Short Communication

Nanocatalysis production of photoactive radicals

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ABSTRACT

Eosin Y (EY) dye can be reduced electrochemically by accepting either one or two electrons. The stable two electron reduction product of EY is also obtained by sodium borohydride (BH) reduction. Although the one- and two-electron reductions have similar potentials (~−1.03 and ~−1.04 V, respectively), gold nanocatalysts change the traditional reduction reaction pathway of EY dye with BH to a selective one-electron reduction instead of two. The resultant one-electron reduction product is a slightly persistent semiquinone intermediate: the same as is produced with the electrochemical one-electron reduction. This is the first example of nanocatalysts guiding a reaction to the same products as the electrochemical pathway. The semiquinone intermediate was found to be photochemically active and decomposed by light into a novel green EY dye after losing two bromine atoms. Whereas in the dark, the semiquinone intermediate radical was found to be reduced by accepting another electron forming a colorless reduced form of EY. It was found that hollow gold nanoparticles were superior catalysts for this reaction than solid gold nanoparticles; this was attributed to the cage effect of hollow nanoparticles. This kind of powerful catalyst induced product specificity will be useful for the synthesis of novel molecules or improving the yield of existing products.

Keywords:
Reduction
Eosin Y
Nanocatalysis
Cage effect
Hollow gold

1. Introduction

Most of the chemically produced compounds in industry are based on catalysts. They increase both product yield and reaction selectivity [1,2]. In addition, they drive the reaction to proceed in pathways that lower its activation energy. Nanoparticles of different shapes and sizes have been used to catalyze different chemical reactions and have shown to have higher efficiency compared with regular catalysts [2−6]. Nanocatalysis proceeds either on the surface of the nanoparticles (heterogeneous) [7−9] or in the solution of the nanocatalyst by forming an active intermediate which results from the reaction of one of the reacting material with the nanocatalyst itself (homogeneous) [4,5,10]. The catalytic reactions in solution proceed through an ionic or a free radical mechanism. In photochemical reactions, light excites the reacting materials to generate radicals, which initiate the reaction through free radical formation mechanism [11]. Semiconductor photocatalysts can also generate free radicals after light excitation [12].

Hollow metallic nanoparticles synthesized via the galvanic replacement technique [13,14] are found to have strong catalytic activity [10,11,15]. This is due to the confinement of the rate determining species in the reaction mechanism within the cage like in a nanoreactor and the large surface area since the inner surface of the hollow nanocatalyst added to the outer surface [1,10,11,15]. The confinement of the reacting species could lead to an increase in its steady state concentration and thus the rate of the reaction. The nanoreactor cage effect was studied by a number of different catalytic experiments using different types of the hollow nanoparticles of different designs [14] (single or double shells made of metals of different physical and chemical properties) or the type of the reaction being studied [1]. The results of these experiments suggest that the reactions studied in different hollow nanoparticles occur within the cage of the hollow nanoparticles [10,11,15].

In this communication, solid and hollow gold nanospheres have been used to catalyze a one-electron reduction of Eosin Y (EY) by borohydride into a slightly stable semiquinone free radical intermediate. This radical is formed by a one electron transfer from the borohydride to the EY through the gold nanoparticles. When the semiquinone free radical is exposed to visible light, it undergoes a photochemical reaction to form a green EY dye, but when it is kept in the dark, a colorless two electron reduced form of EY is formed. The nanocatalyst has no role in the photochemical reaction. This combination of nanocatalysis reaction with the photochemical reaction can be useful in synthesizing new products. The yield of the green dye in case of using solid gold nanosphere is less than that in case of using the gold hollow spheres of the same outer size due to the cage effect.

