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Production of Methanol as a Fuel Energy from CO_2 Present in Polluted Seawater - A Photocatalytic Outlook

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Abstract: The production of methanol by photocatalytic reduction of the CO_2 present in the different polluted seawater systems was explored using P-25, C/TiO_2, and Cu-C/TiO_2 under both UV and sunlight. Both C/TiO_2 and Cu-C/TiO_2 were synthesized by the sonicated sol-gel method. The prepared photocatalyst demonstrated maximum efficiency when the dosage of photocatalysts was 1g/L and the doping level was 3wt% of copper. The maximum methanol yields of two observed polluted seawater systems were 2910 μmol/g and 2250 μmol/g after 5 hour illumination of UV light. However, the 5 hour natural sunlight illumination generated the yield of 990 μmol/g and 910 μmol/g of methanol. The observed results demonstrated that band gap narrowing of the photocatalyst by carbon modification and the restriction of electron-hole pair combination by copper doping both greatly enhanced the photocatalytic reduction of CO_2 to methanol under both UV and natural sunlight.

Keywords: Photocatalysis; CO_2 reduction; polluted seawater; methanol; Cu-C/TiO_2.

1 Introduction

The issues of global warming and energy crisis have become a pronounced issue in the present situation of the world. According to IPCC 2014, the globally averaged combined land and ocean surface temperature statistics, calculated by a linear trend, display a warming of 0.85ºC over the period from 1880 to 2012. During this period, the global mean sea level was elevated by 0.19m [1]. About half of the cumulative anthropogenic CO_2 emission between 1750 and 2011 has occurred in the last 40 years [2]. It is unbalanced when more CO_2 is as a result of burning fossil fuels compared to the natural carbon cycle. Although the output of 29 gigatons (Gt) of CO_2 emitted from burning fossil fuels is a minor compared to the 750 Gt emitted through the natural carbon cycle each year, it adds up because the land and ocean cannot absorb all of the additional CO_2 [3]. Nearly 40% of this supplementary CO_2 is absorbed with the rest remaining in the atmosphere. As a consequence of this is that the atmospheric CO_2 is at its uppermost level in 15 to 20 million years [4].

Energy is considered to be the lifeline of an economy, the supreme dynamic instrument of socio-economic development and recognized as one of the most important deliberate commodities [5]. The relationship between economic development, energy and CO_2 emissions has been a dynamic research area [6-9]. A quickly emergent population and industrialization have caused difficulty for the world's natural resources to keep up with demands. At present, fossil fuels such as coal, oil or natural gas are burned in power plants to produce energy. Moreover, civilization and industrialization have brought not only technology but also pollution and emissions from factories, vehicles and chemical plants, especially with an increase in atmospheric CO_2 by 30% [10]. Due to the shortage of oil and natural gas reserves as well as the strong dependence of developed countries on fossil fuel, there is a great interest in the development of renewable energy sources.

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Presently the oceans remove about a quarter of current CO_2 emission from anthropogenic activities [11]. The intensification in seawater CO_2 level will change the chemical buffering capacity of seawater which will lead to a decrease in the fraction of CO_2 emission taken up by the ocean [12]. This issue highlights the importance of photocatalysis to reduce the CO_2 into energy sources like methanol effectively. Recently, photocatalytic reduction of CO_2 into methanol using semiconductor materials has drawn substantial consideration [13]. Among these TiO_2 is considered to be a promising photocatalyst due to its superior redox ability, low toxicity and photostability. However, its broad band gap (3-3.2eV) makes it difficult to absorb light in the visible region [14, 15]. Carbon modification of n-TiO_2 improved the ability of the photocatalyst to absorb the light in the visible region by lowering its band gap to 2.32eV [16]. Generally, the substitutional carbon will form an additional layer over the valence band which facilitates easy movement of an electron from the valence band to the conduction band. To accomplish the improved photoactivity, many scientists tried to modify TiO_2 by doping with metal [13, 17-20] and non-metal impurities [21, 22]. Numerous advanced studies have investigated the modification of TiO_2, including metal doped TiO_2 nanotubes and nanowires [23, 24]. Consequently, many researchers have successively used C/TiO_2 as a visible light active photocatalyst [25-29]. On the other hand doping of TiO_2 with Cu (II) can enhance the selective production of methanol by suppressing the recombination of an electron and hole pair [13, 17, 30, 31].

To the best of our knowledge, the photocatalytic reduction of CO_2 to methanol present in the polluted seawater using Cu-C/TiO_2 has not been investigated before. From our previous studies [13, 32] the reduction of CO_2 from the pure water and unpolluted seawater has successfully investigated. Hence, the present work is principally focusing on the photocatalytic reduction of CO_2 into methanol as an energy source from two different polluted systems located in the central Red sea coast.

2 Materials and Methods

2.1 Preparation of Catalyst

TiO_2 P25 (Degussa. Japan) was used as a reference photocatalyst without supplementary modification. Cu-C/TiO_2 was prepared by the sonicated sol-gel method. The preparation was carried out by the addition of 30ml of titanium (IV) isopropoxide to the 30 ml of absolute ethanol under constant sonication. 15 ml of 0.01M glucose and 3wt% of copper sulfate were added to the prepared mixture. The pH was adjusted to 3.2 by the addition of 50% HNO_3 followed by 2 hours further sonication. The prepared gel was kept at room temperature around 24 hours followed by dehydration at 80ºC for 12 hours. The obtained powder was then transferred to the crucible and was kept in a muffle furnace at 500ºC for 2 hours. The same procedure was followed to prepare the C/TiO_2 without the addition of the $CuSO_4$.

