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A Cu^{+1}/Cu^{0}-TiO_2 mesoporous nanocomposite exhibits improved H_2 production from H_2O under direct solar irradiation

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ABSTRACT

A photostable sunlight-responsive mesoporous Cu^{+1}/Cu^{0}–TiO_2 (Cu-mpTiO_2) photocatalyst has been fabricated for the H_2 production from water. Structural analysis revealed the anatase polymorph of TiO_2 with mesoporous characteristics and an average particle size of ~32 nm. Mesoporous TiO_2 was observed to possess high surface area (188 $m^2\ g^{-1}$) and pore size (0.32 nm). HRTEM studies suggested the deposition of Cu in Cu^{0} and Cu^{+1} oxidation states with three distinct lattice fringes of 0.21, 0.25, and 0.35 nm for Cu, Cu_2O, and TiO_2 respectively. Cu-mpTiO_2 produced 1000 μmol of H_2 (AQE = 11.39%) under sunlight irradiation, which is severalfold more than obtained with Cu impregnated on commercial Cu–TiO_2 (P25). The photostability of the Cu–mpTiO_2 increased after recycling because the excess Cu^{+1} (binding energy = 533.5 eV) is reduced to Cu^{0} (533.3 eV) and the excess holes in the valance band of Cu_2O oxidize Cu^{0} to Cu^{+1}.

1. Introduction

Titanium dioxide (TiO_2) is considered one of the promising candidates for photocatalytic water splitting after the discovery of the Honda Fujishima effect [1] during the early seventies. However, conventional TiO_2 (P25) has several limitations [2–4] such as low surface area, fast electron/hole recombination, an absorption in the UV region due to a large bandgap (E_g). Many effective structural and optical modifications have been adopted [5,6] to overcome these hindrances. Characteristically mesoporous TiO_2 [7,8] has recently emerged as the best alternative to be an effective material due to its excellent structural and electrical properties, high porosity, and large surface area, which results in effective charge transfer for promoting the quantum yield of several photocatalytic reactions such as photocatalytic water splitting [9,10]. Further efforts are being made to increase the solar-to-hydrogen conversion efficiency by manipulating its band energetic [11] and light absorption ability [12]. Still, hydrogen generation from water over bare mesoporous TiO_2 is very low due to its inability to respond to sunlight/visible light and fast charge carrier recombination. In this regard, noble metal (Au, Ag, and Pt) loading has proven to be very effective [13–15]. Alternatively, doping with transition metals such as Cu, Fe, Co, and Ni has recently turned out to be a cheaper option [16–18]. Several other reports have also revealed the effectiveness of Cu in photocatalytic activity over noble metals [19,20]. The complete mechanism is still less explored due to simultaneous formation of other active Cu species such as Cu_2O and CuO. Copper is supposed to be in elemental (Cu^{0}) or oxide forms (Cu^{+1} or Cu^{+2}). Some earlier reports [21–23] reveal that Cu_2O species are responsible for enhanced photocatalytic activity to generate hydrogen from water. A few reports [24,25] also suggest that CuO is responsible for separation of charge carriers (electrons and holes). Cu_2O (2.1–2.2 eV) [26] is also an important transition metal oxide (p-type) that has the capacity to work under sunlight irradiation, and it is expected to form a p-n junction with n-type TiO_2 to enhance the lifetime of charge carriers.

Ampelli [27] and co-workers studied the effect of impregnation of copper oxide on TiO_2 for enhancement in photocatalytic activity. Similarly, Korzhak et al. [28] reported the hydrogen production on Cu-doped TiO_2 nanocomposite and concluded that when Cu species are loaded onto TiO_2, the expected stabilization of Cu and Cu oxides against photocorrosion results in the enhancement of photocatalytic efficiency. Hence, synthesis of mesoporous TiO_2 and its modification by formation of heterocomposites and metal loading are done to eliminate the drawbacks of commercial TiO_2 (P25), such as low surface area, charge separation, and low quantum efficiency.