Gold hollow spheres (AuHSs) and gold nanospheres (AuNSs) were prepared as reported earlier [16]. Here galvanic replacement of the silver atoms in silver nanosphere template has been used to make AuHSs. Fig. 1A and B shows the TEM images of AuNSs and AuHSs taken by a JEOL 100C TEM machine. The sizes of the AuHSs and AuNSs are 35 ± 6 nm and 36 ± 5 nm, respectively. Although the shapes of the two particles are not symmetrically spherical, they have similar outer shape. The localized surface plasmon resonance (LSPR) peak positions were found at 630 nm and 540 nm for AuHSs and AuNSs, respectively. In a typical...
experiment, 1.5 mL aqueous solution of EY (4 × 10⁻⁵ M) was mixed with 1 mL of AuHSs or AuNSs nanocatalyst for 3 min in 4 mL quartz cuvette. Then 0.5 mL of sodium borohydride (0.12 M) was rapidly injected into the reaction mixture which was allowed to react for a few minutes at room temperature under atmospheric pressure. The concentrations of the AuHSs and AuNSs after mixing with the reacting materials are 5 and 10 pM, respectively [16]. For the uncatalyzed experiment, 1 mL of AuHSs nanocatalyst was replaced by 1 mL of deionized water (DI). For the reaction carried out in the dark, a black box was used to cover the cuvette when the peak at 405 nm reached its maximum intensity. Naringenin radical scavenger (NG) was used with concentration of 5 M in order to examine the participation of free radicals in reaction. Ocean optics HR4000Cg-UV-NIR was used to conduct the optical measurements. The fluorescence measurements were carried-out with a photon technology international fluorescence setup. An Agilent 1100 liquid chromatography was used with LC–MS analyzer and mass spectrometer (Waters Quattro LC). Bruker (500 MHz) was utilized for the NMR measurement. The surface-enhanced Raman spectrum (SERS) of the EY and the products adsorbed on the surface of AuHSs was measured by Renishaw Invia Raman microscope with 785 nm laser.

When Eosin Y dissolves in water, it undergoes hydrolysis into EY²⁻ di-anion. Spectroelectrochemical studies of EY²⁻ reduction reactions showed that two different reduction pathways coexist [17–19]: (1) reduction of EY²⁻ by a single electron to form a slightly stable semiquinone radical (EY³⁻) or (2) two electron reduction of EY²⁻ with the formation of EY⁴⁻ [20]. EY²⁻ solution has an orange color as it has an absorption peak at 516 nm, and EY³⁻ has an absorption peak at 405 nm, while EY⁴⁻ solution is colorless and absorbs in UV with low absorption cross-section. Sodium borohydride (BH) gives two electrons to EY²⁻ and reduces it to the colorless EY⁴⁻ reduced form species. Fig. 2A shows the absorption spectrum of EY²⁻ after mixing with BH at different times. The intensity of the EY²⁻ peak decreases continuously with time and at the end of the reaction, no new absorption peaks were observed. The reaction completed after 40 min and no change in the optical absorption spectrum of the resulting solution was observed over time. Fig. 2B shows the optical measurement of the reduction reaction of EY²⁻ by BH in the presence of AuHSs. The intensity of the EY²⁻ peak

![Fig. 1. TEM image of: A) hollow gold nanospheres of 35 ± 6 nm diameter and B) solid gold nanospheres of 36 ± 5 nm diameter.](Image)

![Fig. 2. The reduction of EY by sodium borohydride: A) without the AuHS nanocatalyst, EY, the color disappears at the end of the reaction due to two electron reduction. B) Using the AuHS nanocatalyst, the color of the reaction changes to pale yellow having absorption band at 405 nm, due to a one electron reduction. C) The pale yellow solution photochemically decays to a green EY dye, which has an absorption peak at 495 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](Image)
decreases with time and a new peak at 405 nm appears 5 min after mixing the solution with the AuHSs nanocatalyst. This peak corresponds to the EY$^{3−}$ radical and the highest concentration is obtained after 10 min. The reduction process of EY$^{2−}$ to EY$^{3−}$ (one electron) or EY$^{4−}$ (two electrons) has the same reduction potential (−1.03 V) [20]. However, EY$^{4−}$ is much more stable than EY$^{3−}$. For that reason, EY$^{3−}$ is not detected in the absence of the AuHS nanocatalyst. AuHS nanocatalyst controls the reduction rate of EY$^{2−}$, and changes the reaction pathway to one electron reduction. The reason for changing the reaction pathway from two electrons to one electron by the gold nanoparticles is that because borohydride injects electrons into the nanoparticles, and then the nanoparticle passes the electron to EY. To examine whether the surface plasmon resonance of gold nanoparticles has an effect on the catalytic properties of gold, platinum and palladium hollow nanospheres of the same size were used to catalyze this reaction. The one electron reduction of EY was observed in case of both platinum and palladium nanocatalysts. After EY$^{2−}$ is reduced to EY$^{3−}$, if the reaction takes place in the dark, EY$^{3−}$ undergoes further reduction to EY$^{4−}$ (colorless). However, under light EY$^{3−}$ forms green EY dye by a photochemical reaction. Fig. 2C shows the reduction of EY$^{3−}$ to EY$^{2−}$ in the first 10 min. After which, the EY$^{3−}$ radical photochemically decays and a new green dye having absorption peak at 495 nm starts increasing in intensity. In order to prove that the AuHS nanocatalyst does not have a role in the photochemical reaction of EY$^{3−}$ into the green dye, the AuHS nanocatalyst was removed from the reaction solution by centrifugation at 10,000 rpm for 5 min, after the 405 nm peak reached its maximum value. Consequently, the supernatant EY$^{3−}$ produced the green dye photochemically, which proves that the nanocatalyst has no role in the photochemical green dye formation.

