the reaction rates.\cite{5,46–50,52,53} Our recent work has shown that nanostructured metals deposited on cotton fabrics remarkably enhance LSPR-induced visible light reductive catalysis reactions.\cite{5} We noticed that among various metals, while Cu@ Fabrics showed very high catalytic activities, copper was prone to oxidation in air and aqueous solutions over time, affecting catalyst recovery and reuse.\cite{5,18} As such, the high inherent catalytic activity of metallic copper fabrics could not be harnessed to their full potential.

In the current work, we address this challenge by reacting Cu@Fabrics with metal ions of Au and Ag through a GR reaction to create bimetallic Cu-Au@Fabric and Cu-Ag@Fabric (further referred to as Cu-Mx@Fabrics where x is the concentration of the metal ion M (Au or Ag) used during the GR reaction). Combining the highly catalytic Cu with LSPR-active Au and Ag not only prevented the oxidation of the underlying copper but also improved the overall catalytic performance of the resultant Cu-Mx@Fabrics through enhancing the optical absorption profile of these hybrid materials and creating synergistic effects of the bimetallic systems. We probed the catalytic performance of these new materials using a model pseudo-first-order reaction involving photoenhanced catalytic reduction of ferricyanide to ferrocyanide in the presence of excess thiosulfate. We also investigated the LSPR-induced catalytic mechanism by studying the mode of electron transfer at the catalyst-reactant interface. The simple approach of fabricating highly photoactive bimetallic nanocatalysts supported on low-cost cotton templates offers new prospects in developing reusable catalysts.

2. Results and Discussion

2.1. Fabrication of Cu-Mx@Fabrics (M = Au or Ag)

The fabrication of Cu@Fabric proceeds via an electroless deposition of nanostructured metallic copper on cotton fabrics as outlined in our previous work.\cite{30} In brief, a multistep process is employed where the cotton fabric is first sensitized with Sn2+ ions, followed by the deposition of Pd0 nuclei onto the fabric through a GR reaction between Sn2+ and Pd2+. The Pd0 nuclei act as a catalyst for subsequent deposition of copper nanoparticles to form Cu@Fabric (3 ± 0.2 mg of Cu deposited on a 1 × 1 cm² cotton fabric). Next, the bimetallic Cu-Mx@Fabrics are fabricated by exposing Cu@Fabric to three different concentrations of either Au3+ or Ag+ ions (10, 100, and 1000 × 10⁻⁶ M). The favorable difference in the reduction potentials between Cu²+/Cu⁰ (0.34 V vs SHE),\cite{30} Cu⁺/Cu⁰ (0.52 V vs SHE),\cite{30} and AuCl₄⁻/Au⁰ (0.85 V vs SHE)\cite{30} or Ag⁺/Ag⁰ (0.80 V vs SHE)\cite{30} allows the GR reaction to proceed spontaneously without any externally applied potential.

It has been suggested that GR reactions typically start at sites with high surface energy including defects, stacking faults, or steps.\cite{30} During the GR process, exposing the Cu@Fabric to AuCl₄⁻ or Ag⁺ would first result in the oxidation of Cu⁰ to Cu²⁺ ions leading to atomic Cu vacancies on the Cu surface (Scheme 1). The electrons generated as a result of the Cu oxidation will migrate to the surface and reduce AuCl₄⁻ or Ag⁺ ions to generate Au⁰ or Ag⁰ seeds. These newly generated seeds are expected to epitaxially deposit on the surface of the Cu nanoparticles due to the good crystalline match between the Cu and Au or Ag (face-centered cubic structures).\cite{30} Once the Cu surface is covered with Au or Ag nanoparticles, it will hinder the direct accessibility of the underlying Cu⁰ atoms to the AuCl₄⁻ or Ag⁺ ions. However, the underlying Cu⁰ atoms can still participate in the GR reaction through electron transfer via the top exposed layer, leading to appearance of discrete islands of Au or Ag on the top layer of the Cu@Fabric.\cite{30} As indicated through the equations in Scheme 1, the amount of Cu²⁺ ions leached from the surface of the fabric during GR reaction depends on the oxidation state of the participating metal ions. In case of reaction with gold ions, for every three Cu ions leached, two Au atoms will deposit on Cu; while during reaction with silver ions, for every Cu ion leached, two Ag atoms will deposit on the Cu fabric.