This study demonstrates the fabrication of recyclable Cu–-mesoporous TiO_2 nanocatalysts (Cu–mpTiO_2) for photocatalytic hydrogen evolution (PHE) from water. This design may increase the surface area of TiO_2 and impregnated Cu in variable

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oxidation states; especially, the sunlight-active Cu (I) state should help in sensitization of $mpTiO_2$. Cu in different oxidation states is supposed to act as both a sensitizer and a co-catalyst for TiO_2 and is also expected to maintain a balance of Cu^{+1} and Cu^0 due to reversible oxidation and reduction on Cu_2O by excess electrons and holes in the conduction band (CB) and valance band (VB), respectively. Furthermore, increasing the porosity characteristics of the nanocatalyst is also predicted to enhance the apparent quantum yield (AQE, %) of PHE from water photolysis.

2. Experimental

2.1. Chemicals and reagents

All the analytical grade chemicals were used as received: titanium butoxide ($Ti(OBu)_4$, 97%, Sigma–Aldrich), cupric acetate ($Cu(CH_3COO)_2$, 99% Loba Chemie Ltd.), methanol and ethanol (99%, SD Fine Ltd.), ethylene glycol (MW = 4000, Loba Chemie Ltd.), and acetone (99%, Sigma–Aldrich). During the whole experiment DI water was used, obtained from Milli-Q (Millipore), an ultrafiltration system (conductivity = 35 mho cm^{-1} at 25 °C).

2.2. Synthesis and characterization of photocatalysts

Mesoporous TiO_2 ($mpTiO_2$) was prepared by template synthesis, in which 2 mL of titanium butoxide ($Ti(OBu)_4$) was added to ethylene glycol (44.4 mL) and stirred for 8 h at room temperature. The mixture was poured into 200 mL of acetone containing 3 mL of DI H_2O and 0.8 mL of acetic acid and further stirred at 35 °C for 3 h, resulting in the formation of mesoporous titanium glycolate precipitate. This precipitate was stirred at 80–100 °C for 8 h to produce $mpTiO_2$, which was further washed with DI water and ethanol, dried at 100 °C, and further calcined at 250 °C for 5 h to get an effective surface area and pore structure.

Copper nanoparticles (Cu NPs) were synthesized separately by a gelatin–sugar based green synthesis method. Gelatin was dissolved in distilled H_2O (30 mg/10 mL) in a 50 mL flask and vigorously stirred until the formation of a clear solution. In another flask, 5 mL NaOH (0.5 M) was added dropwise to the $(CH_3COO)_2Cu$ solution (5 mL, 0.2 M). This solution was quickly poured into the gelatin solution until a deep blue color was formed. The reduction was carried out by 5 mL (1 M) glucose and the solution was sonicated until the formation of brown color, indicating the formation of Cu NPs. The as-prepared Cu NPs were washed under several cycles of centrifugation with DI water and ethanol.

The fabrication of Cu–$mpTiO_2$ nanocomposites was done by wet impregnation. The $mpTiO_2$ (100 mg) was suspended in DI water (10 mL) in a 50 mL beaker and sonicated for 10 min. The required amount (1–10 wt.%) of Cu NPs was added to this suspension and stirred at room temperature for 24 h. The nanocomposite (Cu–$mpTiO_2$) was separated by centrifugation and dried at room temperature for further analysis.

