Abstract

The hydrogen (H_2) is the most viable future energy carrier due to its high gravimetric energy density and non-polluting nature. The direct conversion of solar to green H_2 via photocatalytic water splitting has a great potential and the optofluidic microreactors (OFMRs) are highly useful in this regard. The OFMRs in photocatalysis enables the concurrent and fine control of fluid flow, photon harvesting, and reaction with the shorter transfer path lengths, which in turn improve the photocatalytic reaction performance. However, due to complex and expensive fabrication, these devices are not well established in practical applications. In this study, we describe a simple, rapid, and inexpensive method to fabricate microchannels with various geometries on the glass substrate and tested them for the production of green H_2 via photocatalytic water splitting after coating with a sustainable photocatalyst. The adhesive tape as mask resulted in deeper channels (up to 550 µm), and higher etch factor (1.2) as compared to those obtained with UV photolithography. The semi-circular shaped microchannel with sharp edges and without any wall irregularities was obtained with adhesive tape as mask and using 49% HF solution as chemical etchant at room temperature for 120 min.

The CdS photocatalyst was coated, using sol-gel method, on OFMRs with various geometries, such as serpentine, planner and micropillared, and tested them for H_2 production. The effect of OFMR geometry, liquid flow rate (0.05 – 1 mL min^{-1}) and sacrificial reagent (SR, Na_2SO_3/Na_2S) concentration (0.05 – 0.5 M) on the H_2 generation under visible light was studied. A higher H_2 production rate was observed with the serpentine OFMR as compared to that in planar and micropillared OFMRs. The serpentine OFMR, having higher surface-to-volume ratio, induced the micromixing that enhanced the mass transfer of the sacrificial reagent and resulted in higher H_2 formation. A maximum H_2 production rate of 2.65 µmol h^{-1} cm^{-2} was observed at a reactant flow rate of 1.0 mL min^{-1} and a sacrificial reagent (Na_2SO_3/Na_2S) concentration of 0.5 M. There is a necessity to enhance the mixing, which results in the mass transfer enhancement. The serpentine OFMR was used for the gas-liquid photocatalytic H_2 production. The effect of gas and liquid flow rates on the H_2 production rate in the presence of 0.1 M SR (Na_2SO_3/Na_2S) under the UV light (254 nm) irradiation was investigated. A higher H_2 production rate (0.298 µmol h^{-1}) was observed at the gas and liquid flow rates of 1 and 0.8 mL min^{-1}, respectively.

An effective corrugated serpentine OFMR (C-SOFMR) with advanced features, such as expansion/contraction and wavy microstructures, was fabricated using the adhesive tape based method as described before. A flow visualization study reveals a laminar flow with no back mixing in plain serpentine OFMR (P-SOFMR), and stretching and folding of fluid along with back mixing in C-SOFMR. Further, the CdS nanowires on g-C_3N_4 nanosheet (CN/CdS) heterojunction was synthesized *in situ* both P-SOFMR and C-SOFMR and utilized the device for the photocatalytic green H_2 generation. The CN/CdS heterojunction endowed with narrow band gap energy (2.01 eV). The longer CdS nanowires (~110 nm) benefit the electronic interface with CN in the CN/CdS heterojunction and lead to the spatial separation of excitons along the CdS axial direction. The charges generated were utilized efficiently for the HER reaction in both P-SOFMR and C-SOFMR at higher flow rates attributing to the rapid micro-mixing and mass transfer. The CN/CdS2 heterojunction showed the highest photocatalytic activity (6.38 µmol h^{-1} in C-SOFMR and 6.16 µmol h^{-1} in P-SOFMR at 1.0 mL min^{-1}) due to its good optronic properties.

The new approach developed in this study is a step forward in fabricating highly efficient, advanced and inexpensive optofluidic microdevices for the green hydrogen production directly from solar energy.