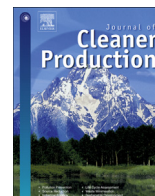




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Assessment of clean H₂ energy production from water using novel silicon photocatalyst

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ABSTRACT

Nanosheets of silicon have attracted a great deal of attention due to its tunable optical and electronic properties. However, the development of facile and easily scalable synthesis process has remained a great contest. Endeavor has been made in this research to find a waste inferred effective photocatalyst to deliver hydrogen (H₂) through visible light responsive water splitting.

One-pot solid phase reaction was applied to synthesis catalyst and adopted ultrathin structure. The photocatalytic efficiency of catalyst was examined by XRD, XPS, and UV–VIS absorption spectra, PL, FESEM, HRTEM and EDX. The HRTEM and FESEM images revealed the interconnected nanosheets with Si having the average thickness of 5 nm and their band gaps were 2.3–2.5 eV corresponding to the absorption of visible light range. The H₂ production rate on photocatalyst was originated to 3200 μmol h^{−1} without utilizing any conciliatory electron givers, voltage or pH alteration, which beats the Pt, Ru, Rh, Pd and Au stacked photocatalyst ever detailed up until this point. The significant increase in photocatalytic activity could be the fast charge migration and separation from the silicon-hydrogen and silicon-hydroxyl bonds on Si surface and facilitation of charge separation could results from the multiple reflections of visible light on ultrathin nanosheets. It has been confirmed that the electron/hole recombination rate in ultrathin nanosheets of Si declined due to the oxidation of Si surface. It would be presumed that the approach of surface chemistry of silicon could not be limited towards the photocatalytic water splitting and could be applicable to remedy water pollution.

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1. Introduction

As of late, expanding convergence of ozone harming gas discharges in the environment has concerned in extensive consideration due to intensifying the global warming brought about by the greenhouse impact. A conclusion has been drawn by environmental change authority that the decreasing the ozone harming gas discharge must be accomplished by executing clean energy system to stop climatic change (Teo et al., 2019). Using water more

proficiently and transforming to H₂ fuel is one of the auspicious energy transformation systems to take care of climate change issue.

Binary or multi-doped supported oxynitrides, sulphides photocatalyst catalysts were reported over the previous decades (Pan et al., 2017). Heterojunction structured photocatalyst was found to be efficient for hydrogen production under illumination with visible light; for example CaFe₂O₄ (Kim et al., 2013); N-doped TiO₂ (Kim et al., 2015); TiO₂/Fe₂O₃ (Alsayegh et al., 2019) and Cu₂ZnSnS₄-PtCu₂ (Yu et al., 2014). Lamentably, photocatalytic reaction is not facilitated without using electron donor in the reaction medium leading incompetent utilization of sunlight. In fact, the advancement of complex oxides, for example, Rh-SrTiO₃ (Iwashina and Kudo, 2011) PbBi₂Nb₂O₉ (Kim et al., 2004), Sr_{1-x}NbO₃ (Sun et al., 2012); oxynitrides SrNbO₂N (Maeda et al., 2011), LaTiO₂N (Kasahara et al., 2002); and Pt (Au_{0.4}/Pt_{0.75}-TiO₂ (Rather et al., 2018) reported to

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split water into H_2 with the irradiation of visible light yet the perplexing synthesis procedure and moderate activities are principle obstacle towards its pertinence for effective H_2 generation.

Layered oxide materials containing a combination of Co, Cu, Ti, Cd have been reported for water splitting, such as Au/TiO₂ (Shouei et al., 2019), Co₃O₄/Co(OH)₂ (Yang et al., 2017), CuWO₄ (Ramezanalizadeh and Manteghi et al., 2018), α -Fe₂O₃ and Fe/Co-N₄/TiO₂ (Gao et al., 2019), K₂Sr_{1.5}Ta₃O₁₀ (Yao and Ye, 2007), CdS/TiO₂ (Reverberi et al., 2016) and LiCa₂Ta₃O₁₀ (Mitsuyama et al., 2008). Although these catalysts led to the splitting of water under the illumination of visible light, the degradation of active phase during subsequent reuse limits their applicability. Advanced hybrid molecular assembly techniques have been used to investigate the production of H_2 through water splitting (Sheridan et al., 2016). However, splitting process associated with the electron donor or voltage operation presents a substantial challenge. The substitution of noble nanoparticles such as Pd, Ti, Au, Pt have been attempted attention for photocatalytic water splitting. Trapping of photo-generated electrons on the noble metal's reduction site is beneficial for water splitting reaction (El-Emam and Özcan, 2019). While greater H_2 production efficiencies can be obtained by precious metal containing photocatalyst, the minimal cost with high proficiency materials desire to meet the future energy demand.

Silicon has been regarded as semiconductor material for solar hydrogen production (Lee et al., 2018) and Peng et al. (2011) attempted to relate the appropriate band energy of silicon with the photoelectrochemical reaction. After performing a number of theoretical simulations, Zhang et al. (2011) explored the photocatalysis over silicon for the hydrogen production from water, yet its applicability needs experimental validation. Further, it has been shown by other workers (Liu et al., 2015) that the photocatalytic hydrogen evolution performance of silicon catalyst greatly impacts on the surface function of catalyst. This result is consistent with the data reported by Ryu et al. (2016) who attempted to produce Pt/Si photocatalyst for H_2 production through water splitting. However, the expensive platinum co-catalyst remains challenge for practical application. Rice husk has been exploited an attractive cheap candidate for pure silicon (Bose et al., 2018). Thus, the synthesizing nano-structured with enhanced surface functionality Si composite could be a noble approach for H_2 evolution from pure water under visible-light in absence of any sacrificial reagent. Most strategies for generating hydrogen from water require a lot of conciliatory electron contributor and are cost-restrictive. The best energies to acquire hydrogen from water require the utilization of costly valuable metals, for example, platinum, and are in this manner not competitive approach to energy generation. In addition, the complex catalyst synthesis process, low hydrogen production rate and non-toxic photocatalysts driven by sunlight persist a major contest for hydrogen production.

Numerous efforts have been devoted to synthesize silicon based photocatalyst using a variety of strategies to facilitate the charge separation of photocatalyst. Natural clay was chemically reduced and exfoliated by Ryu et al. (2016) to synthesis mesoporous Pt/Si nanosheets. However, the lower degree of exfoliation and chemical reduction during synthesis of catalyst limits the improvement of photocatalytic performance. Silicon nanowires from Si wafer are synthesized by Liu et al. (2015) for photocatalytic water splitting using metal-assisted etching process. However, using the hydrofluoric acid (HF) during fabrication process most frequently to remove oxide layer and silicon hexafluoride (SiF₆) compound from the catalyst surface facilitate the detrimental precipitates to the environment. A two-dimensionally grown single-crystal silicon nanosheets was synthesized by Kim et al. (2014) through chemical vapor deposition of SiCl₄. The supersaturation of reactant SiCl₄/H₂ ratio in the gas-phase growth process limits the free standing property of single crystal 2D Si nanostructures and thus is not

suitable for cost effective large-scale production. Therefore, the complex photocatalyst synthesis process, low hydrogen production rate, high cost of co-catalyst and non-toxic photocatalysts driven by sunlight remain major issues. Hence, it would be very important to assess the catalytic activity of rice husk derived nanosheets of silicon for hydrogen generation under illumination with visible light without utilizing any electron contributor.

