Article

Upcycling of Wastewater via Effective Photocatalytic Hydrogen Production Using MnO₂ Nanoparticles—Decorated Activated Carbon Nanoflakes

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Abstract: In the present work, we demonstrated the upcycling technique of effective wastewater treatment via photocatalytic hydrogen production by using the nanocomposites of manganese oxide-decorated activated carbon (MnO₂-AC). The nanocomposites were sonochemically synthesized in pure water by utilizing MnO₂ nanoparticles and AC nanoflakes that had been prepared through green routes using the extracts of Brassica oleracea and Azadirachta indica, respectively. MnO₂-AC nanocomposites were confirmed to exist in the form of nanopebbles with a high specific surface area of ~109 m²/g. When using the MnO₂-AC nanocomposites as a photocatalyst for the wastewater treatment, they exhibited highly efficient hydrogen production activity. Namely, the high hydrogen production rate (395 mL/h) was achieved when splitting the synthetic sulphide effluent (S²⁻ = 0.2 M) via the photocatalytic reaction by using MnO₂-AC. The results stand for the excellent energy-conversion capability of the MnO₂-AC nanocomposites, particularly, for photocatalytic splitting of hydrogen from sulphide wastewater.

Keywords: manganese oxide; activated carbon; nanocomposite; photocatalyst; green synthesis; hydrogen production

1. Introduction

Upcycling of wastewater via effective solar-assisted photocatalytic hydrogen production is vital for future green energy technology because this technique would become readily available as an ecofriendly and inexpensive method for treating industrial wastewater as well as developing alternative energy sources. Among various attractive methods for water splitting (i.e., hydrogen production), photocatalysis is one of the emerging techniques for the development of energy conversion technology [1–3]. For photocatalytic hydrogen production, developing a novel semiconductive material is essential to enhance the charge separation because the large number of photo-generated charge carriers may promote the photocatalysis reaction [4]. In general, semiconductor materials exhibit the increased
potential energy from the photocatalytic reaction because of their flexible constitution and diversity of properties [5]. Even though a variety of inorganic semiconductors showed a potential hydrogen production ability through photocatalytic reactions, there has been a serious drawback in water-splitting due to its absorption of visible light and bandgap variations [6]. As an alternative, transition metal oxides have become a prominent candidate for photocatalytic hydrogen production because of their modulated interface, tunable bandgap, high specific surface area, and good electron transport [7,8]. Among various metal oxides, MnO$_2$ acts as a diverse material in technical and fundamental aspects. For example, MnO$_2$ exhibited various feasibilities in wide application areas; e.g., catalysis, molecular adsorption, sensors, energy storage electrodes, etc. [9–13]. In addition, MnO$_2$ can also be available for environmental technology such as dye degradation [14,15], wastewater treatment [16,17], photocatalytic degradation of organic pollutants [18–23], and photo-electrochemical hydrogen production [24,25].

To move a step closer to feasible applications, recently, intensive research was conducted to synthesize high-quality MnO$_2$ [26,27]. However, most of the well-known synthesis techniques are based on chemical approaches, which generally require toxic and/or hazardous precursors [28]. To release this, many researchers have been devoted to developing a green synthesis method, particularly, using biomass natural resources (e.g., plant and fruit extracts) as chemical reagents [29,30]. For instance, the ecofriendly-synthesized MnO$_2$ nanoparticles showed similar structural and morphological properties to the chemically synthesized ones [31,32]. Furthermore, those MnO$_2$ nanoparticles could be utilized in catalysis because of their excellent physicochemical properties [33].

Meanwhile, adding activated carbon (AC) into catalysts is also of great interest for improving the photocatalytic reaction. In other words, since low-cost AC has several advantages (e.g., high porosity, specific surface area, and excellent adsorption), catalytic performances could be improved during photocatalytic hydrogen production [34]. Additionally, many earlier studies reported that biomass AC could improve the catalytic ability for reformation of carbon dioxide [35] and enhance the energy-storage performances [36–39]. Despite such vast benefits, to our best awareness, no studies on the MnO$_2$-AC nanocomposite-based wastewater treatment have been conducted yet. We, therefore, investigated the formation of high-performance MnO$_2$-AC photocatalysts via ecofriendly routes for efficient hydrogen production.

