



Photocatalysis in a packed bed: Degradation of organic dyes by immobilized silver nanoparticles



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ABSTRACT

Complete photocatalytic degradation of methyl orange, methylene blue and rhodamine chloride was accomplished using immobilized silver nanoparticles as catalysts and tethered calix[7]hydroquinone molecules as nano-reactors. The nanoparticles were immobilized on quartz beads that were assembled in a packed bed configuration. The large interfacial area afforded by the packed bed geometry, presentation of the nanoparticles as a single, tethered layer, and the optically transparent packing material facilitated intimate interaction between the catalyst, dye solution and radiation. The degradation was accomplished using either UV or visible radiation and the nanoparticles displayed self-cleaning and anti-poisoning properties thereby demonstrating excellent durability and catalytic efficiency. The single-layer coverage of Ag nanoparticles facilitates use of very small amounts of the photocatalyst for degradation of relatively large amounts of dye. The method addresses multiple issues that constrain scale-up of photocatalytic systems that deploy nanoparticles as catalysts.

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Introduction

Organic dyes discharged by textile industries are one of the major sources of contamination of water. It is estimated by the World Bank that about 20% global industrial pollution comes from textile industry [1]. Various approaches, such as adsorption, sedimentation and coagulation, have been employed to treat pollutant containing effluents [2]. However, these classical methods usually generate secondary waste products which must be treated further. Photodegradation of organic dyes by semiconducting nanoparticles (NPs) wherein the catalytic mechanism is mainly due to the photo-excited electron–hole pairs [2–4] has been widely investigated. The excited electrons help generate active radicals (HO^{*}) which together with the positive holes contribute to the oxidation of organic dyes. In order to facilitate excitation by visible radiation than by ultraviolet, many methods have been investigated to decrease the band gap of semiconducting NPs, such

as modifying the crystal lattices of NPs by doping [2,5], surface modification by deposition of conjugated polymers [6,7] or noble metals [8]. Recently, silver nanoparticles (AgNPs) have attracted much attention as photocatalyst to degrade organic dyes due to their low electronic band gap that promotes high activity under both UV and visible light *via* the surface Plasmon resonance mechanism [9–11].

Despite their demonstrated performance, there are many challenges that have limited NPs from being used as commercial catalysts, such as their ease of aggregation, difficulty in post-treatment recovery/recycle and short durability. Surfactants are typically used to protect NPs from aggregation; however, the capping molecules on the surfaces of NPs block the mass transport and electron transfer and thus reduce the activity [12,13]. Furthermore, recovery of the NPs from the reaction medium is difficult and expensive. This necessitates immobilization of NPs on solid surfaces to provide stability and thus facilitate the reuse of NPs. AgNPs have been immobilized on different solid surfaces such as glass slides [14], silica nanofibers [15], amidoxime fibers [16], carbon nanotubes [17], zeolite and amorphous SiO₂ [18]. In all these cases, AgNPs were formed by direct physical adsorption of AgNPs or precursors on surfaces of solids; however, the NPs were usually not strongly attached on the surfaces, which not only resulted in a low surface coverage of the NPs on the substrates (less than 10% estimated from TEM images) [18,19], but also led to their reduced catalytic durability. The rapid decrease in effectiveness with time of AgNPs may be

Abbreviations: NPs, nanoparticles; AgNPs, silver nanoparticles; MO, methyl orange; MB, methylene blue; RAC, rhodamine chloride; APHS, *p*-aminophenyl-trimethoxysilane.

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caused by the loss of the nanoparticles due to lack of sufficient functional groups on the solid surfaces to stabilize the AgNPs. Yao et al. [19] found that NPs immobilized on the support with more functional groups resulted in better spatial distribution, improved number density and long-term durability. Though supported NPs on organic films usually have good long-term durability due to robust immobilization, fully embedded NPs in organic films are easily poisoned by the accumulation of organic dyes on the surface because their catalytic efficiency is very low due to the reduced access to the NPs [20]. On the other hand, a monolayer of NPs tethered on organic films will provide robust immobilization and access to NPs, and thus bestows the NPs with high catalytic efficiency, long-term durability and anti-poisoning property, which is desired for an efficient catalytic system.

The need for separating the nanocatalyst from the reaction medium in typical stirred tank configurations demands that photocatalysis be conducted in batch mode. This requires the onerous task of separating the catalysts from the medium by methods such as centrifugation to remove the small particles in each recycle process [21,22] and imposes a serious limitation in practical applications. Clearly, a semi-continuous/continuous mode of operation will be amenable to scale-up. Thus, while past studies have focused on improving one aspect or another of the photocatalytic system, such as activity, immobilization, light exposure and durability, a comprehensive solution that addresses all these issues has not been proposed. In this work, photocatalysis is carried out in a packed bed configuration wherein the catalytic nanoparticles are immobilized on the surface of the packing material and the dye solution is pumped through the packed bed. Optically transparent quartz beads used as the packing material facilitate interaction between the NPs, radiation and reactant, in addition to their utility as the substrate for immobilization. The feasibility of the proposed method is supported by the work of Vella et al. [23] who studied the irradiation model in quartz wool packed bed, and demonstrated that light can be sufficiently distributed in a transparent packed bed through scattering and refraction.