The emphasis was given in this study to synthesis waste derived nanosheets of silicon photocatalyst that can irradiate under visible light irradiation. A simple one-step solid phase reaction strategy was reported to synthesis ultrathin structure of catalyst which could decrease the complexity of synthesis. No report on the waste derived silicon nanosheet photocatalyst was presented for water splitting to the best our knowledge. The photocatalyst with much preferable hydrogen production performance over the current precious-metal-free photocatalyst was perceived in this study without utilizing any electron contributors.

2. Materials and methods

2.1. Catalyst preparation

Solid state strategy was employed to synthesis photocatalyst, shown in Fig. 1. In the fabrication of photocatalyst, rice husk used for the preparation of photocatalyst was typically prepared by the treatment with hydrochloric acid (20%) at 90 °C for 1 h and subsequently the husk were being treated with HF (10%) at the same temperature for 1 h to reduce the metallic impurities as well as to chemisorb the surface functional group onto the catalyst surface (Liu et al., 2015). The Si-H bond generated by HF treatment is inevitably advantageous for photocatalysis over Si (Shao et al., 2009). Electron deficient H atom over Si surface could act as electron sink to improve charge detachment (Peng et al., 2011). The treated rice husks were being heated in furnace under oxidizing condition at 750 °C for 3 h. The calcined sample was blended with Mg nanopowder purchased from Sigma-Aldrich. The ratio of the mixture was maintained 1:1.1 for solid phase reaction at 750 °C for 3 h in a close reactor (Fig. 2A) to obtain photocatalyst.

Top-irradiated reactor with circulated gas system was used to determine the activity of photocatalyst (Fig. 2B). Evacuation was performed to remove the air from the reactor and the dispersion of 1.0 g powdered catalyst the deionized water (370–390 mL) was executed during the reaction. Irradiation of the reactor with cooling jacket system was implemented by xenon lamp ($\lambda > 420$ nm). The video for photocatalytic reaction system was given in Fig. S1. Agilent gas chromatograph was used to measure the H_2 evolution during reaction. It was coupled with TCD (thermal conductivity detector) and a molecular sieve (Agilent US). The amount of H_2 was measure using auto injection system where Ar was used as carrier gas. The identification of H_2 was accompanied by reference standard H_2 and compared with the retention time. The integration of peak intensities compared with standard H_2 to generate a calibration curve. The mole of hydrogen evolution was calibrated by the area of standard H_2 from gas chromatography and was converted into μ mol. Finally, the accumulative H_2 evolution for 1 h reaction time was measured. The detail procedure was provided in supplementary information-S2. The measurement of the H_2 was given in detail in Table S1. The following equation was used to calculate the rate of hydrogen production.

$$\text{Hydrogen generation rate} = \frac{\text{Hydrogen generated in moles}}{\text{irradiation time}} \quad (1)$$

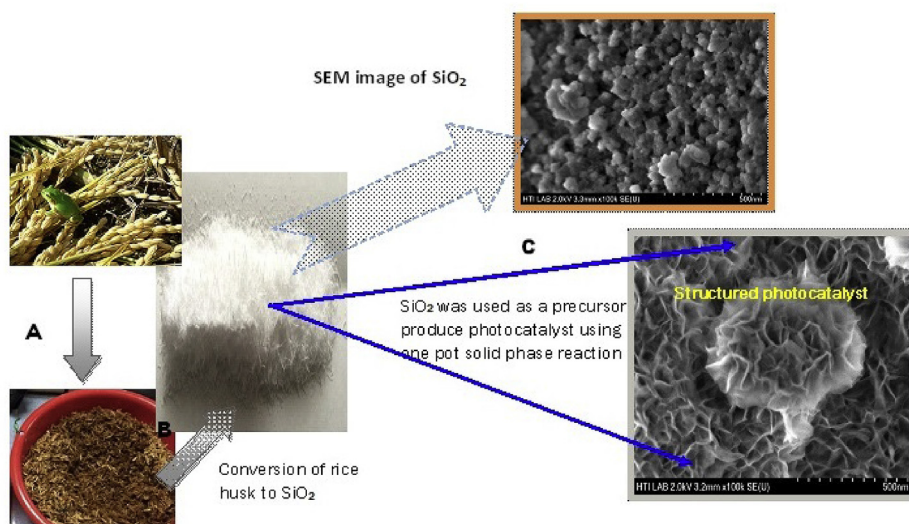


Fig. 1. Illustration of the preparation of the Si/MgO by the solid phase reaction method; (A) Treatment of rice husk; (B) conversion of silica from rice husk; (C) Photocatalyst was prepared using solid phase reaction in which SiO_2 was used as a precursor.

2.2. Sample characterization

Powder X-ray diffractometer (XRD6000, Shimadzu) with radiated $\text{Cu K}\alpha$ was used to identify the structure of the catalyst at 2.7 kW and 30 mA. The data of crystalline phase were recorded over a range of $10\text{--}80^\circ$ (2θ) with a step of 2° . The identification of the phase of catalyst was conducted with the standard of JCPDS database file. The observation of sample morphology was accompanied by the FESEM (Hitachi SU8000) with accelerated 12 kV voltage. The examination of elemental composition of the catalyst was carried out by EDX with a detector system 7 of ThermoscientificNoran. HRTEM with accelerated 200 kV voltage was used for obtaining the morphology of the catalyst.

UV–Visible spectrophotometer (PerkinElmer Lambda 950) was

used to characterize the absorption property of light for the catalyst. The absorbance property of the catalyst was converted into reflectance intensity using Kubelka-Munk technique. X-ray photoelectron spectroscopy (XPS) radiated with $\text{Al K}\alpha$ (1486 eV) was employed to measure the oxidation state of catalyst. Monochromator was used to record XPS spectra of the sample in operation at 25.6 W. Reduction of charging effects carried out by charge neutralizer and 10 eV energy was maintained during the collection of data. Minimization of surface hydrocarbon of the catalyst was accomplished by heating of sample at 100°C prior to the measurement. The correction of binding energy was performed by using reference C 1s binding energy of 284.8 eV. The electron-hole recombination characteristics of photocatalyst were measured by using photoluminescence (PL) spectra (PerkinElmer LS55)