Herein, we report experimental data on the effective photocatalytic hydrogen production from wastewater using a novel nanocomposite of the MnO$_2$-AC photocatalyst that had been prepared by green approaches. The MnO$_2$-AC nanocomposites were fabricated through a simple sonication process in pure water by using MnO$_2$ nanoparticles and AC nanoflakes that were synthesized using Brassica oleracea (cabbage) and Azadirachta indica (neem leaf) extracts, respectively. We observed the high photocatalytic activity of the MnO$_2$-AC nanocomposites, resulting from the increase in photo-generated electron and hole carriers in the composite system. In this article, the material preparation and the improved hydrogen production characteristics of the MnO$_2$-AC nanocomposites are discussed in detail.

2. Experimental Details

2.1. Synthesis of MnO$_2$ Nanoparticles

Figure 1 schematically illustrates the experimental procedure for the synthesis of the MnO$_2$-AC nanocomposites. To synthesize the composite structure of MnO$_2$-AC, as a primary task, we prepared the MnO$_2$ nanoparticles by reducing potassium permanganate (KMnO$_4$: 99.7%, Sigma-Aldrich, St Louis, MO, USA) using the reduction agent of Brassica oleracea, which had been extracted from cabbage (Perambalur, Tamil Nadu, India). Firstly, 0.1 M of KMnO$_4$ (30 mL) was mixed with 50 mL of Brassica oleracea in dropwise, and the mixture solution was left for 15 min. Thereafter, the brownish colloidal suspension was stirred at 600 rpm for 1 h by using a home-built magnetic stirrer. During this step, molecular constituents (e.g., anthocyanins and cyanides) of Brassica oleracea act as effective reduction agents [40,41] to reduce KMnO$_4$ into the form of nanocrystalline MnO$_2$. The obtained product was then washed by deionized (DI) water and an ethanol–water mixture to remove both template extracts.
and unreacted chemicals. After further washing, filtering, drying, and grinding, the powder type of MnO₂ nanoparticles were obtained.

![Diagram showing the process of deriving biomass AC](image)

**Figure 1.** Schematic illustration for the fabrication of MnO₂ nanoparticles, AC nanoflakes, and MnO₂-AC nanocomposites.

### 2.2. Derivation of Biomass AC

Next, we derived the biomass AC powders by using *Azadirachta indica* (neem leaves) that had been collected from Perambalur, Tamil Nadu, India. Firstly, the neem leaves were washed and dried several times to get clean *Azadirachta indica*. Then, the dried leaves were carbonized at 500 °C for 2 h. Subsequently, the carbonized ashes were purified through the hydrolysis treatment using DI water to increase the uniformity of the AC nanoflakes [37,38]. After drying the water-treated ashes at 120 °C for 10 h, filtering and grinding processes were performed to obtain the uniform AC nanopowders.

### 2.3. Synthesis of MnO₂-AC Nanocomposites

Using the above materials, we synthesized the MnO₂-AC nanocomposites. Firstly, MnO₂ nanoparticles and AC nanoflakes were mixed in DI water with the ratio of 1:1. Next, to form the MnO₂-AC nanocomposites, the mixture solution was then sonicated by using the UD-211 ultrasonic disruptor (Tomy Digital Biology Co., Tokyo, Japan) under ultrasonic power of 100 W for 1 h at 20 kHz. After sonication, the solution was dried at 120 °C for 12 h to get the powder type of the MnO₂-AC nanocomposites. Finally, the powders were grinded and filtered to obtain free-flow fine MnO₂-AC nanoparticles.