The concentrations of the Cu ions leached through metallic Cu oxidation and the Au or Ag concurrently deposited on the fabric surface via reduction of the respective metal ions during GR reactions were quantified using atomic emission spectroscopy (AES). The concentration of the leached Cu ions increases with increasing Au or Ag concentration (Figure S1, Supporting Information). Further, significantly higher amounts of Cu ions are leached when the GR reaction is carried out using Au³⁺ ions in comparison with that of Ag⁺ ions. This observation resonates well with the equations provided in Scheme 1. However, higher than theoretically expected Cu ion leaching during the GR experiments suggests that the reaction solutions facilitate additional direct leaching of Cu ions beyond that through the GR reaction. This suggests that during the GR reaction, a complex interplay between the leaching of Cu ions and the concomitant deposition of either Au or Ag on the surface of the Cu fabric takes place.

2.2. Characterization of Cu-Mx@Fabrics

Figure 1 shows representative scanning electron microscopy (SEM) images of the Cu-Mx@Fabrics post-GR reaction, containing bimetallic nanoparticles coated on the individual threads interwoven within the cotton fabrics. Consistent with our previous work, pristine Cu@Fabric shows nanostructured...
Scheme 1. Schematic showing the process of GR reaction on the surface of the Cu@Fabric with either Au^{3+} or Ag^{+} ions to create bimetallic photoactive fabrics.

Figure 1. SEM images obtained from the bimetallic Cu-M@Fabrics after GR reactions. a) Cu-Au_{10}@Fabric; b) Cu-Au_{100}@Fabric; c) Cu-Au_{1000}@Fabric; d) Cu-Ag_{10}@Fabric; e) Cu-Ag_{100}@Fabric; and f) Cu-Ag_{1000}@Fabric. Scale bars correspond to 20 µm for the main figure and 200 nm for the inset.
quasispherical Cu nanoparticles of 50–100 nm in diameter (Figure S2, Supporting Information).[5] Following the GR reaction, with increasing concentrations of Au$^{3+}$ ions (Figure 1a–c), the surface roughness of the fabrics increase due to the creation of quasispherical AuNPs. At low Au$^{3+}$ ion concentration ($10 \times 10^{-6}$ M), the Au nanoparticles show a diameter of 20–50 nm (Figure 1a). The diameter of the Au nanoparticles increases as a function of Au$^{3+}$ ion concentration (Figure 1b,c) such that at $1000 \times 10^{-6}$ M Au$^{3+}$ ion concentration, the Au nanoparticles show a diameter $\approx 70–100$ nm (Figure 1c). This is due to the initially deposited Au nanoparticles acting as the nucleation sites for further growth which is consistent with our AES results. A similar trend is observed when Ag$^{+}$ ions are used for the GR with Cu@Fabric (Figure 1d–f), where lower Ag$^{+}$ ion concentration results in Ag nanoparticles of diameter 10–30 nm deposited on the surface of the Cu@Fabric (Figure 1d). The particle size increases to $\approx 50–60$ nm when the reaction proceeds at $1000 \times 10^{-6}$ M Ag$^{+}$ ion concentration (Figure 1f). This increase in the size of Au or Ag nanoparticles is similar to that observed in previous studies employing the GR process for the fabrication of bimetallic nanostructures.[30]

The GR process could also be visually observed. The deposition of Cu nanoparticles (CuNPs) on the surface of the cotton fabric gave it a reddish color. Post-GR reaction, the deposition of either Au nanoparticles (AuNPs) or Ag nanoparticles (AgNPs) resulted in a color change. For instance, depending on the concentration of Au, the fabric changed color from red to bluish-black, while the deposition of AgNPs resulted in a silvery-black color (Figure S3, Supporting Information). These colors arise due to the collective surface plasmon resonance (SPR) absorption of the nanostructured Cu,[5,54] Au,[55,56] Ag,[5,57] and the combinations of these. The energy-dispersive X-ray (EDX) spectrum of the Cu@Fabric showed characteristic energy lines of Cu Lα (0.930 keV), while the EDX spectra from the Cu-M@Fabric showed additional energy bands arising from either Au M (2.123 keV) or Ag Lα (2.984 keV) depending on the metal ion used to create the bimetallic nanostructures (Figure S4, Supporting Information). The intensity of the Au M and Ag Lα lines also increased with increasing concentration of the metal ion used. This confirms that the amount of AuNP or AgNP deposited on the Cu@Fabric is dependent on the concentration of the metal ion used during the GR process. The EDX elemental mapping of the fabrics containing the respective metals further confirms that both metals in the bimetallic nanostructures were distributed uniformly throughout the surface of the cotton fabric (Figures S5 and S6, Supporting Information).