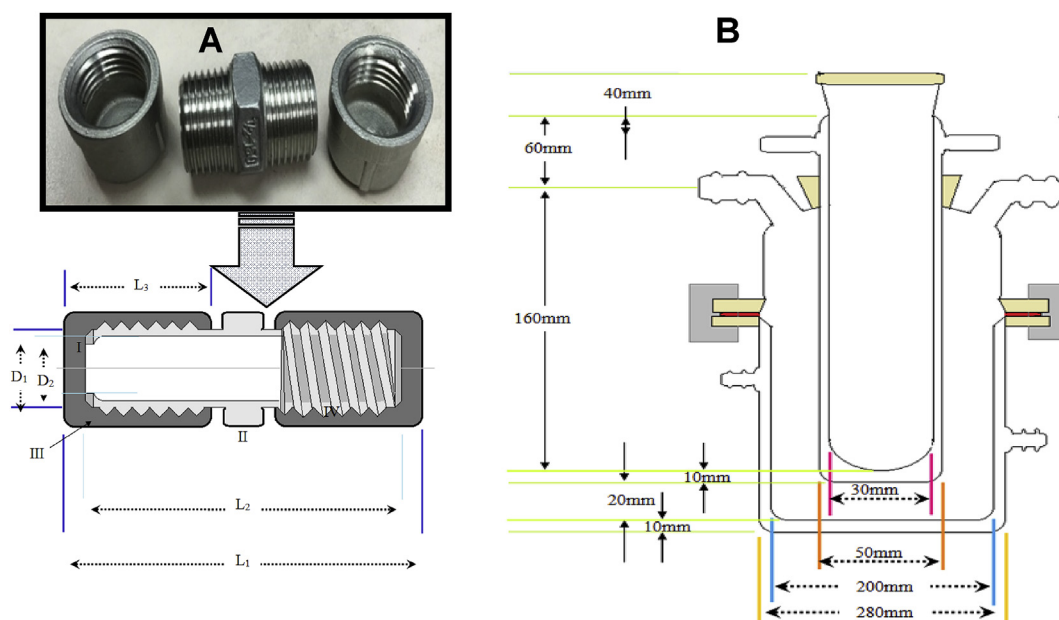


Fig. 2. A Photo of the homemade reactor design used to perform solid phase reaction to produce photocatalyst. L_1 : length of reactor (5 cm); L_2 : length of body (4.5 cm); D_1 : external diameter of body (3 cm); D_2 : internal diameter of body (2 cm); L_3 : length of vent cap; I: vent cap; II: connection; III: connection type; and IV: threads. B. Experimental setup of the water splitting system using photocatalyst.

connected with xenon (Xe) lamp.

3. Results and discussion

To well understand the structural information of photocatalyst, a comparison of FESEM and HRTEM images are demonstrated in Fig. 3A and B. The catalyst with an average diameter of 240 nm was observed (Fig. 3C). The structures of catalyst are composed of many interconnected nanosheets with average thickness of 5 nm (Fig. 3D), which could enable a superior electrical conductivity

(Awual et al., 2019a). The crystallinity of catalyst was gained by X-ray diffraction (XRD) (Fig. 3E). The diffraction peaks at 36.47° , 42.90° , 62.33° , 74.70° , 78.74° are associated with the formation of MgO (JCPDS file no. 01-075-0447). Strong crystalline peaks at 28.39° , 47.27° , 56.15° , 58.68° , 69.15° and 76.38° corresponds to crystal planes of (111), (220), (311), (222), (400) and (331) on Si (JCPDS No. 01-089-2749). SEM-EDX elemental mapping was used to identify the metal in the catalyst (Fig. 4A–D), which is consistent with results of XRD. Ultrathin layer structured Si was characterized to identified the surface functional property of the catalyst

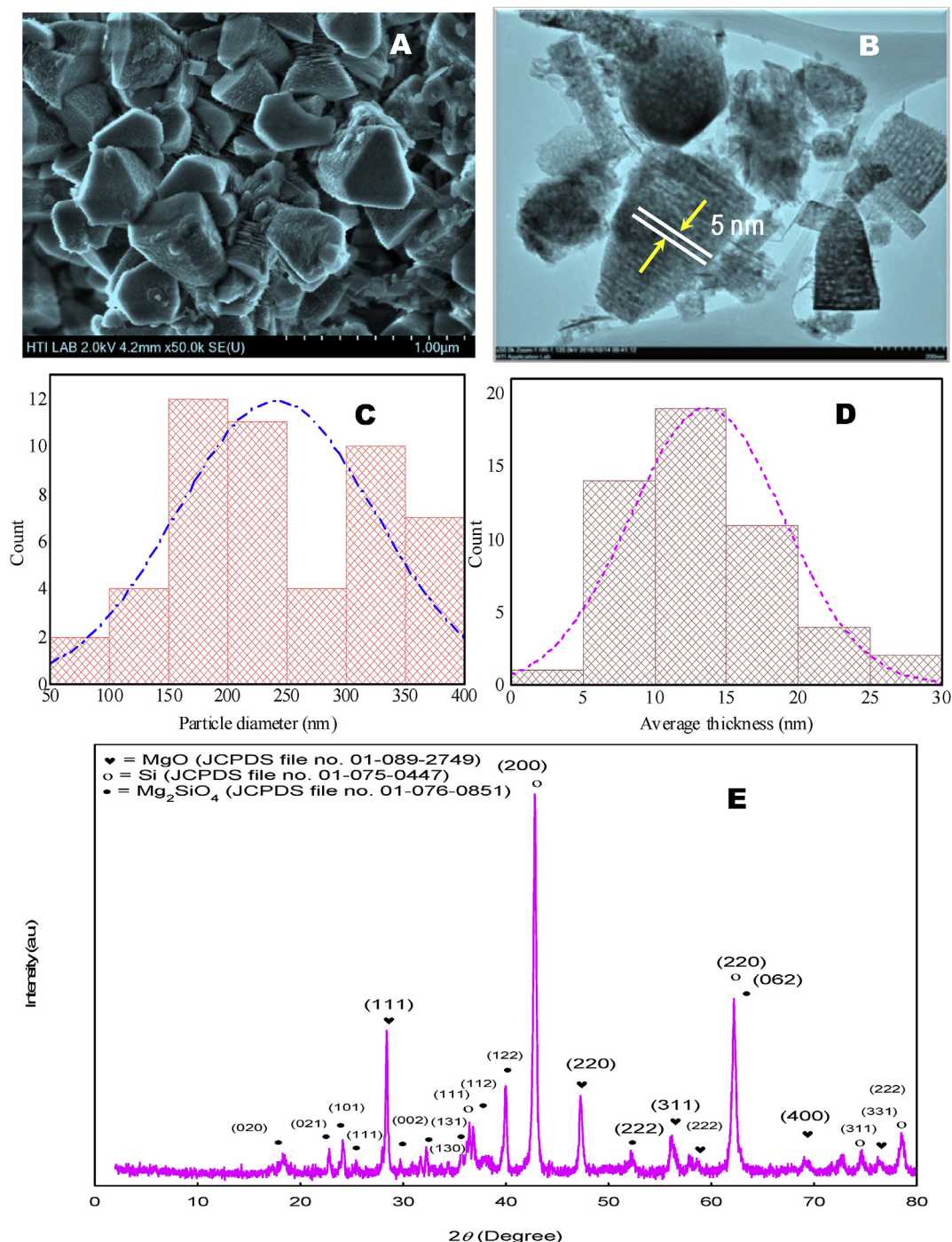


Fig. 3. Structural and chemical characterization of as prepared catalyst. **A.** Field emission scanning electron microscopy image of catalyst. **B.** High resolution transmission electron micrograph of catalyst. **C.** The particle diameter of catalyst. **D.** The thickness of nanosheets of catalyst. **E.** X-diffraction of photocatalyst.