### 2.4. Characterization of Material Properties

The crystallographic properties of the MnO₂ nanoparticles and the MnO₂-AC nanocomposites were investigated by X-ray diffraction (XRD) using a Rigaku Miniflex 300 system (Rigaku, Tokyo, Japan). The functional groups of MnO₂ and MnO₂-AC were recognized by Fourier transform infrared (FTIR) spectroscopy using a Spectrum-100 system (Perkin Elmer, Shelton, CT, USA). The surface area and the pore characteristics were analyzed through Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods by using a Belsorp-mini II equipment (MicrotracBEL, Osaka, Japan). The topographical and the compositional properties were examined by field-emission scanning electron microscopy (FE-SEM) and in-situ energy dispersive X-ray (EDX) spectroscopy.
using a SIGMA-VP system (Zeiss, Jena, Germany). The optical properties were evaluated by UV-VIS spectroscopy using an S-3100 system (Scinco, Seoul, Republic of Korea).

2.5. Measurement of Photocatalytic Performances

The photocatalytic performances of MnO₂ and MnO₂-AC were characterized via direct solar irradiation at Chennai, India. The optical power of the incident sunlight was measured by using a LX-101A lux meter (HTC Instruments, Mumbai, India) at the beginning and end of each experiment. All the experiments were conducted for 1 h during 12 pm to 2 pm to avail the maximum solar irradiation. The average solar irradiance was found to be 725 W/m². For photocatalytic hydrogen production, firstly, the prepared photocatalyst was dispersed in a photolytic solution, containing synthetic sulphide wastewater (1 L). The effects of the sulphide ion (0.05–0.30 M), sulphite ion (0.05–0.30 M), and photocatalyst concentrations (0.1 to 0.3 g/L) on the maximum hydrogen production were examined. The photocatalytic hydrogen production was undertaken in a trapezoidal photo-reactor (5 L), and the amount of hydrogen production was measured by using an inverted measuring cylinder (Figure S1). The photocatalyst is kept under suspension with the help of the recirculation mode by using a peristaltic pump.

3. Results and Discussion

3.1. Topographical and Compositional Properties

The topographical and the compositional properties of the synthesized materials were investigated by FE-SEM and in-situ EDX, respectively. In the case of bare MnO₂, a bundle of spherical nanoparticles was aggregated with the shape of the nanogravel field (Figure 2a,b). Similarly, the MnO₂-AC nanocomposites exhibited an agglomerated topography, where the tiny MnO₂ nanoparticles were decorated onto the AC nanoflakes (Figure 2c,d). From the EDX spectra (Figure 2e,f), one can confirm that both the MnO₂ nanoparticles and the MnO₂-AC nanocomposites contain their main species of Mn, O, and C. Small amounts of Pt and K came from conductive coating for SEM measurements and residual K ions intercalated at MnO₂ surfaces, respectively. Although the K ions may somewhat affect the hydrogen production efficiency [42,43], we believe that the effect of residual K ions would be negligible because the small amount of K ions were detected only in EDX spectrum but not in other material characterizations, as can be seen from Figures 3–5.

![Figure 2](image-url)

**Figure 2.** (a) Low- and (b) high-magnification FE-SEM images of MnO₂ nanoparticles. (c) Low- and (d) high-magnification FE-SEM images of MnO₂-AC nanocomposites. EDX spectra of (e) MnO₂ nanoparticles and (f) MnO₂-AC nanocomposites.
3.2. Crystallographic Properties

Figure 3a displays the XRD patterns of MnO₂ and MnO₂-AC. The MnO₂ nanoparticles exhibited the diffraction patterns at 18.5, 29.5, 33.0, 36.0, 39.5, 44.2, 47.5, 48.6, 57.3, 60.7, and 64.6°, corresponding to (200), (310), (400), (211), (420), (301), (510), (411), (600), (521), and (002) lattice phases of tetragonal α-MnO₂ (JCPDS no. 44-0141), respectively [28,39,44]. In the composite of MnO₂-AC, two additional peaks from C (002) and C (100) phases were observed at 23.2 and 43.2° because of the agglomeration of AC and α-MnO₂ [36–38,45,46]. Using Scherer’s law [47–49], the average crystalline size of the MnO₂ and MnO₂-AC were calculated to be approximately 32 nm and 28 nm, respectively.

