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Sono-photocatalytic production of hydrogen by interface modified metal oxide insulators

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ABSTRACT

Dielectric oxide materials are well-known insulators that have many applications in catalysis as well as in device manufacturing industries. However, these dielectric materials cannot be employed directly in photochemical reactions that are initiated by the absorption of UV–Vis photons. Despite their insensitivity to solar energy, dielectric materials can be made sono-photoactive even for low energy IR photons by modifications of the interfacial properties of dielectric materials by noble metals and metal oxides. In this investigation, by way of interface modification of dielectric MgO nanoparticles by Ag metal and Ag₂O nanoparticles, IR photon initiated sono-photocatalytic activity of MgO is reported. The observed photocatalytic activity is found to be the synergic action of both IR light and sonication effect and sonication assisted a multi-step, sub-bandgap excitation of electrons in the MgO is proposed for the observed catalytic activity of Ag/Ag₂O coated MgO nanoparticles. Our investigation reveals that other dielectric materials such as silver coated SiO₂ and Al₂O₃ also exhibit IR active sono-photocatalytic activity.

1. Introduction

Photocatalytic systems consist of semiconductor particles (photocatalysts) which are in close contact with a liquid or gaseous reaction medium in which the catalytic activity is initiated by using energy from light. When the semiconductor photocatalyst is exposed to light with an appropriate energy, an electron-hole pair is generated by excitation of an electron from the valence band (VB) to the conduction band (CB) [1]. After initial charge separation, the electron in the CB band and the hole in the VB participate in the reduction and oxidation reactions respectively at the semiconductor interface. Important applications of photocatalysis are diverse from environmental remediation [2] (in the treatment of water and air) to alternative fuel [3–5] (photocatalytic hydrogen generation) and hence, photocatalysis reactions have been widely investigated. In photocatalytic reactions, high bandgap semiconductors such as TiO₂, ZnO, SrTiO₃, etc are the commonly used light-harvesting materials due to their appropriate band energy positions for oxidation as well as reduction reactions [6,7].

Among the dielectric oxide materials, SiO₂, ZrO₂, Al₂O₃, and MgO are the most representative materials that have been employed in important technological applications due to their wide band gaps

(6.0–8.0 eV) and thermal stabilities (melting points ~ 2000–2800 °C). However, due to the large bandgap energy, that requires high energy photons (< 5 eV) for electron excitation from the VB to the CB, reactive charge carriers are not generated under direct bandgap excitation with the UV–Vis light [8]. Consequently, no interest has been paid on the use of high bandgap oxides as photocatalysts and only a handful of research articles have been published. In a short recent report, H₂ formation has been noted on SiO₂ and Al₂O₃ nanoparticles under UV irradiation in CH₃OH:H₂O solution and the observed photocatalytic activity has not been attributed to either conventional photocatalysis or a photochemical process [9,10]. Similarly, photocatalytic activities have been reported on MgB₂ under IR and visible light irradiations [10].

Nevertheless, these dielectric materials are one of the most significant and important metal oxides for theoretical and experimental studies due to their unusual stability to photocorrosion. Their optical properties of crystals can be essentially modified by the presence of impurity ions and radiation-induced defects [11]. Due to the presence of extrinsic and intrinsic defects, including those related to surface states in wide bandgap oxides, red-shifted absorptions relative to the fundamental absorption threshold of wide band gap oxides have been noted [12]. This leads to a way of developing wide bandgap solids as

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potential competitors for the semiconductor photocatalysts by energy upconversion despite these metal oxides are not active photocatalysts. It is known that ultrasound waves initiate chemical reactions through the acoustic cavitations and the simultaneous use of light and ultrasound irradiation can accelerate the reaction by the synergistic effect of acoustic and solar energy. Hence, sono-photocatalysis is a promising method for the production of hydrogen and degradation of organic and inorganic pollutants present in water [13–16]. Hence, in this investigation, MgO as a model dielectric material, the sono-photocatalytic activity of these high dielectric materials with low-energy IR radiation was demonstrated by modification of interface properties of metal oxide insulators. MgO was selected as a model dielectric compound owing to its simple lattice structure which can be a host for a number of transition metal ions. Properties of MgO nanoparticles were modified by control deposition of Ag and Ag₂O on MgO particles and their sono-photocatalytic activity for hydrogen production with water:methanol mixture by IR radiation was reported.

