Photocatalytic degradation of hexavalent chromium emerging contaminant via advanced titanium dioxide nanostructures

C. Athanasekou, G.Em. Romanos, S.K. Papageorgiou, G.K. Manolis, F. Katsaros, P. Falaras *

Institute of Nanoscience and Nanotechnology, N.C.S.R. Demokritos, Terma Patriarchou Grigoriou & Neapoleos, 15310 Agia Paraskevi Attikis, Athens, Greece

HIGHLIGHTS

- Cu/Cu$_2$O nanoparticles decorated TiO$_2$–alginate beads were synthesized.
- The photocatalytic efficiency for Cr^{6+} reduction was independent of the acidity.
- 10 g L^{-1} of photocatalysts cleaned a 5 ppm Cr^{6+} solution in only 15 min.

ARTICLE INFO

ABSTRACT

Photocatalysis is an attractive advanced treatment process that can be used for water purification from emerging contaminants, including hexavalent chromium (Cr(VI)) removal. Up to now, photocatalytic reduction of Cr(VI) has been investigated mostly using titania (TiO$_2$) photocatalysts in acidic water solutions. In this work, copper (Cu) and cuprous oxide (Cu$_2$O) nanoparticles (NPs) decorated TiO$_2$–alginate beads were synthesized and studied in the photocatalytic reduction of Cr(VI) to Cr(III) under UV/Vis irradiation. The target was to overcome the drawback of pristine TiO$_2$ which requires acidified solutions to achieve enhanced photocatalytic reduction of hexavalent chromium. Moreover, the spherical and uniform size of the photocatalytic beads ensures efficient mass transfer, addresses the problems of limited irradiation into slurries and facilitates separation of the catalyst after the photocatalytic treatment. The hexavalent chromium reduction efficiency of the Cu/Cu$_2$O decorated TiO$_2$/alginate beads was satisfactory at pH range 2–6 and practically did not depend on the treated solution acidity. Small quantities (10 g L^{-1}) of the newly synthesized photocatalytic beads succeeded to remove all toxic loads from a 5 ppm Cr^{6+} solution in only 15 min under UV light irradiation. These low-cost developed and non-toxic photocatalysts seam greatly promising for Cr(VI) pollution cleanup.

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1. Introduction

Following the chrome electroplating industrial revolution, which provides everyday life with decorative, corrosion resistant chrome layered objects, landfill waste disposal of chromium containing compounds is a common practice arising. Hexavalent chromium [Cr(VI)] is carcinogenic and related pollution constitutes an extremely serious threat, especially for the precious water resources human beings live on. The reduction of Cr(VI) to the one hundred times less toxic Cr(III) is an important task as it restricts the distribution of a priority pollutant rather resistant to chemical reduction and even to bioremediation. Typical chromium removal treatments such as coagulation, metal adsorption (including the use of resins) and reverse osmosis, usually need high instal-

lation and maintenance costs that can be afforded only in large-scale applications. On the contrary, photocatalytic treatment is a low cost, environmental friendly, efficient, flexible and feasible advanced technique to eliminate emerging pollutants, with TiO$_2$ being the most widely used semiconductor catalyst. This is due to its exceptional optoelectronic and physicochemical properties combined with endurance to aggressive conditions, large availability and lack of toxicity towards both humans and the environment. Thus, hexavalent chromium removal using metal oxide photocatalysts was investigated in the literature, insisting on TiO$_2$ mechanistic aspects [1–6]. In addition, the photoreduction of Cr(VI) from acidic aqueous solution using TiO$_2$-impregnated glutaraldehyde-crosslinked alginate beads was recently reported in the presence of Fe(III) ions in the pollutant solution [7]. However this approach aggravated the process complexity and is not practical at an industrial scale.

* Corresponding author.
  E-mail address: p.falaras@inn.demokritos.gr (P. Falaras).

Methods for optimizing the photocatalytic activity of TiO_2 as well as its vis-light response, often employ non-metal doping [8], surface decoration with transition metals nanoparticles (NPs) or doping with transition metals ions. Besides affecting electron-hole recombination, doping metal ions into the TiO_2 lattice essentially decreases the semiconductor's band gap and therefore, the energy needed for photo-excitation, turning TiO_2 into a visible-light responsive catalyst. Cu has extensively been studied as dopant into the TiO_2 lattice [9–14]. In most of the cases, the preparation method makes use of copper salts incorporated into the titanium alkoxide precursor solutions during the sol-gel synthesis of TiO_2. In fact, despite the induction of visible light response, doping with copper may have adverse effects on the photocatalytic efficiency of TiO_2. In a photocatalytic process, the band-gap excitation and formation of free charge carriers (an electron and a hole) is followed by deactivation which can be either the successful donation of the carrier to the acceptor molecules at the surface, leading to the desired redox reactions, or an unwilling recombination process.

The carriers' recombination can occur either on the surface or/and in the bulk of the catalyst, both damaging the efficiency of the photocatalytic reaction. Recent literature works report on intensive efforts to develop copper decorated titania photocatalysts. However, the new catalysts suffer for serious electron-hole recombination problems, mostly due to the existence of copper oxide (CuO) acting as electron-hole recombination site [9]. On the contrary, stable Cu_2O NPs bring the advantage of beneficial charge carrier separation since they permit the transfer of photo-generated electrons from the Cu_2O conduction band to the TiO_2 conduction band as well as the transfer of photogenerated holes from the TiO_2 valence band to the Cu_2O valence band, respectively. In addition, the co-existence of Cu(0) species (Cu_2O) further promotes the photocatalytic activity, since the photoinduced electrons of Cu_2O are transferred to the conduction band of TiO_2 and from there injected to the pollutant [15,16].