2.3. Characterization and photocatalytic activity

The optical properties of the photocatalysts were studied by UV–visible spectrometry (Analytic Jena, Specord 205, Germany) and Fourier transform infrared spectrometry (Carry 660, Agilent Technologies, California, USA). Structural and crystal properties were studied by X-ray diffraction (PANalytical Xpert Pro, Almelo, Netherlands, Cu Kα at 1.54 Å, 45 kV, and diffraction angle between 20° and 80°). Morphological characteristics were determined by high-resolution transmission electron microscopy (HRTEM, FEI Technai G2 F20 operating at 200 kV) and field emission scanning electron microscopy (FESEM, SU8180, Tokyo, Japan). Porosity and surface area of the photocatalyst were studied by a Brunauer–Emmett–Teller (BET, BEL mini-II, Micro Trac Corp. Pvt. Ltd, Tokyo, Japan)-based N_2 adsorption–desorption method at cryogenic temperature. Furthermore, the oxidation state of the photocatalyst before and after sunlight reaction was analyzed by X-ray photon spectroscopy (XPS, KRATOS Axis 165 Shimadzu, UK) with Mg Kα radiation (1252.6 eV at 75 W).

The photocatalytic activity of different photocatalysts was carried out in a Pyrex reaction tube (20 cm^3), placed horizontally to sunlight (Fig. ESI-1 in the Electronic Supporting Information) and containing 30 mg photocatalyst and 5 mL reaction mixture (4:1 water: methanol). Methanol was used both as sacrificial agent and hole scavenger. The reaction mixture was purged with argon for 10 min and irradiated under direct sunlight during the months of May 2016 (06–11 and 19–21 May) and August 2016 (27 August), with average solar radiation of ~637 W/m^2 and ~34.8 °C temperature. The H_2 produced during the reaction was analyzed by gas chromatography (GC, Nucon Ltd., India) with a thermal conductivity detector (TCD) and molecular sieve column (5X A, Lab India Ltd., Mumbai). The temperatures of the injector, detector, and column oven were set at 30 °C and the amount of H_2 produced during the reaction was quantified by comparing it with standard 180 PPM H_2 (Sigma Gasses Ltd., New Delhi, India). Moreover, the apparent quantum efficiency (AQE, %) of the photocatalyst × was calculated using the equation [29]

$$\mathrm{AQE}\ (\%) = \frac{n \times \Delta G}{W \times S \times T} \times 100,$$

where n denotes the moles of H_2 produced (moles/L), ΔG is total free energy change for the water splitting reaction (237 kJ/mol), W represents the sun radiation (W/m^2), S is the surface area of the reaction tube (m^2), and t is the time of the reaction (s). The recycling experiments were performed by separating the photocatalyst from the earlier reaction mixture washing it several times with DI water and drying it at room temperature before the next cycle.

3. Results and discussion

3.1. Optical and structural properties

Optical absorption analysis revealed (Fig. 1) that $mpTiO_2$ and Cu–$mpTiO_2$ photocatalysts exhibited absorption edges at ~418 nm and ~512 nm respectively. The red shift in Cu–$mpTiO_2$ along the formation of a new band around λ_{max} = 741 is ascribed

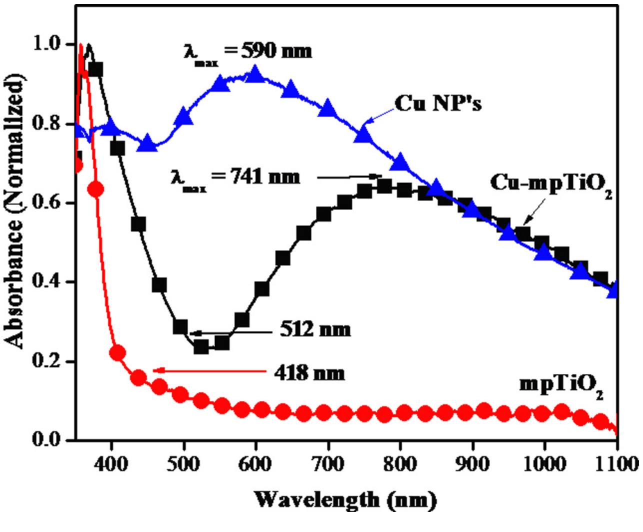

Fig. 1. Normalized optical absorption spectra of different photocatalysts.