The oxidation states of the Cu, Au, and Ag in cotton fabrics were further confirmed using X-ray photoemission spectroscopy (XPS) (Figure 2). The pristine Cu@Fabric shows characteristic 2p$_{3/2}$ and 2p$_{1/2}$ splitting components (spin–orbit splitting $\approx 19.7$ eV) for Cu 2p core levels corresponding to zerovalent (Cu$^0$) and Cu$^{2+}$ oxidation states, consistent with our previous report.[18,58] In addition, the presence of weak satellite peaks suggests the presence of a small amount of surface oxides due to the propensity of pristine Cu to rapidly oxidize in air.[39,66] The Cu 2p core levels for the Cu-Au$_{100}$@Fabrics instead show that as the concentration of the Au ions is increased during the GR process, it stabilizes the surface of the Cu@Fabric against potential surface oxidation. This is evident from the presence of weak satellite peaks corresponding to copper oxides in the Cu 2p core level spectrum of the Cu-Au$_{100}$@Fabric (Figure 2a star mark), which are undetectable in Cu-Au$_{1000}$@Fabric and Cu-Au$_{10000}$@Fabric. Post-GR reaction with gold ions, the Cu-Au$_{x}$@Fabrics show additional Au 4f core levels with characteristic 4f$_{7/2}$ and 4f$_{5/2}$ splitting components (spin–orbit splitting $\approx 3.7$ eV) at $\approx$84.5 and 88.2 eV corresponding to Au in the zerovalent oxidation state (Figure 2b).[61] The Cu 2p core levels for Cu-Ag$_{x}$@Fabrics show similar trends except that no surface oxidation was seen even at the lowest Ag$^{+}$ ion concentration (Figure 2c). These samples show additional peaks corresponding to Ag 3d core levels with characteristic 3d$_{5/2}$ and 3d$_{3/2}$ splitting components (spin–orbit splitting $\approx 6$ eV) at $\approx$368.2 and 374.2 eV, corresponding to zerovalent metallic Ag (Figure 2d).[62] In both of these bimetallic fabrics, XPS analysis also show a concentration-dependent trend wherein the intensity of the peaks corresponding to the GR metal (Au or Ag) relative to the original metal (Cu) increases as a function of GR metal ion concentration (Figure S7, Supporting Information). Importantly, XPS analysis reveals that the GR reactions help in...
stabilizing the surface of Cu@Fabric against oxidation, which may have important implications in enhancing the stability of the Cu-M@Fabric when used as a catalyst.

Considering that efficient absorption of light is central to the photoenhanced catalytic activity of bimetallic fabrics, optical spectroscopy both in transmission (T) and reflection (R) was used to determine the optical properties of Cu-M@Fabrics (Figure 3). The pristine Cu@Fabric shows an absorption peak at ≈500–600 nm, attributable to the SPR properties of the nanostructured copper. A similar trend is observed when Ag impurity in the bimetallic systems can significantly deteriorate the overall catalytic performance. For reasons, we have focused our subsequent discussion on Cu-Au@Fabrics, while briefly discussing about Cu-Ag@Fabrics to draw general trends between the two systems. Irrespective of the nature of the catalyst, when we performed the same catalytic reaction using different metal deposited on the Cu@Fabric on its work function, photoelectron spectroscopy in air (PESA) was used during the GR process. As evident from Table 1, the work function of the bimetallic nanostructure gradually increases or decreases toward the work function of either pristine Au or Ag, respectively. In fact, at the highest concentration of the metal ions employed during GR reaction, the work functions of Cu-M@Fabrics become similar to those of pristine Au or Ag. Considering that PESA is a surface-sensitive technique, our findings suggest that even if the hybrid Cu-M@Fabrics contain small amounts of noble metals, their surface characteristics most likely become similar to those of pristine noble metals.