![Figure 3](image)

**Figure 3.** (a) XRD patterns and (b) FTIR spectra of MnO₂ nanoparticles and MnO₂-AC nanocomposites.

The chemical bonding states of the samples were further elucidated through the FTIR measurements. The MnO₂ nanoparticles revealed their major IR absorption bands (Figure 3b). The absorption band at 3419 cm⁻¹ originates from –OH stretching [50], the vibrational modes at 1643, 1565, and 1419 cm⁻¹ arise from –OH bending [51,52], and the IR absorbance at 1121 cm⁻¹ comes from the Mn–OH vibration. In addition, MnO₂ showed to involve some vibration modes at 503, 616, 710, and 868 cm⁻¹, arising from Mn–O–Mn stretching in α-MnO₂ [28,44,51]. In the MnO₂-AC composites, those Mn–O–Mn stretching modes became significant because the adsorbed C atoms might increase the ionic interaction at the MnO₂ surface [53,54]. These verify that MnO₂-AC was well-aggregated with the stable conformation of the composite system.

3.3. Textural Characteristics

Figure 4a displays the N₂ adsorption–desorption isotherm curves of the MnO₂ nanoparticles and the MnO₂-AC nanocomposites. All three samples reveal the Type-IV isotherm characteristics with the distinctive Type-H3 hysteresis curves (classified by IUPAC). These are indicative of the mesoporous feature in the solid-state material system [38,39,55,56]. Through the BET analysis, the specific surface area \( (A_{ss}) \) was determined to be 64, 822, and 109 m²/g for MnO₂, AC (see also Figure S2a), and MnO₂-AC, respectively. Figure 4b shows the pore characteristics of MnO₂ and MnO₂-AC. Both samples clearly revealed their pore sizes in a nanometer scale; i.e., the average pore sizes of MnO₂ and MnO₂-AC were estimated to be approximately 8.78 and 7.66 nm, respectively. Through the BJH analysis, additionally, we confirmed that the MnO₂-AC nanocomposites have a larger total pore volume (i.e., 0.0204 cm³/g) than that of the MnO₂ nanoparticles (i.e., 0.0141 cm³/g). In addition, the average pore size and total pore volume of the AC (Figure S2b) are 2.8 nm and 0.0459 cm³/g, respectively. The larger pore volume of MnO₂-AC is thought as resulting from anchoring of mesoporous MnO₂ nanoparticles with mesoporous AC nanoflakes, and is beneficial for enhancing the photocatalytic hydrogen production, as discussed in detail later.
1.90 eV, respectively, as represented in Figure 5b. From Tauc’s plots, additionally, the optical bandgap within a photon energy spectrum of the natural sunlight, we assessed their photocatalytic hydrogen production. The photon energy values for those absorption bands can be confirmed to be approximately 2.34 and 2.42 eV, respectively, as represented in Figure 5b. From Tauc’s plots, additionally, the optical bandgap ($E_g$) was extrapolated to be approximately 2.42 and 2.41 eV for MnO$_2$ and MnO$_2$-AC, respectively, and those are consistent with the literature value [64].

3.4. Optical Properties

The optical properties of the MnO$_2$ nanoparticles and the MnO$_2$-AC nanocomposites were characterized by means of the Schuster–Kubelka–Munk (SKM) model [57,58] through UV–VIS absorption measurements. Both samples showed the optical absorption bands at the visible wavelength regions (Figure 5a). Namely, the d–d transitions of Mn ions were observed at around 500–550 nm and 620–680 nm. The former is ascribed to the intra-band transition from Mn$^{2+}$ core shells via $^{4}T_1 \rightarrow ^{6}A_1$ [59–61], and the latter is attributed to emission from the Mn dimers (i.e., Mn$^{2+}$-Mn$^{2+}$) [62,63]. The photon energy values for those absorption bands can be confirmed to be approximately 2.34 and 1.90 eV, respectively, as represented in Figure 5b. From Tauc’s plots, additionally, the optical bandgap ($E_g$) was extrapolated to be approximately 2.42 and 2.41 eV for MnO$_2$ and MnO$_2$-AC, respectively, and those are consistent with the literature value [64].