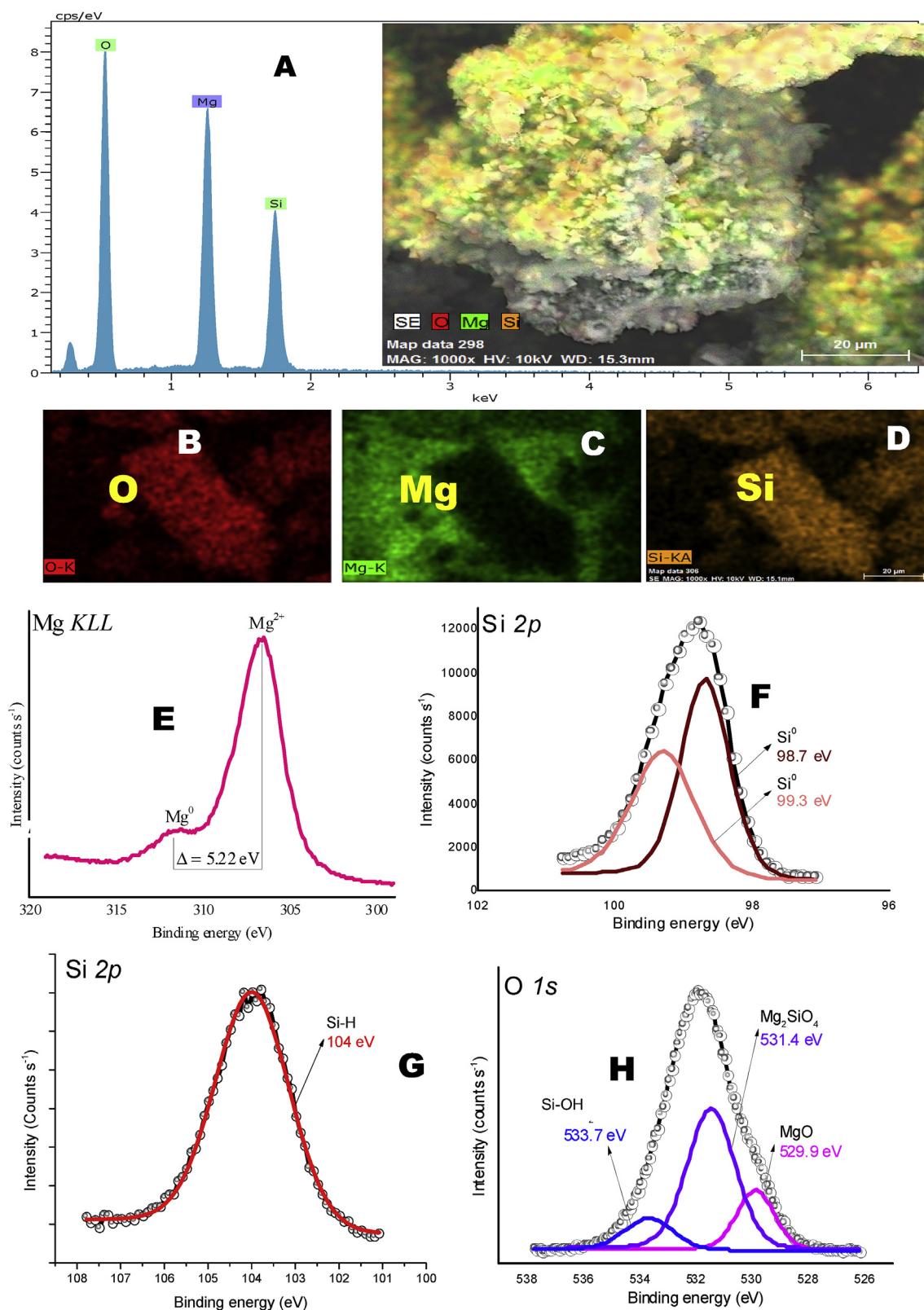


Fig. 4. A. Elemental mapping of used catalyst. B. O Distribution. C. Mg distribution. D. Si distribution. E. XPS spectra of Mg KLL F. XPS spectra of Si 2p. G. XPS spectra of Si 2p. H. XPS spectra of O 1s for catalyst.

(Fig. 4E–H). Shifting the binding energy from 311.8 eV to 5.22 eV indicates the transformation of Mg into MgO (Wu et al., 2016), as shown in Fig. 4E. In general, MgO has been regarded as an acid-base nature of catalyst support. Julkapli and Bagheri (2016) have shown that these acid-base properties could enhance the photocatalytic efficiencies by transforming electron from support to catalyst surface. Other workers (Meshkani and Rezaei, 2011; Awual et al., 2019b) have discussed similar phenomenon and concluded that the chemisorption of surface functional group could improve due to its Lewis basicity character. Hence, MgO was utilized in this investigation to increase the catalyst efficiency by increasing surface functional group on its catalyst surface. The binding energy of 99 eV could be ascribed to the formation of Si (Fig. 4F). Prominently, the broad peak recognized at 104 eV associated with the hydrogen bonding onto the silicon surface (Ryu et al., 2016). Liu et al. (2015) fabricated the Si-H bonds on silicon photocatalyst by the treatment of hydrofluoric acid (HF) in its preparation steps and it was assumed that after such a treatment the Si-H bonds were essentially formed on silicon surface. A similar method has been used by Ryu et al. (2016) who attempted to prepare Si-H bonds on silicon nanosheets for hydrogen evolution from a water–methanol mixture. Further, it has been shown by other workers (Huang et al., 2008) that the involvement of acid treatment in Si

nanowire fabrication generate Si-H bonds on its surface. Peng et al. (2011) agreed quite well with the preparation of Si-H bonds on bare Si surface reported by Huang et al. (2008). Liu et al. (2015) have shown that the facilitation of electron-hole detachment is occurred on Si–H surface and served as hydrogen creation sites. The peak at 531.4 eV could be ascribed to silicates while 529.9 eV resembles with the MgO (Yin et al., 2014), shown in Fig. 4H. The peak at ~533 eV (Fig. 4H) could be associated with hydroxyl bonding onto the silicon surface (Carniato et al., 2007). The solid phase reaction leaves Si-OH bonds on ultrathin layers of Si which could act as back reaction center to suppress the formation of H₂ (Liu et al., 2015).