2. Experimental

Silver oxide coated MgO nanoparticles were prepared by the wet chemical method reported previously [17] and the silver coated MgO catalyst is denoted as Ag(AgO)/MgO hereafter. For the preparation of Ag(AgO)/MgO catalyst, 500 mg of MgO (Sigma-Aldrich, 99% AR) was suspended in 15 ml of dist. H₂O by sonication. For the well dispersed MgO solution, 15 ml of 0.04 M AgNO₃ (BDH, 99%, AR) in water was added with vigorous stirring and stirring was continued for 30 min for better mixing of AgNO₃ with MgO suspension. Then a stoichiometric amount of ammonia solution (BDH, 33%, AR) was added dropwise to the solution for the full conversion of AgNO₃ to Ag₂O. The resulting mixture was heated at 150 °C until the resulting powder gets completely dry. The solution mixture was stirred thoroughly throughout the synthesis to avoid the formation of larger particles. Since the decomposition of Ag₂O to Ag occurs at a temperature over 200 °C, the resultant powder was sintered at 200 °C for 30 min. The prepared Ag (AgO)/MgO catalyst was characterized by X-ray diffraction analysis (XRD), X-ray photoelectron Spectroscopic analysis (XPS), Scanning electron microscopic analysis (SEM), High-resolution transmission electron microscopy (HRTEM), Diffuse reflectance spectroscopy (DRIFT). Chemical composition, the crystal structure of the catalyst were studied by using powder X-ray diffractometer with the PANalytical X'Pert diffractometer (X'Pert PRO MPD, PW3040/60) with Cu-K α ($\lambda = 0.154060$ nm) radiation (40 kV, 40 mA). X-ray diffractograms were obtained before and after the activation of the catalyst. The composition and oxidation states of Ag(AgO)/MgO photocatalyst composite were analyzed by X-ray photoelectron spectroscopy thermo ESCALAB 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific Inc.) equipped with an Al K radiation source. The surface morphology of the Ag(AgO)/MgO catalyst was examined by HITACHI SU6600 Variable pressure FE-SEM. Energy dispersive X-ray analysis of Ag₂O/MgO sample was recorded by energy dispersive x-ray diffraction analysis associated with the HITACHI SU6600 FE-SEM scanning electron microscope to find the elemental distribution of the catalyst. The size and morphology of silver nanoparticles were characterized by Transmission electron microscopy (TEM) on a JEM-2100 microscope. The diffuse reflectance spectrum of finely grounded Ag₂O/MgO, photocatalyst was recorded using Shimadzu UV-2450 UV-VIS spectrophotometer in reflectance mode. Diffuse reflectance spectra of MgO and Al₂O₃ was recorded along with Ag₂O for comparison purposes. BaSO₄ was used for the filling of the sample at the reflectance apparatus. Luminescence properties of solid Ag(AgO)/MgO catalyst powder was done using a Shimadzu RF 5000 recording spectrofluorophotometer instruments.