### 2.3. Heterogeneous Reductive Photocatalysis

The interesting optical properties of bimetallic fabrics combined with high porosity, absorbency, and potential access to a large number of catalytically active sites resulting from the hierarchical ordering of cotton fibrils within the fabrics prompted us to explore their catalytic properties. We chose a model pseudo-first-order reaction involving catalytic reduction of ferricyanide to ferrocyanide ions in the presence of excess thiosulfate ions and monitored the decrease in the absorption maximum of ferricyanide ions at ≈420 nm in the presence of various catalysts. All Cu-M@Fabrics could catalyze the reaction under both dark and visible light illumination, albeit with different catalytic efficiencies (Table 2). The Cu-Au@Fabrics offered improved catalytic activity over the pristine Cu@Fabric, whereas the catalytic performance of Cu-Ag@Fabrics was reduced compared to the pristine material. For instance, when Cu-Au@Fabric is used, the reaction proceeds to 95% completion within 19 min under dark conditions, while it takes 35 min in the case of Cu-Ag@Fabric and 26 min by pristine Cu@Fabric (Figures S8 and S9, Supporting Information). We believe that Au-mediated improvement in the catalytic efficiencies and Ag-mediated deterioration of catalytic properties of bimetallic fabrics are due to the inherent catalytic properties of these materials. In our previous work, we have regularly observed that Cu is not only an inherently better catalyst than Ag, but also in certain cases even the small amounts of Ag impurity in the bimetallic systems can significantly deteriorate the overall catalytic performance.
under visible light illumination, the reaction proceeded to completion faster, taking 10, 24, and 17 min, respectively for Cu-Au_{100}@Fabric, Cu-Ag_{100}@Fabric, and Cu@Fabric (Table 2). The improvement in the catalytic efficiency during photoillumination in all the cases can be attributed to the LSPR properties of the Cu, Au, and Ag nanoparticles, as interaction of light with LSPR-active materials is known to influence the conduction band electrons resulting in the enhancement of the local electromagnetic fields on the surface of nanoparticles, thereby enhancing overall catalytic efficiencies.

The influence of the composition of catalytic fabrics on the reaction kinetics is further evident from the plots of ln(A_t/A_0) versus time (Figure 4; Figure S10, Supporting Information), where A_t is the absorption maximum of ferricyanide ions at time (t) and A_0 is the absorption maximum of ferricyanide ions before the beginning of the reaction. The reaction rates determined from the linear region of the ln(A_t/A_0) versus time plots are outlined in Table 2. For the Cu-Au_{x}@Fabric catalyst, the time taken for the reaction to reach 95% completion generally tends to decrease with an increasing Au concentration under both dark and photoillumination conditions (Figure 4). Interestingly, at the lowest gold concentration (Cu-Au_{10}@Fabric), a distinct lag-phase during the early time points of the catalysis reaction is observed, which does not exist at higher gold concentrations (Cu-Au_{100}@Fabric and Cu-Au_{1000}@Fabric). In our previous work, we have noted that copper oxides tend to show a lag phase during catalysis.[5,6,70] In the current case, it is expected that the low amounts of Au present in the Cu-Au_{10}@Fabric is not sufficient enough to avoid formation of copper oxides, whereas in Cu-Au_{100}@Fabric and Cu-Au_{1000}@Fabric samples, the higher Au content passivates the Cu surface with oxidation-resistant Au thereby minimizing Cu oxidation. It is also noted that for Cu-Au_{10}@Fabric, while the lag phase is more prominent under dark conditions, the lag phase is significant reduced during photoillumination, clearly demonstrating the beneficial effects of photoredox catalysis over dark catalysis. Further, while under dark conditions the reaction rate continues to increase with increasing gold concentration, under photoillumination conditions the reaction seems to have reached a saturation state with the intermediate gold concentration (Cu-Au_{100}@Fabric showing the best performance). Following this, the catalytic efficiency moderately decreases, suggesting that the Cu-Au_{100}@Fabric offers an optimal loading of Au nanoparticles to promote efficient transfer of electrons from the surface of the catalyst to the reactants in solution under photoillumination. It is well known that under photoillumination conditions, an optimal amount of metal loading is critical for the highest performance, beyond which the photocatalytic efficiency begins to deteriorate.[2,7,9,14–16] In terms of catalytic reaction rates, the best photocatalyst obtained from this study is Cu-Au_{100}@Fabric with a reaction rate of 0.56 min^{-1} under photoillumination conditions (Table 2).

