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Efficient photocatalytic hydrogen generation by Pt modified TiO₂ nanotubes fabricated by rapid breakdown anodization

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ABSTRACT

Photo-assisted hydrogen generation studies of platinum loaded titanium (IV) oxide nanotubes suspended in ethanol–water mixture were carried out at room temperature. The TiO₂ nanotubes synthesized by rapid breakdown anodization technique were loaded with Pt nanoparticles by chemical reduction of aqueous chloroplatinic acid solution using sodium borohydride. The chemisorption (active) surface area of the synthesized nanocomposites for hydrogen was measured by pulse chemisorption method using temperature programmed desorption reduction oxidation equipment and found to decrease with increase in platinum loading in the range 1–10 wt%. The platinum supported nanotube composites were characterized for phase and morphology by XRD, TEM and SEM. The hydrogen generated by the photocatalytic reduction of water from water–ethanol mixture at different wavelengths of incident light, using the Pt-TiO₂ nanocomposite photocatalyst, was determined by using a proton exchange membrane based hydrogen meter. The highest hydrogen generation efficiency was observed at 1–2.5 wt% of Pt loading. The maximum photocatalytic hydrogen generation of 0.03 mol/h/g of Pt-TiO₂ was observed with a 64 W UV light source ($\lambda = 254$ nm). The photoluminescence property of the Pt loaded TiO₂ has been correlated with the hydrogen generation efficiency and the reaction mechanism briefly discussed.

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1. Introduction

Sustainable energy and environment are the two important concerns of our modern society. Presently, the major source of energy for industrial and economic purposes is fossil fuels. Depletion of fossil fuel reserves and pollution caused by combustion of fossil fuels is a major concern. Hydrogen, an effective energy carrier, is considered as a possible alternative

to reduce the strong dependence on fossil fuels and environmental pollution. When H₂ becomes the primary energy carrier the hydrocarbon economy (oil economy) will be replaced by hydrogen economy. Currently 95% of the H₂ production is from steam reforming of natural gas, which has an indirect dependence on fossil fuels. Hydrogen generation by photo splitting of water, being an environmentally friendly and economically viable process, has been considered as the

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best alternative. The first report on photocatalytic splitting of water on TiO₂ electrode by Fujishima and Honda created new paradigm in energy conversion and environmental remediation using solar photons [1]. Currently, various research groups are working on H₂ generation by water splitting using solar energy. The principle behind photolysis of water using TiO₂ is that, when TiO₂ is in contact with water the photo excited conduction band electrons can reduce water, to generate hydrogen, if the conduction band level is more negative compared to the H⁺/H₂ reduction potential. Compared to bulk, nano-structured TiO₂ have enhanced photocatalytic properties due to quantum confinement and heightened reactivity associated with their molecular electronic structure and/or an increase in surface to volume ratio. When the size of the particles become comparable with the de-Broglie wavelength of the charge carriers, which lies between 5 and 25 nm for oxide semiconductors like TiO₂, the wave function of charge carriers spread over the entire particle do not need to diffuse anymore to accomplish reactions with species present at the surface, thereby increasing the quantum yield [2]. For photocatalytic applications quasi one-dimensional TiO₂ nanostructures such as nanotubes, nanowires and nanorods are expected to be more efficient compared to nanoparticulates. Among the quasi one-dimensional nanostructures, nanotubes are preferred because of their high surface area. The photocatalytic efficiency of TiO₂ is limited due to the high recombination rate of photo-generated electron–hole pairs. To resolve this issue and enhance the photocatalytic activity, methods like deposition of noble metals and their oxide particles, sensitization by means of dyes, and chemical modification have been proposed [3–11]. Noble metals like Pt, Au, and Pd have been reported to be very effective in enhancing the photocatalytic efficiency, when loaded on TiO₂ [12]. Since the Fermi levels of the noble metals are lower than the TiO₂ conduction band, when loaded on to TiO₂, the photo excited TiO₂ electrons migrate toward the noble metal Fermi levels leaving the holes in the valence band [13], thereby reducing the electron–hole recombination rate and hence enhancing the photocatalytic efficiency. As the number of electrons on the noble metal particles increases, the Fermi level shifts toward TiO₂ conduction band generating more energy levels for electron transfer. The Fermi level of the TiO₂-noble metal composite photocatalyst should be more negative than the H₂ evolution level ($E_{\text{H}_2/\text{H}_2\text{O}}$) [14,15] to enable effective transfer of the accumulated electrons to the protons adsorbed on the noble metal-TiO₂ interfaces and noble metal surfaces. Among the noble metals, Pt has found to be more effective and they act as catalyst for the hydrogen evolution, by reducing the activation energy of water reduction [16]. Various techniques such as evaporation, irradiation, thermal decomposition and chemical reduction have been adopted for Pt loading [17–20]. Chemical reduction technique has several advantages over other techniques in terms of high yield, narrow size distribution etc [21–24].