For photocatalytic reaction, finely ground 12.5 mg of Ag(AgO)/MgO catalyst was dispersed in 20 ml of 10% methanol in 25 ml borosilicate flask and tightly sealed with a gas septum. Prior to irradiation, the flask

with catalyst was sonicated for 5 min in a dark room. Then the flask was irradiated with six IR emitting diodes (890 nm) and the experiments were conducted in a dark room to avoid UV and visible light. The sono-photochemical experimental set-up is shown in Fig. S1. The ultrasonic irradiation of the aqueous samples was performed in a 1000 ml stainless steel sonicator bath (15 cm L \times 10 cm W \times 20 cm H) (VWR) at a frequency of 34 kHz with the applied power of 200 ± 3 W at a constant temperature of 30 ± 1 °C. The system was sonicated continuously during irradiation. The gaseous products were quantitatively analyzed using a Shimadzu gas Chromatograph GC-9AM with TCD detector with a packed charcoal column using Ar as the carrier gas. Control experiments were carried out with the IR source in the absence of the catalyst and without IR source in the presence of catalysts. The spectrum and circuit diagram of the IR lamp source used for the irradiation are shown in Fig. S2.

3. Results and discussion

3.1. Characterization of catalyst

The Ag/Ag₂O coated MgO photocatalyst was prepared by controlled deposition of adsorbed Ag⁺ cation on MgO particles surface by the addition of ammonia solution [17]. The catalyst consists of 24% (w/w) of silver (Ag₂O or Ag) and 76% (w/w) of MgO. The formation reactions of Ag/Ag₂O on MgO particle interface is given in the Supporting Information (SI) in detail and the X-ray diffraction patterns of Ag (Ag₂O)/MgO catalyst is shown in Fig. 1. The major diffraction peak at 38.3° can be attributed to both hexagonal Ag₂O (2 0 0) and Ag (1 1 1). [18] The peaks at 53.1°, 65.2° and 70.3° can be attributed to the (2 2 0), (3 1 1) and (2 2 2) plans of cubic Ag₂O respectively (JCPDS No. 72-2108). The peaks located at 64.2° and 77.29° could be attributed to the (2 2 0) and (3 1 1) planes of metallic Ag (JCPDS No. 07-0783) [19]. The characteristic diffraction patterns corresponding to MgO crystalline were observed at $2\theta = 41.25^\circ$ (2 0 0), 62.1° (2 2 0) and 72.6° (3 1 1) [20,21]. Additionally, the presence of diffraction peaks corresponding to amorphous Mg(OH)₂ indicates that some MgO particles contain less crystalline amorphous Mg(OH)₂ particles. Furthermore, as shown in Fig. 1, the similar diffractograms of the Ag(Ag₂O)/MgO catalyst before (Fig. 1a) and after (Fig. 1b) IR irradiation inferred that there is no significant changes occur in the composite structure upon IR irradiation. Also, extra diffraction peaks corresponding to any alloy formation between Ag and Mg were not observed confirming that the catalyst contains only Ag, Ag₂O, and MgO(Mg(OH)₂). Hence, the X-ray

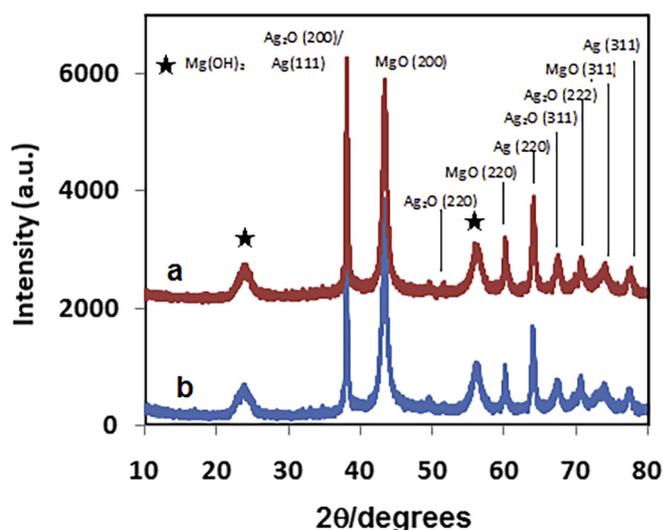


Fig. 1. XRD patterns of Ag(Ag₂O)/MgO (a) before irradiation and (b) after irradiation.

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