In order to confirm that the reaction involves formation of the EY$^{3−}$ semiquinone radical, which photochemically forms the green dye, NG is added to the reaction mixture. If the reaction proceeds via radical formation, the radical scavenger captures the radicals and changes the reaction rate. Fig. 3A shows the absorption intensity of EY$^{2−}$, EY$^{3−}$, and the green EY dye versus the time in the presence and absence of NG, after mixing EY$^{2−}$ with BH and AuHSs in light; the inset panel shows the changes taking place in the first 10 min. During which, the intensity of the peak corresponding to the pure dye EY$^{2−}$ decreased rapidly with time, however the NG is found to decrease the rate of decay of EY$^{2−}$. Moreover, the peak at 405 nm assigned to the EY$^{3−}$ radical increased with time. It seems that NG decreases the rate of EY$^{3−}$ formation. After 10 min from mixing, the band at 495 nm starts to appear and increases in intensity with time while the intensity of the peak at 405 nm decreases with time. The NG also decreases the rate of the green EY dye formation. In order to confirm the cage nanoreactor effect of AuHSs, gold nanospheres of solid structure of with twice as much concentration as AuHSs were used to catalyze the reduction reaction of EY$^{2−}$ into the green EY dye. Fig. 3B shows the decrease of the absorption peak intensity of EY$^{2−}$ with time after mixing with BH and AuNSs catalyst and the formation of EY$^{3−}$ which has an absorption peak at 405 nm. Unlike the reduction by AuHSs the peak that corresponds to EY$^{2−}$ showed up after 7 min of the reaction catalyzed by AuNSs and not after 2 min. The intensity of the peak that corresponds to the EY$^{3−}$ in AuNSs is less intense compared with that in case of using AuHSs as a catalyst. In the first 10 min after mixing the reacting materials, the NG has smaller effect on the reduction reaction of EY$^{2−}$ catalyzed by AuHSs compared with using AuHSs. One of the main differences between the catalysis by AuHSs and AuNSs is that, the yield of green produced by AuHSs is higher than that in case of AuNSs. The NG prevents the photochemical decomposition of EY$^{3−}$ into the green dye in case of AuNSs. These differences in the catalysis by AuHSs and AuNSs support the idea that hollow structure nanoparticles are more active in catalysis compared with the solid structure with twice as much concentration due to the cage effect that we proved in our former studies [1,10,11,15].
medium) the position of the peak maximum is at 490 nm and at pH less than 7 (acidic medium) it blue shifted to 477 nm (see Fig. S4). Based on the previously taken measurements, the reduction reaction of EY can be summarized in Fig. 4B.

2. Conclusions

In summary, gold nanocatalyst was found for the first time to catalyze the reduction of the Eosin Y dye to form a photochemically active intermediate by one electron reduction. This intermediate can photochemically (non-catalytic) release two bromine atoms and give a green EY dye or it can thermally (non-catalytic) reduce to EY$^{4-}$ in the dark. The lower molecular weight dye (EY green) absorbs and fluoresces photons of higher energy than the regular EY. The fact that gold nanoparticles control the number of electrons that is given to EY indicates that the reduction electron transfer proceeds through the nanoparticles. The high efficiency of the hollow structure gold nanoparticles in the production of the EY green dye compared with the solid shape suggests the cage nanoreactor effect.

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Appendix A. Supplementary data

SEM image of AuH@S shell is shown in Fig. S1. GC–MS of EY dye and the green EY dye is shown in Figs. S1 and S2. Fig. S3 are the surface-enhanced Raman spectrum of EY and the green EY dye, and the final product formed on dark experiment. Fig. S4 is effect of the pH of the solution on the maximum absorption peak position of Eosin Y and the newly prepared green dye. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.04.021.

References