UV–Visible spectrophotometer was conducted to understand the light absorption properties and the band gap of the catalysts. The results from UV–Visible spectrophotometer are shown in Fig. 5A–B. From the UV–Visible results, Tauc plots were drawn as reported by literature (Kamarulzaman et al., 2015) using Eq. (2).

$$(\alpha h\nu) = C' (h\nu - E_g)^{1/2} \quad (2)$$

Where α is materials co-efficient of absorption, λ is the wavelength, h is the Planck's constant, C' is the constant of proportionality, ν is the recurrence of light and E_g is the energy of the band-gap. The absorption coefficient is evaluated (Rusdi et al., 2011; Islam et al.,

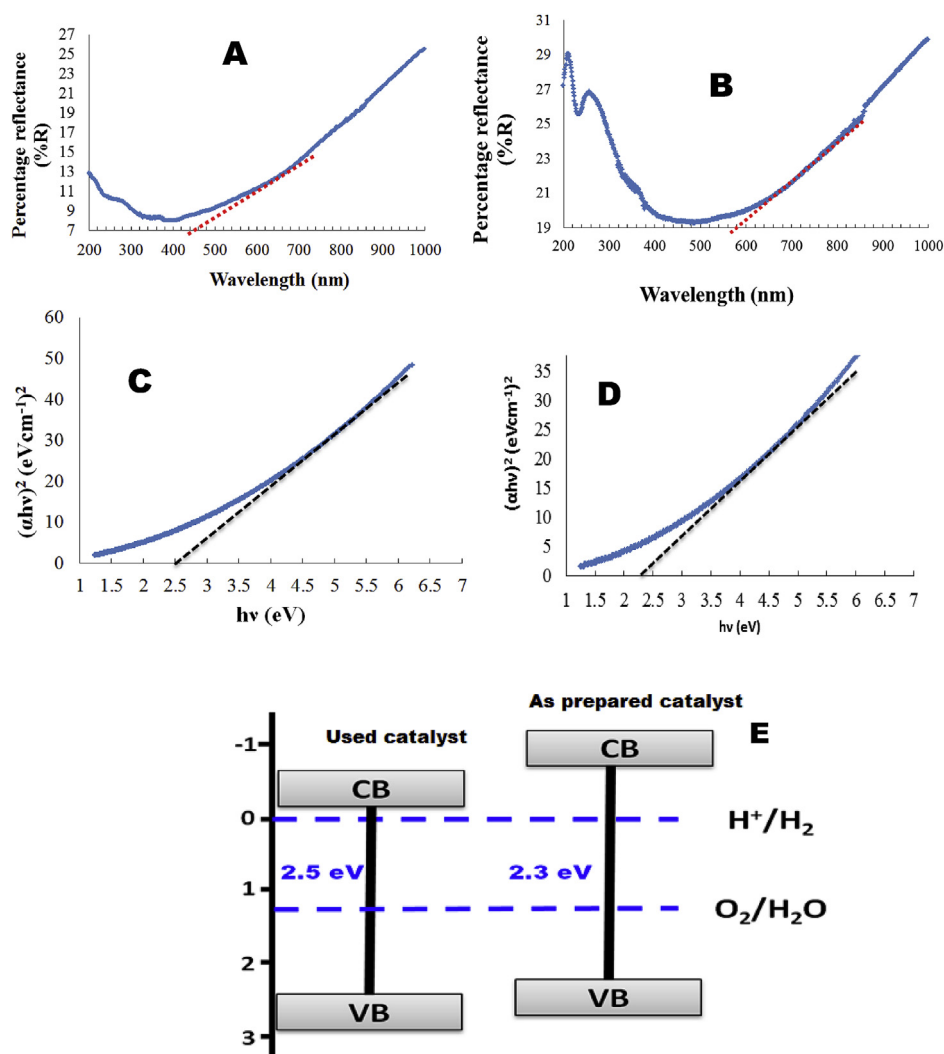


Fig. 5. Ultraviolet–visible diffuse spectra of photocatalyst; A. As prepared catalyst, B. Used catalyst. C. Tauc plots of used catalyst; D. Tauc plots of as prepared catalyst. E. Band positions of Si/MgO photocatalyst. F. The role of photogenerated electrons and holes on catalytic system.

2019) using Eq. (3).

$$\alpha = k \ln \frac{R_{\max} - R_{\min}}{R - R_{\min}} \quad (3)$$

Where, k indicates constant, $R_{\max}$ indicates highest reflection, $R_{\min}$ indicates lowest reflection, combining Eq. (2) and Eq. (3) gives-

$$(\alpha h\nu)^2 = C' (h\nu - E_g) \quad (4)$$

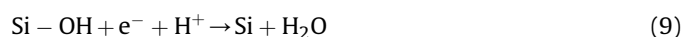
The $(\alpha h\nu)^2$ vs. $h\nu$ was plotted in the graph and extrapolated the graph until reach to the x-axis to determine the band gap of the catalyst (Fig. 4C–D). The conduction band (Ec) position and valence band position (Ev) of the photocatalyst was determined by Eq. (5) and Eq. (6) (Matsumoto, 1996), as shown in Fig. 4E.

$$E_c \text{ (V vs RHE)} = 1.23 - E_g \text{ (eV)/2} \quad (5)$$

$$E_v \text{ (V vs RHE)} = 1.23 + E_g \text{ (eV)/2} \quad (6)$$

The band energy positions move to high when a component with a low electronegativity occurs in the structure, and the other way around, while the non-transitional metal is remained in fixed position. The estimated band gap fresh and used catalysts were 2.5 eV, and 2.3 which attributes to the energy for the carrier separation in the evolution of O_2 and H_2 (Fig. 5E). The band gap for this catalytic system would be favorable for electron excitation in presence of light (Mancipe et al., 2017).

From the foregoing discussions, hydrogen and hydroxyl bond on ultrathin slices of Si could be associated with the oxidation/reduction reaction during hydrogen production. Simulating the water splitting on silicon surface, a conclusion has been reached by Zhang et al. (2011) that the dissociation of water would take place preferentially on Si surface when irradiate in water (Eq. (7)). The holes on Si ($Si-h^+$) could act as oxidation center where H^+ would trap by Si-H bonds to provide proton reduction sites for H_2 production (Liu et al., 2015). Other workers (Ryu et al., 2016) have discussed a similar phenomenon and have suggested that the reduction reaction could be proceeded by adsorption of electron on the functional surface on Si as provide Eq. (8) and Eq. (9). It might be referenced that the concealment of H_2 evolution could be associated with Eq. (9).



The role of photogenerated electron and holes on the photocatalyst is shown in Fig. 6A. The role of photogenerated electrons and holes on Si/MgO system could be explained on the basis of the dynamic interaction of charge separation and surface bonds formation (Ryu et al., 2016). Construction of internal field at ultrathin layer interface could enhance the photogenerated carriers separation (Zhang et al., 2016).