A potential advantage of nanostructured bimetallic fabrics over colloidal systems is their reusability over multiple cycles.

Table 2. Reaction rates for ferricyanide reduction in the presence of different catalysts.

| Samples               | Reaction rate for dark [min^{-1}] | Reaction rate for visible light [min^{-1}] | Time taken to 95% completion dark [min] | Time taken to 95% completion visible light [min] |
|-----------------------|-----------------------------------|-------------------------------------------|----------------------------------------|-----------------------------------------------|
| Cu@Fabric             | 0.15 ± 0.01                       | 0.25 ± 0.02                                | 26                                     | 17                                           |
| Cu-Au_{10}@Fabric     | 0.18 ± 0.01                       | 0.46 ± 0.02                                | 25                                     | 12                                           |
| Cu-Au_{100}@Fabric    | 0.21 ± 0.01                       | 0.56 ± 0.01                                | 19                                     | 10                                           |
| Cu-Au_{1000}@Fabric   | 0.25 ± 0.01                       | 0.36 ± 0.02                                | 16                                     | 12                                           |
| Cu-Ag_{10}@Fabric     | 0.09 ± 0.03                       | 0.23 ± 0.02                                | 45                                     | 25                                           |
| Cu-Ag_{100}@Fabric    | 0.11 ± 0.01                       | 0.24 ± 0.02                                | 35                                     | 24                                           |
| Cu-Ag_{1000}@Fabric   | 0.14 ± 0.01                       | 0.24 ± 0.01                                | 36                                     | 28                                           |

Figure 4. Plots of ln(A_t/A_0) versus time for Cu-Au_{x}@Fabric in the a) absence and b) presence of visible light.
We therefore assessed the catalytic performance of the best-performing Cu-Au\textsubscript{100}@Fabric for 15 consecutive reactions under photoillumination conditions (Figure 5) and compared it with the pristine Cu@Fabric\textsuperscript{[5]} and Cu-Ag\textsubscript{100}@Fabric (Figure S11, Supporting Information). The rate constant and the catalytic efficiency for the Cu-Au\textsubscript{100}@Fabric showed a higher degree of stability in comparison to the Cu@Fabric. Although Cu@Fabric in itself is a good catalyst, our previous work has shown that the surface of pristine Cu@Fabric is prone to oxidation, which led to a significant drop in the catalytic efficiency by the 5th cycle, such that over a 50% loss in catalytic conversion efficiency was observed by the 15th cycle.\textsuperscript{[5]} In contrast, after GR reaction with Au\textsuperscript{3+} ions, the stability of the bimetallic Cu-Au\textsubscript{100}@Fabric catalyst is remarkably enhanced with minimal loss of catalytic activity even after 15 consecutive catalytic cycles (Figure 5). This shows that the addition of Au nanoparticles on the surface of Cu@Fabric not only improves its photocatalytic efficiency, but also protects the catalyst from surface oxidation leading to higher catalyst stability. Interestingly, while Cu-Ag@Fabrics showed reduced catalytic performances over pristine Cu@Fabric, the stability test reveals that the Cu-Ag\textsubscript{100}@Fabric catalyst remains stable over 15 catalytic cycles (Figure S11, Supporting Information). These results imply that the GR reactions offer a simple strategy to enhance the stability of important catalysts such as copper.

