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Catalytic oxidation of methylene blue by dendrimer encapsulated silver and gold nanoparticles

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Dedicated to Professor Cedric Holzapfel on the occasion of his 80th birthday.

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ABSTRACT

The catalytic oxidation of methylene blue was investigated in the presence of dendrimer generation five terminated NH_2 encapsulated silver (AgDENs), and gold (AuDENs) nanoparticles as catalyst. The synthesis process of encapsulated metal nanoparticles were monitored by UV/vis spectrophotometry and their average diameters determined by transmission electron microscopy analysis, respectively. The kinetics was monitored using UV/vis spectrophotometry, under pseudo-first order conditions, resulting in observed rate constants k_{obs}. Langmuir–Hinshelwood approach was applied to model the kinetic process. The adsorption of methylene blue on the catalyst surface is related to the type of metal nanoparticle present, and presents the rate-determining step.

1. Introduction

Nanosciences have recently evolved as a major research field. The nanosciences gained interest in several areas, including optoelectronics, sensing, medicine and catalysis [1,2]. The use of transition-metal nanoparticles in catalysis is due to their high ratio of surface atoms to volume and thereby bring selectivity and efficiency to heterogeneous or homogeneous catalysis [3,4]. An important factor in transition-metal nanoparticle synthesis is the use of protective agents to stabilize dispersed nanoparticles and avoid their agglomeration. The agglomeration is the formation of larger sized transition-metal nanoparticles with an eventual decrease in catalytic activity [5]. In order to preserve their specific magnetic properties, and to protect nanoparticles from both oxidation and agglomeration, the application of the colloid template synthesis has been proposed [3]. Encapsulated nanoparticles have been successfully employed by using carbon, silica, metal oxides, organic polymers and surfactants [6]. Previous work demonstrated that the stabilization and size of nanoparticles depends on the amount of stabilizers, and the balance between amount of metal and stabilizer.

Dendrimers are nearly perfectly monodisperse (basically meaning of a consistent size and form) macromolecules with a regular and highly branched three-dimensional architecture, and are generally prepared using either a divergent method or a convergent one [7,8]. Dendrimers are well-suited for hosting metal nanoparticles [3]. The host function of dendrimer in metal nanoparticle synthesis is controlled by internal functional groups on the dendrimer that coordinate to the metal nanoparticle surface with minimal passivation [9,10]. Among the potential applications of dendrimer encapsulated metal nanoparticles, catalysis is one of the most promising, because it is relatively easy to tune the structure, size, and location of catalytically active sites; and dendrimers have the potential to combine the advantage of both heterogeneous and homogeneous catalysts [3]. The properties of dendrimer based catalysts, such as selectivity, activity, and stability are dependent on the location and nature of the metal [10].

Catalytic properties of silver and gold nanoparticles have been known for decades, and have been reviewed extensively [11], particularly for nanoparticles included into vesicles of surfactants and water-soluble or insoluble polymers [12].

The catalytic oxidation of methylene blue has been used as an illustration of metal nanoparticle activity by many groups [13]. To

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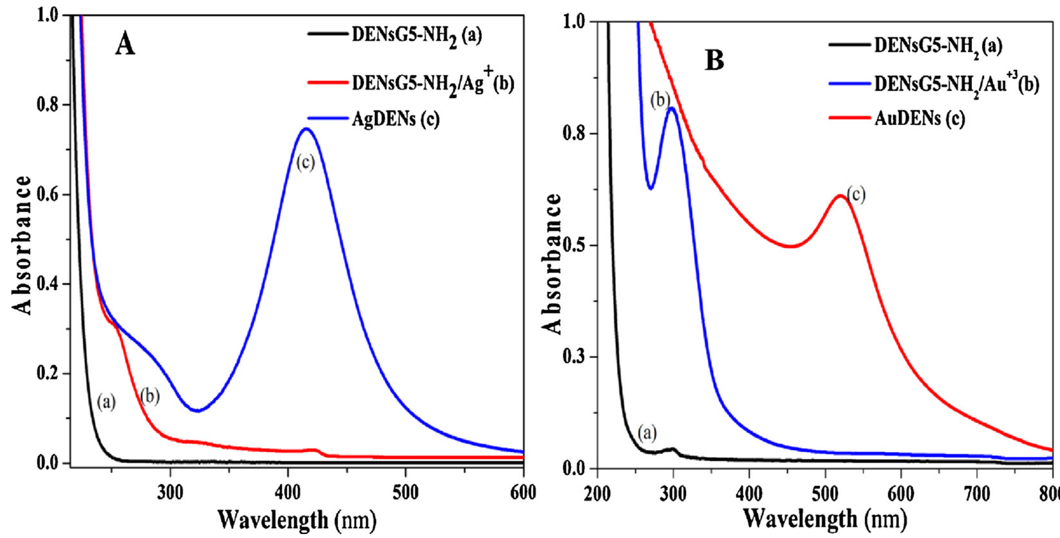