In the present paper, Cu/Cu_2O nanoparticle-impregnated TiO_2/alginate beads were developed and their potential use as photocatalysts for Cr(VI) reduction was investigated as a function of the pH, and initial Cr(VI) concentration. Proceeding with partial decoration of the positively-charged titanium oxide surface with well dispersed and stabilized copper nanoparticles (NPs), we prepared the active photocatalyst following an innovative, highly efficient and fully controllable method for the decoration of the TiO_2 surface. Thus, we have proved the photocatalytic reduction efficiency of the hexavalent chromium (Cr^{6+}) is almost independent of the solution pH and there is no need of additional adjustment. In parallel, a more efficient charge carrier separation is induced by the Cu_2O decorated composite material that results in more effective photocatalyst than the pristine TiO_2.

2. Material and methods

2.1. Chemicals

All reagents were of analytical grade and were used without further purification. Potassium dichromate, Ethylene glycol, EtOH, HCl and Polyethylene glycol were obtained from Sigma-Aldrich, 1.5 diphenylcarbazide (DPC), Copper (II) nitrate trihydrate 99% and Glutardialdehyde (Pentane-1,5-dial) from Acros Chemicals. Degussa TiO_2 P25 was provided by Evonik Industries AG. Cr(VI) stock solution ($0.05\ g\ L^{-1}$) was prepared by dissolving 141.4 mg $K_2Cr_2O_7$ (Aldrich) in 1000 ml ultrapure water. The solutions of different concentrations used were obtained by dilution of the stock solution and the pH values were adjusted to the required values by adding negligible amounts of 0.1 M NaOH or H_2SO_4 solutions.

Sulfuric acid was preferred over nitric acid for pH control due to its inability to oxidize copper at low concentrations ($SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2(g) + 2H_2O$; $E_0 = +0.17$, $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$; $E_0 = 0.96$, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E_0 = +0.52$). DPC stock solution ($5\ g\ L^{-1}$) was prepared by diluting 250 mg 1.5 diphenylcarbazide in 50 ml acetone and stored in a drown bottle. Sodium alginate was purchased by SIGMA (SIGMA, medium viscosity from *Macrocystis pyrifera*).

2.2. Synthetic procedure

About 100 mL of the precursor solution was prepared by mixing 2 g of SA powder and 2 g of TiO_2 powder (Degussa P25) in ultra-pure water followed by 24 h stirring until a homogenous solution was achieved. The mixture was outgassed for 24 h and then injected dropwise using a peristaltic pump and a syringe (10 mL) with a needle (0.5 mm in diameter) into 500 ml Cu^{2+} solution of 20,000 ppm (cross-linker solution), under gentle stirring at 25 °C. The resulting Cu-alginate gel-TiO_2 spheres formed were left upon contact with the cross-linker solution under stirring for 24 h to stabilize to equilibrate and were subsequently filtered. The excess of cross-linker solution was removed by filtration and washing several times with distilled water. The prepared beads together with 0.5 g polyethylene glycol were added to 25 ml ethylene glycol and the mixture was boiled under reflux at 220 °C for 4 h [17]. Finally, the beads were filtered, washed with Millipore water left to dry at room temperature until no weight change was observed. The advantage of using the dry beads over the gel beads were accurate measurement of the mass, better handling nature, gain in mechanical strength. For the preparation of the blank beads the cross-linker solution was a mixture of 800 ml glutaraldehyde, 9 ml EtOH and 184 ml HCl 5 N. The rest of procedure was the same. Comparative photo of the blank and Cu-beads is shown in Fig. 1.

2.3. Characterization

Elemental Analysis was conducted in a Perkin Elmer 2400 CHN Elemental Analyzer which uses a combustion method to convert the sample to simple gases (CO_2, H_2O, N_2). Each sample is first oxidized in pure oxygen environment, the product gases are measured as a function of thermal conductivity and finally all quantitation is performed on a weight percent basis. Sample masses were between 2 and 4 mg (weight accuracy 0.001 mg). X-ray diffraction analysis was conducted in a Rigaku R-AXIS IV Imaging Plate Detector mounted on a Rigaku RU-H3R Rotating Anode X-ray Generator. Micro-Raman measurements were performed using a Renishaw inVia dispersive micro-Raman spectrometer with 250 mm focal length and equipped with a high sensitivity, deep-depletion CCD detector. The percentage determination of elements in these samples was performed by an energy-dispersive X-ray spectrometer (EDX) attached on a FEI Quanta Inspect Scanning Electron Microscope (SEM) with tungsten filament operating at 10 kV in order both improve signal scanning depth and minimize the organic components degradation. Core-level X-ray photoemission (XPS) spectra were collected with a PHOIBOS 100 (SPECS) hemispherical analyzer at a pass energy of 7 eV with a Mg X-ray source (1253.6 eV). The take-off angle was set at 37° relative to the sample surface. The binding energy scale was calibrated using the position of both the Au 4f7/2 and Ag 3d5/2 peaks at 84 and 368.3 eV, respectively measured on clean gold and silver foils.

2.4. Photocatalytic experiments

The diphenylcarbazide (metal ion indicator, DPC) colorimetric method, described in Standard Methods [18], was used to determine the concentration of the different Cr species. The redox