In the present study, anatase phase TiO₂ nanotubes, of particle size comparable to the de-Broglie wavelength of the charge carriers in TiO₂, were fabricated by rapid breakdown anodization technique and loaded with different amounts of Pt via chemical reduction using NaBH₄. The samples

were then characterized using FESEM, TEM and XRD. The chemisorbed surface areas of the as prepared as well as Pt loaded TiO₂ were analyzed using temperature programmed desorption reduction oxidation (TPDRO) equipment. The H₂ generation rates from Pt/TiO₂ suspension in ethanol–water mixture upon ultra violet (UV) light irradiation were investigated. The photoluminescence property of the Pt loaded samples were studied and correlated with the photocatalytic H₂ generation efficiency. The details of the experimental set-up used for H₂ estimation, optimization of Pt catalyst loading and the results obtained are also briefly discussed.

2. Experimental

2.1. Materials

Analytical grade Ti metal of 0.5 mm thickness (Alfa Aesar), Pt electrode (Arora Mathey) of 1 cm × 1 cm area, perchloric acid (HClO₄), chloroplatinic acid (H₂PtCl₆ × H₂O), sodium borohydride (NaBH₄), ethanol, acetone and isopropyl alcohol, of Alfa Aesar make, were used without further purification. All solutions were prepared using high purity DI water.

2.2. Preparation of platinum supported titania nanotubes

2.2.1. Synthesis of TiO₂ nanotube powders

Anatase TiO₂ nanotube powders were synthesized by, previously reported, potentiostatic rapid breakdown anodization technique [25–27]. The Ti foil anode and Pt foil cathode were clipped by means of crocodile clips and dipped into the electrolyte solution (0.1 M perchloric acid), maintaining 15 mm distance between the electrodes. A constant potential of 10 V was applied between the electrodes using a programmable DC power supply (Agilent N6700series). The variation in current as a function of time, during the anodization process, was measured using a digital multimeter (Agilent 34401A) interfaced to a computer. The anodization process was continued till the foil transformed completely into TiO₂ powder. The white powder obtained was washed several times with DI water, centrifuged and kept in a Petri dish overnight for drying.

2.2.2. Deposition of platinum on TiO₂ nanotubes

The Pt/TiO₂ photocatalyst was prepared by adding excess of NaBH₄ to a colloidal suspension of 0.20 g TiO₂ nanotube powder in about 80 ml of aqueous solutions of H₂PtCl₆ of varying concentrations (0, 25, 50, 75, 100, 150 and 200 ppm of Pt), under stirring. After the chemical reduction, the Pt loaded suspension was centrifuged and washed repeatedly with distilled water and ethanol followed by drying at 50 °C for 6 h. The wt% of Pt deposited on TiO₂ was estimated assuming complete reduction of H₂PtCl₆. The as prepared photocatalyst's color varied from white to black with increase in Pt loading. The pH of the H₂PtCl₆ solution, TiO₂ dispersed H₂PtCl₆ solution and solution after NaBH₄ reduction was monitored using a pH meter. The Pt concentrations in the H₂PtCl₆ solution before and after NaBH₄ reduction were measured using Inductively Coupled Plasma Optical Emission Spectrometer (ICPOES).

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