The excitation of photon energy beyond its band gap energy assist to transfer electron from Si to the Si-H and Si-OH surface bonds to generate H_2 and H_2O respectively, while the photogenerated holes (h^+) from Si promotes to released H^+ cations from water (Ryu et al., 2016), as shown in Fig. 6A. Liu et al. (2015) also explored the effect of surface chemical bonds in silicon photocatalyst on the generation of hydrogen under visible light irradiation. It was concluded that the facilitation of H_2 production could occur by trapping electron on Si-H surface. At the same time, Si-OH

bonds can also be partially excited by absorbing photons (H^+) and subsequently form H_2O with protons (Fig. 6A). This reaction could act as back reaction centers to suppress the production of H_2 in this system.

Hydrogen production efficiency of photocatalyst was assessed under irradiation with visible light (Fig. 6B). The estimated maximum value of hydrogen production reached to $3200 \mu\text{mol h}^{-1}\text{g}^{-1}$. Only H_2 gas produced during splitting of water from the catalyst as evident from Fig. 6C, which concur very well with the information reported by Liu et al. (2015). This outcome implied that the generation of H_2 in photocatalytic framework was not occurred along a customary water-splitting process. This perception is steady with the outcomes shown beforehand by Liu et al. (2015) who demonstrated silicon nanowires for photocatalytic water splitting. Activity of the photocatalyst for hydrogen production through water splitting was compared in Table S1. The attention of recent work has been directed towards the synthesis of modified Co, Ti and Pt supported $g\text{-C}_3\text{N}_4$ to attain high efficiency H_2 production from water (Awual, 2016; Awual et al., 2017). Deficiency of suitable active sites for reduction on polymer surface and low hydrogen evolution reaction activity for water splitting are the main drawbacks of supported $g\text{-C}_3\text{N}_4$ catalyst. Therefore, it was presumed that nanosheet structured photocatalyst based on La, Rh, Au, Pd, Cd co-doped heterostructure could be more efficient to achieve overall water splitting with the presence of sacrificial reagent under visible light irradiation (Table S2). In any case, the employments of Pt-based catalyst for the hydrogen production are exceptionally costly respectable metals, bringing about extra expenses and trouble of large scale production.

Attraction has been paid to use silicon semiconductor due to its novel opto-electrical properties. Noble metal functionalized Si catalyst was shown excellent H_2 production from water in the presence of methanol (Table S2). Despite the fact that the definite investigational condition was not the equivalent for one another, the H_2 production rate for the rice husk inferred photocatalysts observed in this investigation is the most elevated worth contrasted with the precious metal supported photocatalyst, for example, Pt, Pd Cd, Ti, Co, Ru and Au, beforehand demonstrated under irradiation with visible light illumination without any conciliatory reagent or change of pH, as shown in Table S2. Thus, the utilization of earth-bounteous Si could make the procedure of water splitting progressively achievable as a way to develop clean hydrogen as a vitality source from water. What's more, there are a few investigations concentrating on how hydrogen can be one of the most effective future energy source giving better environment and sustainability. Among the conceivable hydrogen generation techniques considered in the literature, this rice husk derived ultrathin structured photocatalyst could be more sustainable due to its high catalytic performance, environmentally sustainable, abundant sources and reduced cost.

Plausibility of water splitting by using silicon photocatalyst was explored by Liu et al. (2015) and reported that the generation of Si-H radicals on silicon surface facilitates the separation of photoexcited electrons from holes. Ryu et al. (2016) have discussed on the applicability of silicon nanosheet for hydrogen evolution from water and have suggested that the formation of ultrathin layer on silicon catalyst maximize contact to transfer photogenerated electron resulting in high catalytic activity. Pan et al. (2017) concluded from their work that the interactions of hydrogen radicles with silicon catalyst surface may increase separation of electron. Further, it has been assumed that the bonding of Si-H on Si surface plays a key role for visible light responsive hydrogen production (Shao et al., 2009). From the foregoing discussion, the strong dependency of such surface bond on Si catalyst seems to suggest that the photocatalytic hydrogen evolution performance of silicon