\textbf{2.4. Mechanism of Electron Transfer during LSPR-Induced Reductive Photocatalysis}

To understand the influence of the electron transfer processes during the catalytic reaction facilitated by these bimetallic fabric catalysts, open-circuit potential (OCP) versus time and electrochemical impedance spectroscopy (EIS) studies were carried out. OCP provides vital information on the charge accumulation/dissipation processes at the interface of the catalyst and the reactant (solid/solution interface) while EIS provides information on the ability of the catalyst to transfer electrons. OCP versus time experiments were performed under conditions similar to the catalysis reaction, where a steady state potential was first obtained in 1 × 10\textsuperscript{-3} M [Fe(CN)\textsubscript{6}]\textsuperscript{3-} solution before the addition of thiosulfate (Figures S12 and S13, Supporting Information). In all cases, a steady state potential was obtained within the first 200 s, at which point, S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} ions were introduced to facilitate the conversion of ferri- to ferrocynaide. Further, in all cases, a rapid decrease in the OCP was observed which may be attributed to the accumulation of negative charge on the surface of the catalyst, as control experiments where OCP was measured with only S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} ions showed a lower OCP value. Comparison of both the catalysts (Cu-Au vs Cu-Ag) under different experimental conditions showed insignificant difference in the OCP potentials. This suggests that the accumulation of charge at the catalyst surface is not a limiting factor for the catalytic activities observed in our study.

The resistance to charge transfer at the solid–liquid interface, i.e., how fast the electron is transferred from the surface of the catalyst to the reactant was further measured using EIS. The EIS data are represented as Nyquist plots (Figure 6), where the width of the semicircle component determines the resistance to the charge transfer.\textsuperscript{[5,6]} In the case of pristine Cu@Fabric (Figure S14, Supporting Information), a pronounced semicircle component is observed suggesting the resistance to charge transfer, which is reduced when the reaction proceeds under visible light illumination (decrease in the width of the semicircle). This decrease in the charge transfer can be attributed to the LSPR effect of Cu nanoparticles. Additionally, the semicircle feature suggests the presence of semiconducting copper oxides in addition to pristine Cu nanoparticles in pristine Cu@Fabric. Therefore, in the case of Cu@Fabric, the enhancement in the catalytic rates is a combinatory effect of LSPR and charge separation mechanism facilitated by the semiconductor-metal junction.\textsuperscript{[5,6]} Following the GR reaction with Au\textsuperscript{3+} ions, at lower gold concentrations, Cu-Au\textsubscript{10}@Fabric shows that the semicircle component is still present, suggesting the presence of an oxide in addition to Cu and Au nanoparticles. This suggests that in case of Cu-Au\textsubscript{10}@Fabric the mechanism of charge transfer at the solid–solution interface would be similar to that observed for pristine Cu@Fabric catalyst. In contrast, both the Cu-Au\textsubscript{100}@Fabric and Cu-Au\textsubscript{1000}@Fabric containing higher concentrations of gold do not show a semicircle component affirming that the deposition of larger amounts of Au on the surface of Cu@Fabrics through GR reactions prevents surface oxidation of Cu. In this case, a diffusion-limited electron transfer process dominates such that photoillumination reduces the resistance to charge transfer, enhancing the photocatalytic efficiencies of these systems. Conversely, in the case of the Cu-Ag@Fabric, no semicircle component is observed even at the lowest Ag\textsuperscript{+} ion concentration (Cu-Ag\textsubscript{10}@Fabric), and instead a diffusion-limited electron transfer process is observed that governs the catalytic mechanism. Similar to the Cu-Au@Fabrics, the photoexcitation of the Cu-Ag@Fabric catalysts...
leads to an improvement in electron transfer rate by reducing the resistance to charge transfer. These observations align well with the photocatalysis results, wherein irrespective of the poor performance of Cu-Ag\textsubscript{x}@Fabrics, an improvement in their catalytic performance was observed during photoillumination. As such, the electrochemical investigations confirm that i) the GR reaction prevents surface oxidation, ii) the mechanism of the catalytic activity of the bimetallic fabrics is dominated by diffusion-limited electron transfer processes, and iii) photoillumination assists in overcoming the resistance to charge transfer from the catalyst surface to the reactants in the solution.