In our previous work, we have reported synthesis of well-dispersed AgNPs that were immobilized on surfaces with non-flat topography using calix[7]hydroquinone nanoreactors [24]. In this work, we employ this approach to synthesize and immobilize monolayer of AgNPs on surfaces of quartz beads which will serve as packing material and investigate the photocatalytic performance of the AgNPs by batch and continuous packed-bed configurations. Furthermore, quartz is advantageous as a substrate due to its high transparency to ultraviolet and visible irradiation. AgNP-laden quartz beads were packed in a quartz tube and the tube was subjected to irradiation from lamps mounted at the periphery of the tube. Photo-degradation of methyl orange (MO), methylene blue (MB), rhodamine chloride (RAC) and as well as their mixtures in the packed bed was investigated. The high coverage of the quartz surface by the AgNPs afforded by using calixarene nanoreactors coupled with the single-layer coverage which facilitates accessibility of the AgNPs to organic dyes due to absence of surfactants, accessibility to radiation enabled by the use of transparent supports, and the high interfacial area provided by the packed bed configuration contribute to a highly efficient, effective and continuous system for dye degradation by photocatalysis.

Materials and methods

Materials

p-Aminophenyltrimethoxysilane (APhS, Gelest), sodium hydro-sulfite (Aldrich), silver nitrate (ACS, Merck), iodocyclohexane (98%, Aldrich), poly(methyl vinyl ether-alt-maleic anhydride) (Gantrez)

(Mn ~ 311,000, Mw ~ 1,080,000) (Aldrich), methyl orange (MO, Merck), methylene blue (MB, Sigma–Aldrich) and rhodamine 6G chloride (RAC, Sigma–Aldrich) were used as received. Triethylamine (GC grade, Fluka), acetone (AR, Merck), toluene (HPLC grade, Tedia), tetrahydrofuran (HPLC grade, Tedia), dimethylacetamide (HPLC grade, Tedia), dimethylformamide (HPLC, Fisher), pyridine (ACS grade, Merck), acetonitrile (AR, Merck), ethyl alcohol (anhydrous) (HPLC grade, Tedia), sulfuric acid (GR grade, Fischer), hydrogen peroxide (30%, Merck) were used without further purification. 4-Methoxycalix[7]arene was synthesized in our laboratory. Structures of APhS, Gantrez, MO, MB, 4-methoxycalix [7]arene were shown as Supporting information, Scheme S1. Silicon wafers were obtained from Engage Electronics Pte Ltd., Singapore.

Fabrication of calix[7]hydroquinone nanoreactor

APhS and Gantrez were deposited on the surface of the silicon wafer by a previously described method [25]. Briefly, it involves sequentially immersion of the silicon wafer in 6 mM APhS in toluene and 0.2% (w/w) Gantrez in THF, and thus populating the surface of the wafer with carboxylic acid groups. Subsequently, 4-methoxycalix[7]arene was assembled on the surface with carboxylic acid groups by immersing the samples in 0.05% (w/w) 4-methoxycalix[7]arene in a mixture of THF and pyridine (10:1, v/v), which has been described in our previous work [24]. Calix[7] hydroquinone nanoreactors were fabricated through the demethylation of 4-methoxycalix[7]arene monolayer by following the method of Zuo et al. [26].

The fabrication process on the surfaces of silicon wafer and glass beads is similar.

In situ synthesis of silver NPs on the surface of quartz beads

Prior to incorporation of NPs, the substrate containing the calix [7]hydroquinone layer was pretreated by a 5% sodium hydrosulfite aqueous solution for 1 h to reduce any oxidized calixarene molecules. The samples were then rinsed with de-ionized water thrice.

Ag NPs were synthesized *in situ* in the organic layer by immersing the samples in 10 mL silver nitrate solutions (0.2% w/w). The solution was agitated by a shaker for 3 h. Afterwards, the samples were rinsed with de-ionized water and dried in vacuum. The resulting AgNPs were dispersed and stabilized in the organic layer, which is shown as Scheme 1.

Photocatalytic study in batch mode

0.3 g of quartz beads (1 mm in diameter) coated with AgNPs was added to 2 mL MO aqueous solution (10 ppm) in a petri dish, and the mixture was stirred under the irradiation of UV light (4 W). The MO solution was characterized by UV–vis spectroscopy periodically.

Photocatalytic study in a packed bed

1.2 g of quartz beads coated with AgNPs was filled in a quartz tube of 20 cm in length and 3 mm in diameter. The photocatalytic reaction was carried out under irradiation of UV (100 W, germicidal UV lamp) or visible light (30 W, fluorescent lamp), and the setup is shown as Scheme 2. The dye solution (10 ppm) was injected through a syringe pump (NE4000 double syringe pump) at one end of the tube at different flow rates and the effluent was collected from the other end. The flow was sustained for 5 h at each flow rate and the effluent was analyzed by UV–vis spectroscopy. For the purpose of characterizing the durability of the packed bed, the

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