3.5. Photocatalytic Hydrogen Production Efficiencies

Since the bandgap and the absorption energy values of both mesoporous MnO$_2$ and MnO$_2$-AC are within a photon energy spectrum of the natural sunlight, we assessed their photocatalytic hydrogen production efficiencies using sulphide-based wastewater under sunlight illumination. Here, it should be noted that we varied the sulphide and the sulphite ion concentrations from 0.05 to 0.30 M to examine the effects of sulphur concentrations on photocatalytic hydrogen production. Firstly, we explain the photocatalytic hydrogen-production activity of the MnO$_2$-AC nanocomposites for the sulphide...
ion-added wastewater treatment. To make a similar condition to industrial sulphide wastewater, we prepared synthetic sulphide wastewater by mixing sodium sulphide salt into DI water. In addition, 0.1 M sulphite ion was also added as a sacrificial agent to avoid the photo corrosion of the photocatalyst. Figure 6a shows the H₂ production activity of MnO₂-AC (0.1 g/L) as a function of the sulphite ion concentration. As the sulphite ion concentration increased from 0.05 to 0.2 M, the H₂ production rate increased gradually. When the sulphite ion concentration exceeded 0.2 M, however, the hydrogen production rate decreased unexpectedly. Such a sudden decrease of hydrogen production at the higher ion concentration can be explained by photocatalytic corrosion on the catalyst surface, which degrades the hydrogen production efficiency [65,66]. When using sulphite ion-involved wastewater, we observed a similar feature of hydrogen production activities (Figure 6b). Namely, the H₂ production rate increased with increasing sulphite ion concentration up to 0.25 M, whereas that suddenly decreased at the high sulphite ion concentration of 0.30 M due to blocking of active sites by the penetrated sulphite ions [67,68].

![Figure 6](image.png)

**Figure 6.** Hydrogen production rates of MnO₂-AC nanocomposites as functions of (a) sulphite ion concentration (best value 0.2 M), (b) sulphite ion concentration (best value 0.25 M), (c) catalyst dose (best value 0.25 g/L), and (d) cycle number of photocatalytic reaction.

Based upon the above results, we chose the optimal concentrations for sulphide (best value 0.25 M), and sulphite ions (best value 0.2 M), and mixed to those solutions. Then, the effect of the catalyst dosage on the hydrogen production was examined (Figure 6c). As the catalyst dose increased up to 0.25 g/L, the H₂ production rate increased because of the increased number of active sites. For a higher dose of 0.30 g/L, the hydrogen production rate began to decrease because the high density of MnO₂ nanocomposites may give rise to viscosity of the solution, and it will retard the photon collection at the photocatalyst surface and will degrade the oxidation-reduction reaction for H₂ production [67–69]. Next, we tested the reusability of MnO₂-AC as a photocatalytic H₂ production agent for the sulphuric wastewater treatment. For this test, we chose the best values of experimental parameters obtained from the previous experiments (i.e., photocatalyst dose = 0.25 g/L, sulphide ion concentration = 0.2 M,
sulphite ion concentration 0.25 M). In addition, we note that, after every cycle, the MnO2-AC catalyst was washed for each measurement. For this step, the plain solution was separated, and the recovered photocatalyst was washed in DI water several times and reused for the next cycle. As shown in Figure 6d, the rate of hydrogen production gradually decreased as the cycle number increased. This can be interpreted by the catalyst loss of the trace quantity during every recycle [65,70] because the 30% weight loss of MnO2-AC was observed at the end of the fifth recycle.