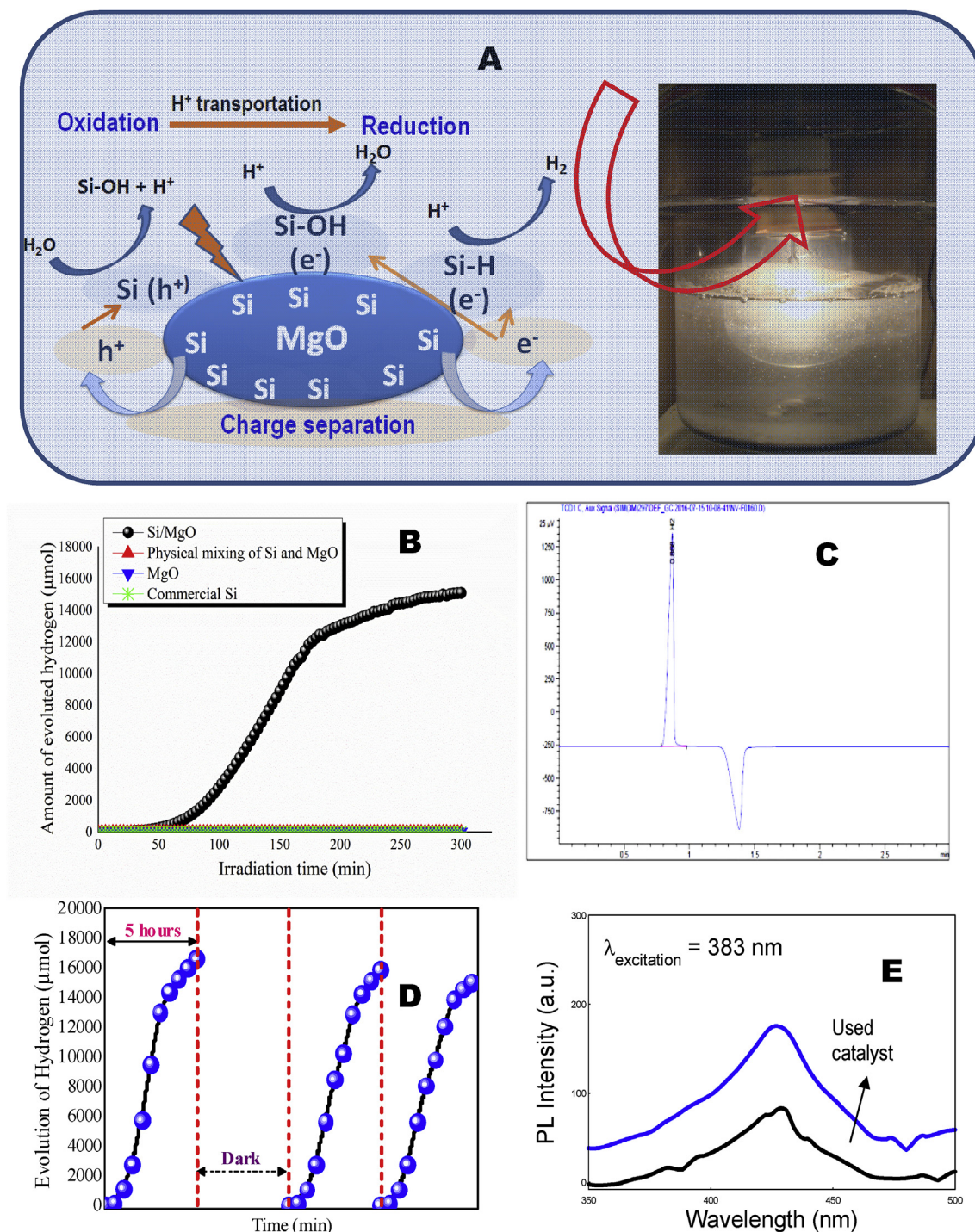


Fig. 6. A. Proposed mechanism for the photocatalytic water splitting. B. Water splitting activity of photocatalyst; Reaction was carried out under visible light. C. A typical GC trace of evolved hydrogen D. Regeneration activity of photocatalyst E. PL of the as-prepared and used catalyst.

catalyst could be attributed to a large extent with its surface functional group. Our results suggest that the formation of Si-H bond on catalyst surface has an important role to generate hydrogen from water in the absence of any reagent or voltage application of voltage.

To investigate the plausibility of recuperating the performance, we have additionally endeavored to reusing trial of the sample after photocatalysis. As appeared in reusing test outcome (Fig. 6D), no noteworthy decrease of H_2 production ($3166 \mu\text{mol h}^{-1} \text{g}^{-1}$) was

found even after 3 continuous keeps running of photocatalyst. In this way, the produced hydrogen noted above appear to be demonstrative might be due to the Si-H formation on Si instead of Si-OH bonds which is apparently an inalienable component for keeping up high pace of hydrogen generation. These evidences accentuated that the tuning of synthesis process is important for efficient for hydrogen generation because of their influence on surface bond. So as to get additional data concerning the recombination a property of electron–holes' on catalysts, the

photoluminescence (PL) of catalyst was estimated (Fig. 6E). It is to a great extent conceded that the higher fluorescence force of utilized catalyst contrasted with as-prepared catalyst could be ascribed to the decrease of charge release proficiency (Hoffmann et al., 1995).

To explore the recovering performance of used catalyst, we have also attempted to conduct characterization of the used sample by FESEM, XRD, XPS and UV–vis studies. To assess the possibility of $\text{Mg}(\text{OH})_2$ conversion from MgO , the used sample was tested by XRD after each cycle of 5h reaction. No $\text{Mg}(\text{OH})_2$ formation was observed in this study, as evident from XRD (Fig. 6A). The binding energy of 50.8 eV for $\text{Mg}(2p)$ peak could be associated with the formation of MgO (Corneille et al., 1994) while the binding energy 531.7 eV could

be indicative of silicates (Fig. 7B and C). Hence, the presence of MgO in the used catalyst, as confirmed from XPS studies indicating the structural stability of used catalyst. It might be noted that the sample was calcined at 700°C before starting the subsequent cycle of reaction. A similar hydration behavior of MgO in water was studied by Gravogl et al. (2018) and no conversion of $\text{Mg}(\text{OH})_2$ from MgO under the exposure to water over 3–5h was reported. However, the prolonged exposure of MgO to water over 24 h could transform MgO to $\text{Mg}(\text{OH})_2$ as concluded by Gravogl et al., (2018). Hence, calcination of sample after 5h of reaction might not affect the conversion of H_2 . The peak intensity associated with the hydrogen bond on silicon surface at 103 eV was reduced after

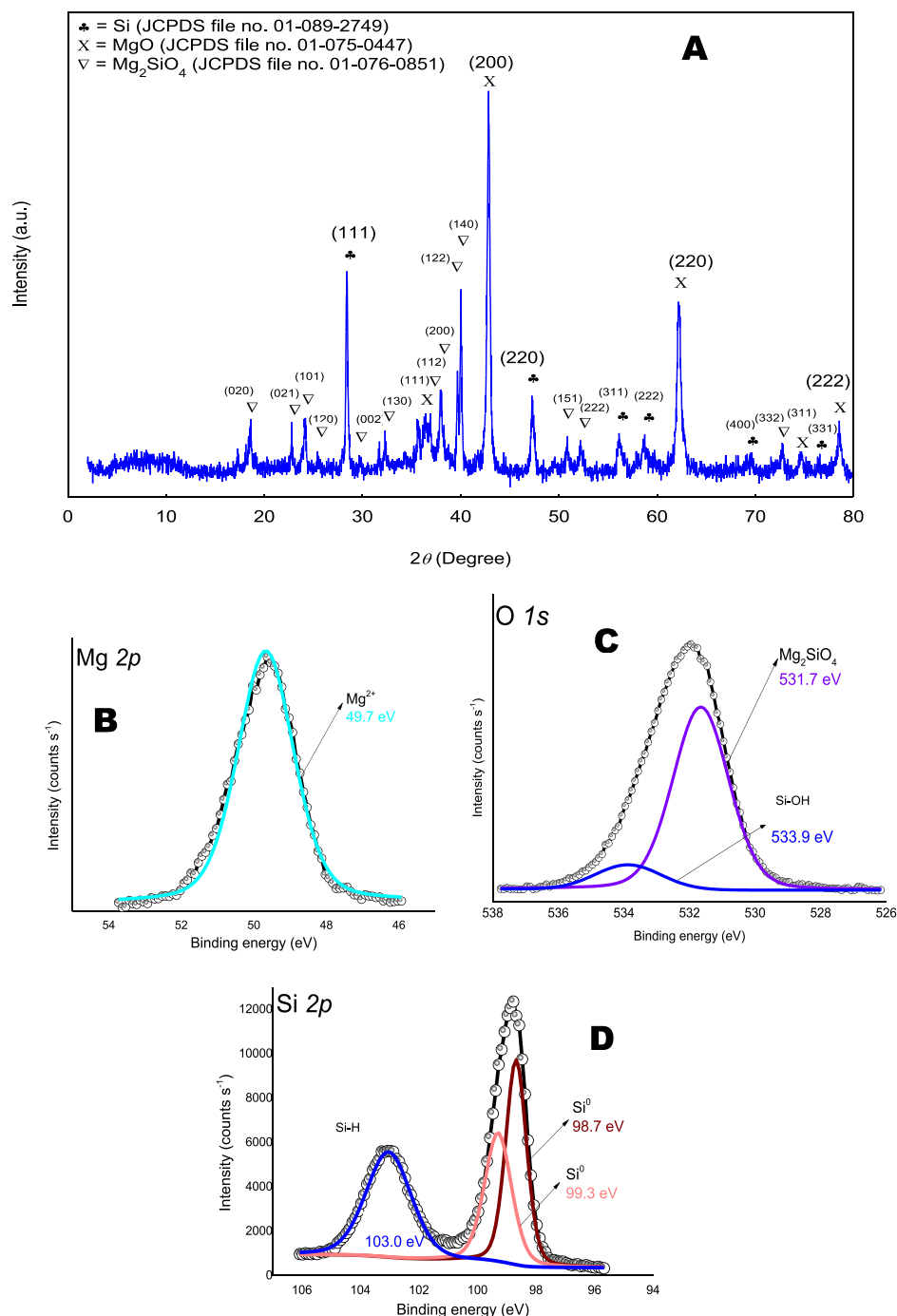


Fig. 7. A. XRD pattern of used catalyst. B. XPS of Mg 2p; C. XPS of O 1s; D. XPS of Si 2p.