3. Conclusion

This study has shown the potential of a simple GR reaction-based strategy to prepare robust visible light-active bimetallic fabrics as reductive catalysts. The study has offered a number of key outcomes. 1) The direct growth of nanostructured catalysts on highly porous and hierarchically ordered low-cost cotton fabrics offers potential for catalyst reusability without the requirement for downstream processing, thereby offering advantages over colloidal catalysts. 2) GR reactions allow conversion of an abundant low-cost metal (Cu) into a bimetallic system (Cu-Au or Cu-Ag) using minuscule quantities of the expensive noble metals, while allowing enhancement in the overall catalytic efficiencies. 3) The appropriate combination of LSPR-active metals significantly influences the optical properties of the bimetallic fabrics, allowing efficient harvesting of visible light to enhance catalytic efficiencies. 4) Importantly, reusability studies show that the GR reactions remarkably improve the stability of the bimetallic fabrics, allowing catalysts to be used over several consecutive cycles without significant loss of activity. Additionally, the mechanistic investigation of the underlying electron transfer processes at the catalyst/reactant interface supports that a diffusion-limited electron transfer process is the rate-limiting step that governs the catalytic mechanism, and as such the photoexcitation of catalysts with visible light can overcome the resistance to charge transfer, improving photocatalytic efficiencies. The proposed GR strategy to directly fabricate bimetallic nanostructures on cotton fabrics may find use in developing multifunctional textiles for various applications.

Figure 6. Nyquist plots obtained in $5 \times 10^{-3}$ M [Fe(CN)]\textsubscript{6}\textsuperscript{3-}/4- and 0.1 M NaCl at OCP for a) Cu-Au\textsubscript{100}@Fabric; b) Cu-Au\textsubscript{1000}@Fabric; c) Cu-Au\textsubscript{1000}@Fabric; d) Cu-Ag\textsubscript{10}@Fabric; e) Cu-Ag\textsubscript{100}@Fabric; and f) Cu-Ag\textsubscript{1000}@Fabric in the absence (black) and presence (red) of visible light illumination.
4. Experimental Section

Materials: Tin(II) chloride (SnCl₂), palladium(II) nitrate (Pd(NO₃)₂), copper(II) sulfate pentahydrate (CuSO₄·5H₂O), sodium hydroxide (NaOH), formaldehyde (HCHO), potassium sodium tartrate tetrahydrate (KNaC₄H₄O₆·4H₂O), gold(III) chloride (HAuCl₄), silver nitrate (AgNO₃), potassium ferricyanide(II) trihydrate (K₃Fe(CN)₆·3H₂O), potassium ferricyanide(III) ([K₃Fe(CN)₆]_), and sodium thiosulfate (Na₂S₂O₃) were obtained from Sigma-Aldrich, Australia. Acetone, methanol, sodium chloride (NaCl), and nitric acid (HNO₃) were obtained from BDH chemicals. Ultra-pure water was generated using a Milli-pore system (Milli-Q). Cotton fabrics were obtained from a local vendor.

Fabrication of Cu@Fabrics: The fabrication of Cu@Fabric and the underlying mechanism are detailed in the previous report.[5] In brief, a 1 cm × 1 cm fabric was first sensitized with SnCl₂ solution for 30 min (0.3 × 10⁻³ m). The sensitized fabric was then exposed to palladium nitrate (3 × 10⁻³ m) for 10 min, resulting in the formation of Pd nuclei. The Pd nuclei on the fabric surface then acted as a catalyst for the deposition of Cu nanoparticles when immersed in a copper bath solution containing a mixture of potassium sodium tartrate tetrahydrate (0.3 m), sodium hydroxide (1 m), copper sulfate pentahydrate (0.1 m), and formaldehyde (1 m). The resultant material contained Cu nanoparticles deposited on the surface of the cotton fabric (Cu@Fabric).

Fabrication of Cu-Mx@Fabrics (M = Au or Ag): The fabrication of the Cu-Mₙ@Fabric started with immersing a 1 cm × 1 cm fabric in a 10 m aqueous solution containing increasing concentrations of either HAuCl₄ or AgNO₃ (x = 10, 100, and 1000 × 10⁻⁶ m) for 1 h at room temperature. Following the reaction, the Cu-Mₙ@Fabric was washed several times with Milli-Q water to remove any potentially unreacted metal ions, and fabrics thus obtained were used as the final material.