Through mimicking the above experiments for MnO2, we obtained the maximum H2 production of 190 mL/h (Figure 7a). Therefore, we can conclude that the hydrogen production efficiency is much better for the MnO2-AC nanocomposites (395 mL/h) than the bare MnO2 nanoparticles, which is higher than the previous reports (Table S1). To help understand the superior H2 production activity in MnO2-AC, we explain the mechanism of photocatalytic hydrogen production using MnO2-AC. The valence and the conduction band edges can be found by using the following equations:

\[ E_{VB} = X - E_e + 0.5E_g \]
\[ E_{CB} = E_{VB} - E_g \]

where \( E_{VB} \) and \( E_{CB} \) are the potential energy values of the valence band and the conduction band, respectively. \( X \) is the electronegativity of the semiconducting material, and \( E_e \) is the free electron energy on the hydrogen scale (4.5 eV), and \( E_g \) is the bandgap energy of the material. In this study, we observed MnO2-AC to possess \( E_g \) of 2.41 eV (Figure 5b); hence, \( E_{VB} \) and \( E_{CB} \) can be 0.4 and \(-2\) eV, respectively. Based on these values, one can illustrate the energy band diagram of the MnO2-AC composite system (Figure 7b). When irradiating sunlight onto the MnO2-AC nanocomposites, the electrons will jump from the valence band to the conduction band. Such an electron excitation will also create the photo-generated holes in the valence band. These photo-generated electrons and holes may cause H2 production with their chemical reactions with sulphuric wastewater as follows:

\[ \text{MnO}_2/\text{AC} \xrightarrow{hv} \text{MnO}_2 - \text{AC} \left( e_{vb}^- + h_{vb}^+ \right) \]
\[ h_{vb}^+ + \text{HS}^- \rightarrow 2\text{H}^+ + S_2^{2-} \]
\[ 2e_{cb}^- + 2\text{H}^+ \rightarrow \text{H} + \text{H} \rightarrow \text{H}_2 \]

![Figure 7. (a) Comparison of photocatalytic hydrogen production rates between MnO2 nanoparticles and MnO2-AC nanocomposites. (b) Photocatalytic hydrogen production mechanism in MnO2-AC nanocomposites.](attachment:image.png)

Namely, the hole carriers may react with the hydrogen sulphide ions, and produce the hydrogen ions. Then, the hydrogen ions will be eventually reduced into hydrogen molecules by reaction with
photo-generated electrons. For this mechanism, H₂ production will be much enhanced when the material system has a larger surface area (i.e., abundant active sites for chemical reaction) and a higher carrier conductivity (i.e., fast promotion of chemical reaction). As a consequence, the MnO₂-AC nanocomposites with high porosity and high conductivity yield a higher H₂ production rate, particularly, compared to bare MnO₂.

4. Conclusions

The MnO₂-AC nanocomposites were prepared by using the biomass resources of Brassica oleracea and Azadirachta indica. The MnO₂-AC nanocomposites showed the aggregated structure of spherical α-MnO₂ nanoparticles-decorated AC nanoflakes. When using the MnO₂-AC nanocomposites as a photocatalytic agent for the sulphuric wastewater treatment, the enhanced hydrogen production rate of 395 mL/h was achieved. We attributed such an excellent H₂ production activity to high conductivity and high porosity of the MnO₂-AC composite system (i.e., fast promotion and abundant active sites for chemical reaction). The results suggest that the ecofriendly-synthesized MnO₂-AC nanocomposite system is useful for upcycling of wastewater via photocatalytic hydrogen production.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/10/8/1610/s1, Figure S1: Schematic illustration of photocatalytic trapezoidal reactor; Figure S2: (a) Nitrogen adsorption–desorption isotherm characteristics and (b) Pore distribution properties of activated carbon; Table S1: Comparison of hydrogen production activity of MnO₂ and MnO₂-AC with other oxide-based photocatalysts reported in previous studies.

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