Fig. 1. UV/vis absorbance spectra of aqueous solutions of A: (a) Dendrimer G5-NH_2, (b) DENsG5-NH_2/Ag^+ metallodendrimer, and (c) AgDENs; B: (a) Dendrimer G5-NH_2, (b) DENsG5-NH_2/Au^{+3} metallodendrimer, and (c) AuDENs. [DENsG5-NH_2] = 5 μM; metallodendrimer ratios: DENs/$M^{n+}{}_{100}$. Characterization spectra were taken using water as a reference.

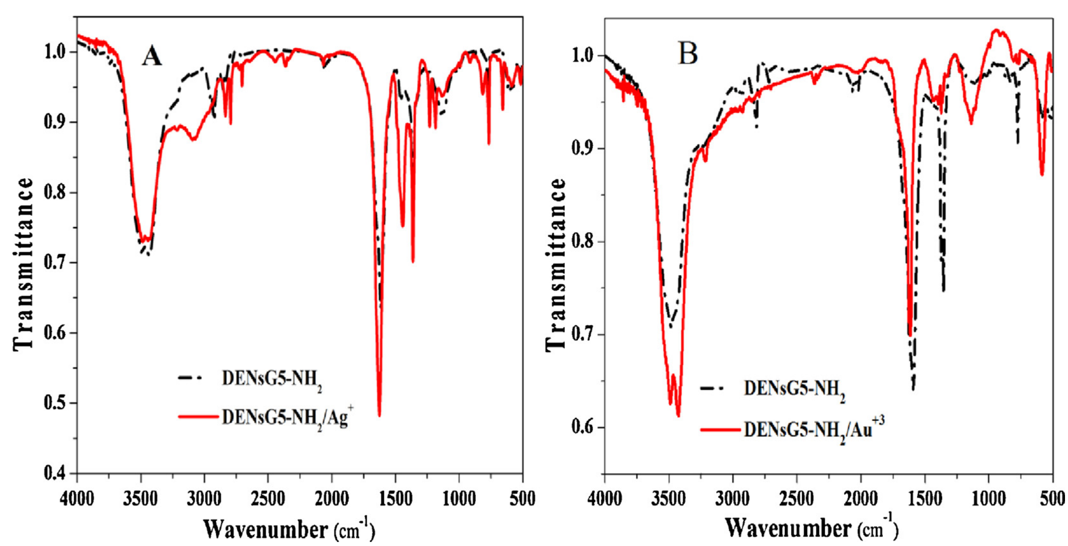

Fig. 2. FTIR spectra for the coordinated silver (A) and gold (B) into G5-PAMAM-NH_2 dendrimer.

the best of our knowledge, while dendrimer encapsulated nanoparticles have been reported as catalysts in CO oxidation [14], there are no reports of DENs as catalysts in methylene blue oxidation. Methylene blue is a heterocyclic aromatic (tricyclic phenothiazine) and cationic dye. It could be applied in medical treatments and staining reagents [15,16]. It has been estimated that 1-15% of the dye is lost during the dyeing process in textile industry and is released into wastewater. Discharge of dyes in water is unacceptable (even <0.005 mg/L) because it causes certain hazards and environmental problems. We note the inhibition of sunlight penetration into water; thus affecting the aquatic ecosystem by the destruction of microorganisms responsible for auto-purification of aquatic ecosystems [17,18]. To avoid this disaster, investigation into the removal of dyes from effluent wastewater is necessary. Three major effective and economical techniques of removing dyes from wastewater have been developed - the oxidation, adsorption, and flocculation or precipitation [19]. The chemical oxidation of organic compounds in wastewater can be used as pre- or post-treatment, decreasing toxicity or destruction of these dyes [20]. The hydrogen peroxide used as oxidizing agents, generates hydroxyl radicals that results in the degradation of organic compounds [21,22].

Methylene blue has been considered as a benchmark compound to evaluate the catalytic activity of metal nanoparticles. The catalytic oxidation process is monitored by UV/vis spectrophotometry following the decrease of the maximum absorbance peak at λ 664 nm which is related to methylene blue concentration [13]. The kinetic data was proceeded according Langmuir-Hinshelwood approach which describe the catalyst as a platform consist to the active sites onto that the reactants absorbed prior to react.

Here we describe the synthesis and the characterization of dendrimer encapsulated silver and gold nanoparticles. The catalytic activity of these metal nanoparticles was evaluated using the oxidation of methylene blue as a model reaction. The kinetic and thermodynamic parameters were determined using the Langmuir–Hinshelwood approach.