Characterization: SEM samples were prepared by attaching the Cu-Mₙ@Fabric sample on an aluminum stub and analyzed using an FEI Scios DualBeam FIB/SEM in conjunction with a monochromator to improve the surface sensitivity of the images (operated at an accelerating voltage of 1–5 kV). EDX spectra and maps were also obtained on the FEI Scios DualBeam FIB/SEM fitted with an Oxford X-Maxn 80 Silicon Drift Detector. X-ray photoemission spectroscopy measurements were recorded using a Thermo K-Alpha XPS instrument with an Al Kα radiation source (photon energy of 1486.6 eV) and overall resolution was 0.1 eV. The C 1s, O 1s, Cu 2p, Au 4f, and Ag 3d core level spectra for the samples were collected and background corrected using Shirley algorithm, as described previously.[6,41] Chemically distinct species were resolved using nonlinear least squares fitting procedure and aligned with adventitious carbon binding energy of 285 eV. Atomic emission spectroscopy measurements were carried out using an Agilent Technologies 4200 Microwave Plasma AES instrument. Optical transmittance (T) and reflectance (R) measurements in the UV–vis–NIR range were conducted on a Perkin Elmer Lambda 1050 spectrophotometer equipped with an integrating sphere. The percentage of light absorption (A) by the samples was calculated as A = 100 – T – R. Photoelectron spectroscopy in air was conducted on samples deposited directly on cotton fabrics using a Riken Keiki AC-2 spectrometer using 10 mW radiation, and the error associated with the work function evaluation was of the order of 0.05 eV.

Heterogeneous Catalysis Reaction: A well-known model reaction of ferricyanide ion reduction in the presence of excess thiouisolate ions was used to evaluate the catalytic efficiency of the Cu-Mₙ@Fabrics [0.1 m Na₂S₂O₃ and 1 × 10⁻³ m K₃Fe(CN)₆]]. All catalysis experiments were performed in dark and visible light conditions [Source: ThorLabs, warm white LED; power output 0.5 W, 10 cm working distance] in 100 mL reaction volumes at 22 ± 2 °C under constant stirring (400 rpm using a magnetic stirrer) using 1 cm × 1 cm fabric as the catalyst. The catalytic reduction of ferri- to ferrocyanide was monitored as a function of time using UV–vis absorbance spectroscopy (Cary 50 Bio spectrophotometer) fitted with a handheld optical fiber probe. Reusability studies were performed by removing the Cu-Mₙ@Fabrics after the completion of the reaction, followed by washing the fabric three times with deionized water, and reusing the same catalyst for the subsequent catalytic cycles.

Electrochemical Measurements: Samples for electrochemical measurements were prepared on a copper foil. The foil was first immersed in an acidic solution containing dilute HNO₃ (10% v/v) for 5 min to remove surface oxide impurities. Following the acid wash, the samples were washed thoroughly with acetone and methanol followed by drying in a stream of nitrogen gas. The sample preparation then followed similar to that described in “Fabrication of Cu-Mₙ@Fabrics (M = Au or Ag)” in the Experimental Section. Electrochemical measurements were carried out using CH Instruments electrochemical analyzer at 25 ± 2 °C under the same conditions as those used for catalysis experiments. A three-electrode set-up was used where the working electrode was the catalyst, the reference electrode was Ag/AgCl (aqueous 3 m KCl), and counter electrode was a platinum wire. Open-circuit potential versus time experiments were carried out in K₃Fe(CN)₆ solution (1 × 10⁻³ m). The OCP was first measured on pristine ferricyanide solution until a stable OCP value was obtained (~200 s). At this time, the required volume of Na₂S₂O₃ (0.1 m) was injected into the cell and the OCP versus time profile was monitored. Electrochemical impedance spectroscopy experiments were performed at the formal redox potential of ferricyanide/ferrocyanide (5 × 10⁻³ m; 0.1 m NaCl) at an amplitude of 10 mV over a frequency range of 0.01–10⁵ Hz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Ag nanoparticles, Au nanoparticles, bimetallic fabrics, Cu nanoparticles, heterogeneous catalysis, surface plasmon resonance

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