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Short Communication

Nanocatalysis production of photoactive radicals

Mahmoud A. Mahmoud *, Guojun Weng

Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA

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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.

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

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* Corresponding author. Tel.: +1 4048944009.
E-mail address: mmahmoud@gatech.edu (M.A. Mahmoud).

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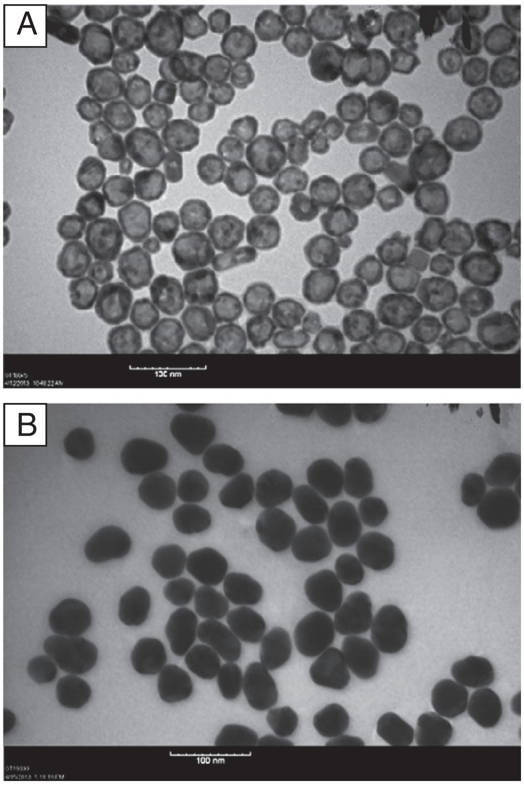

Fig. 1. TEM image of: A) hollow gold nanospheres of 35 ± 6 nm diameter and B) solid gold nanospheres of 36 ± 5 nm diameter.

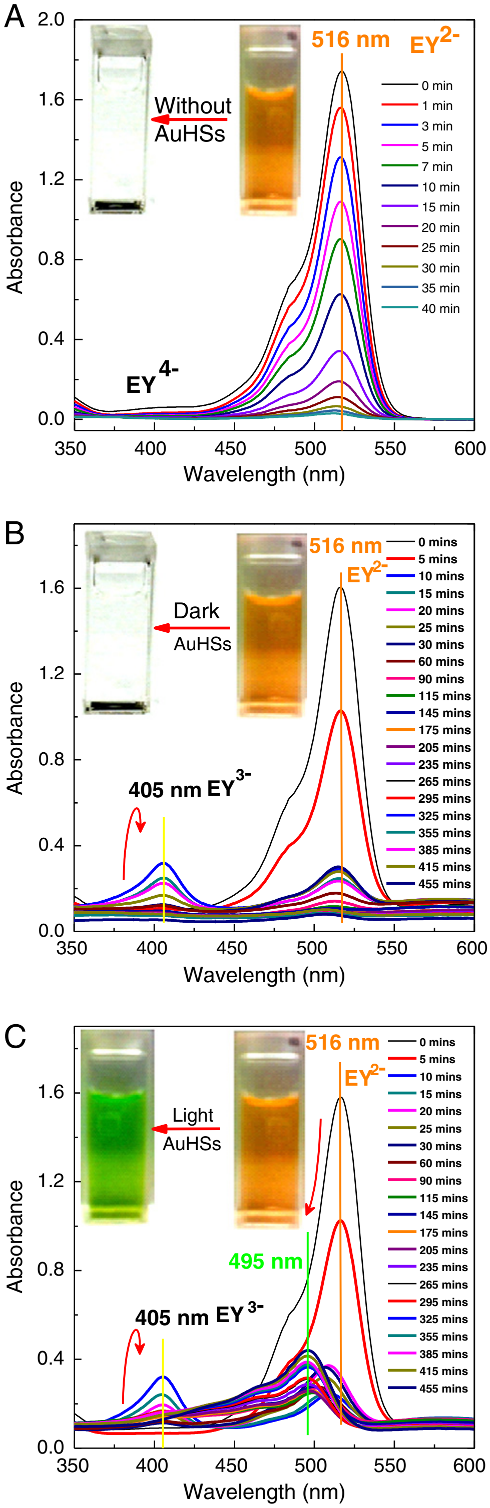

Fig. 2. The reduction of EY by sodium borohydride: A) without the AuHS nanocatalyst, EY, the color disappears at the end of the reaction due to two electron reduction. B) Using the AuHS nanocatalyst, the color of the reaction changes to pale yellow having absorption band at 405 nm, due to a one electron reduction. In the dark, this solution further reduces to a colorless species (EY^{4-}) 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.

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 4×10^{-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 EY^{2-} di-anion. Spectroelectrochemical studies of EY^{2-} reduction reactions showed that two different reduction pathways coexist [17–19]: (1) reduction of EY^{2-} by a single electron to form a slightly stable semiquinone radical (EY^{3-}) or (2) two electron reduction of EY^{2-} with the formation of EY^{4-} [20]. EY^{2-} solution has an orange color as it has an absorption peak at 516 nm, and EY^{3-} has an absorption peak at 405 nm, while EY^{4-} solution is colorless and absorbs in UV with low absorption cross-section. Sodium borohydride (BH) gives two electrons to EY^{2-} and reduces it to the colorless EY^{4-} reduced form species. Fig. 2A shows the absorption spectrum of EY^{2-} after mixing with BH at different times. The intensity of the EY^{2-} 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 EY^{2-} by BH in the presence of AuHSs. The intensity of the EY^{2-} peak