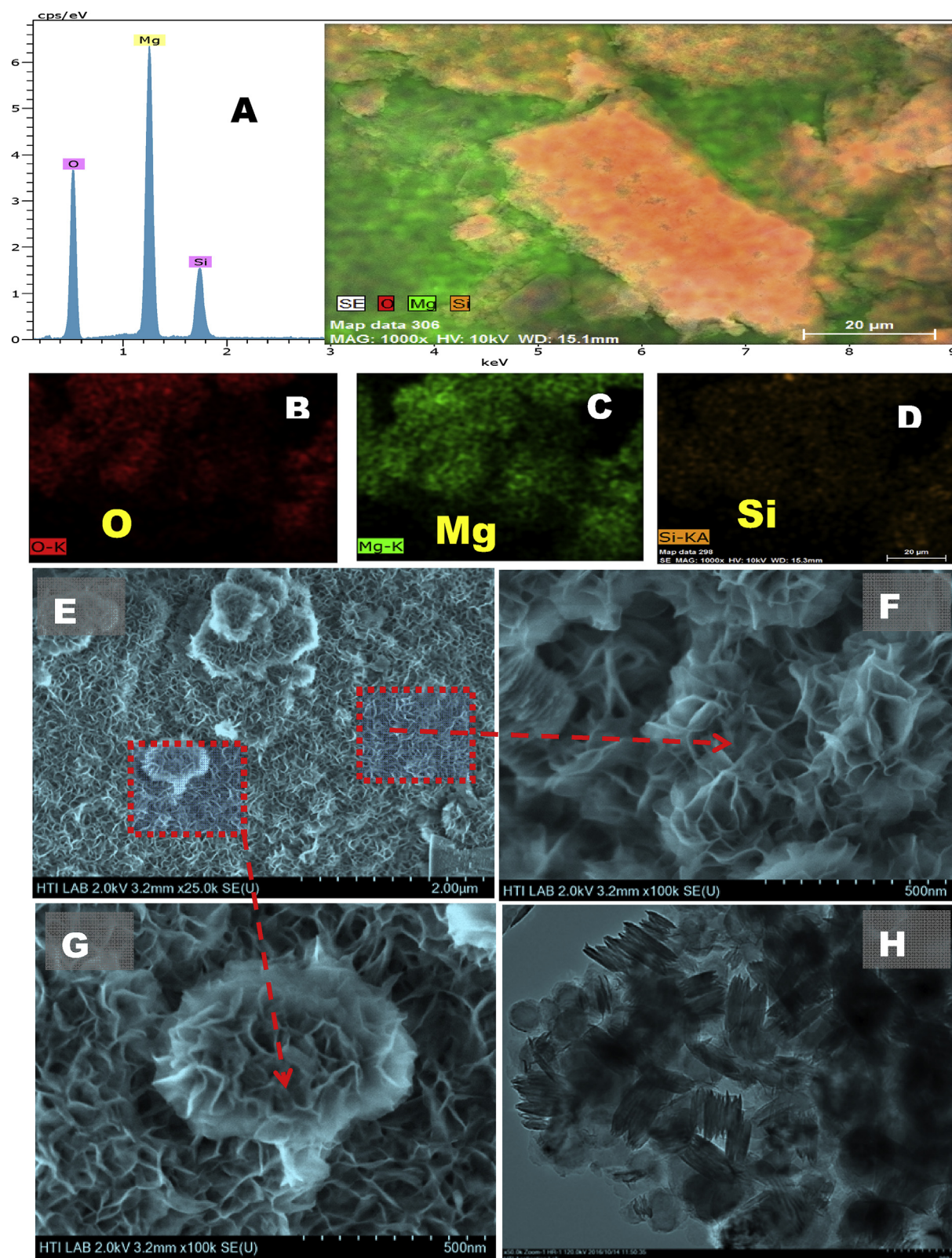


Fig. 8. A. Elemental mapping of used catalyst. B. The distribution of O. C. Mg distribution. D. Si distribution. E. FESEM image of used catalyst. F-G. High magnification FESEM images of used catalyst and H. HRTEM image of used catalyst.

successive reuse (Fig. 7D). Earlier investigations have suggested that the reduction of peak intensity might be due to the decrement of oxide surface on catalyst (Awual, 2019). The result was analogous to that of observed from EDX study (Fig. 8A–D). As appeared in Fig. 8E–G, bloom structured frame forms by amassing of nano-sheets. The crossing of nanosheet assembles the porous structure of the catalyst, as clear from TEM (Fig. 8H). Higher activity of reused nanosheet-structured catalyst noted above might be structure sensitive phenomenon. Shortened charge diffusion path or superficially trapped electron of ultrathin slices might results in adequate photoconductivity during the irradiation with visible light. Erogbogbo et al. (2013) have discussed a similar phenomenon and have suggested that light-trapping efficiency could be improved by scatteredly branched nanosheets. We assumed with future examination, water splitting efficiency could be enhanced by changing and adjusting functional group onto the catalyst surface.

4. Conclusions

A facile approach for synthesis of nano-sliced Si/MgO photocatalyst was developed utilizing solid state procedure. The catalyst illuminated under visible light was proficient for H₂ generation in absence of any electron benefactor or conciliatory agent. The surface property of this catalyst is one of the significant properties influencing photocatalytic efficiency for water splitting, as evident from this study. XPS studies revealed that the enhanced activity of Si/MgO is due to the Si–H binding which act as a reduction site of catalyst. The maximum generated H₂ was reached to 3200 $\mu\text{mol h}^{-1}\text{g}^{-1}$ which is much higher than precious metal free photocatalyst reported in the literature. The resulting Si/MgO exhibited the outstanding stability toward hydrogen production from water even after successive run of catalyst. Considering the ultrathin nanosheet morphology and high photocatalytic efficiency of catalyst, we presumed that the combination of different metals with having lower band gap to frame heterojunctions could further upgrade the photocatalytic efficiency, even allowing H₂ evolution under visible light illumination. In addition with further research, balancing and controlling the surface function group could improve the efficiency of catalyst.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2019.118805>.

Supporting information

Supporting information for this article (the data that support the plots within this paper, details on calculation and measurements of H₂ evolution) are available.

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