2.2 Collection of samples

The samples were collected from 2 locations, the first from Al-Arbaeen lagoon, Jeddah, Saudi Arabia. The samples were highly polluted and anoxic. The second sample was collected from the Al-Shabab lagoon (near Saudi National Water Company), and the sample was oxygenated and polluted. Detailed explanations of the study area have been provided in many studies [33-35].

2.3 Photocatalytic reduction of CO_2

A homemade stirred set annular apparatus was used to achieve the photocatalytic reduction experiment. The apparatus was made up of Pyrex glass and was connected to the CO_2 cylinder through the firmly closed tube. A simple schematic model of the reaction scheme is shown in Figure 1. The desired catalyst loading was added to the sample and before light irradiation, the sample was purged with CO_2 (Certified super-critical fluid grade CO_2 with a maximum hydrocarbon content of less than 1ppm) for 60 minutes in order to saturate the solution. Then the reaction apparatus was closed tightly and the light was irradiated from all sides (UV lamp emitting 365 nm-Sankyo Denki, Germicidal lamp, G15 T8 Japan). The real sunlight experiment was done by exposing the sample reactor in the sunny time between 9.30 am to 2.30 pm. The average solar intensity was 1200 W m^{-2} and it was measured using a 3670i Silicon Pyranometer Sensor attached to Field Scout Light Sensor Reader (Spectrum Technologies, Inc.). The temperature and pH were recorded continuously using the probe sensors.

The polluted seawater samples were drawn at each time interval using a tightly closed syringe, which was connected to the apparatus through the supplementary opening. Different sets of blank experiments were performed to confirm the produced methanol is due to the photocatalytic reduction of CO_2 using Cu-C/TiO_2.

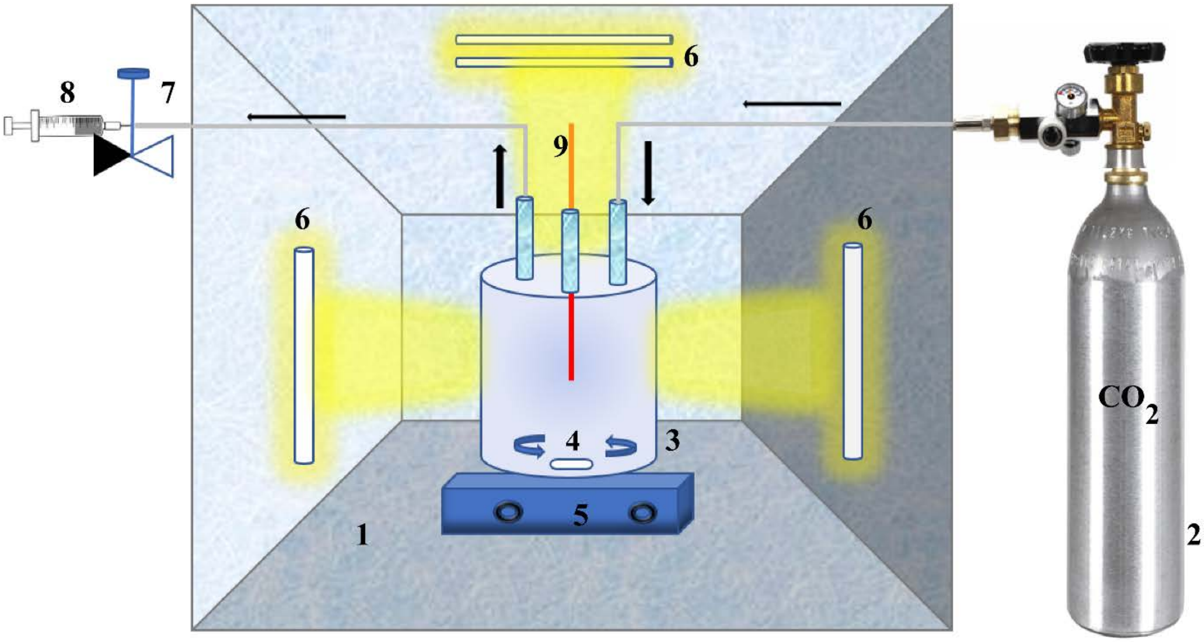

Figure 1: Schematic diagram of photocatalytic reduction experiment.

Table 1: Major parameters along the sampling locations.

Parameters	PSW-1	PSW-2
Temperature (ºC)	30.4	29.8
Salinity (ppt)	33.45	30.5
pH	8.15	7.97
Dissolved Oxygen (mg/l)	4.76	0.85
Alkalinity (mg/l of $CaCO_3$)	220	280
Chloride (ppm)	18515.44	16882.54
Sodium (ppm)	10240.60	9560.42
Total Organic Carbon (ppm)	32.30	48.15

The concentration of CO_2 was measured by both Gas Chromatography (Bruker, GC-450) and titrimetric method ascribed by Strickland and Parson, 1972 [36]. The methanol content was analyzed using the spectrophotometric technique according to the method described by Anpo et al. [17] and Zhan et al. [37].

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussions

In order to evaluate the photocatalytic reduction of CO_2 into methanol under both UV and natural sunlight, P25, C/TiO_2, and 3wt% of Cu-C/TiO_2 photocatalysts were used. The detailed characterization of these photocatalysts was described in our previous studies [13,32]. The photocatalytic reduction experiments were carried out in two different polluted seawater samples collected from different locations. The major constituents of both samples are shown in Table 1.

3.1 Photocatalytic Reduction of CO_2 under UV

The photocatalytic reduction of CO_2 from polluted seawater into the energy-bearing product methanol, has the potential to simultaneous reduce global warming and the energy crisis, since methanol can act as an excellent liquid fuel [38]. The photocatalytic reduction of CO_2 in polluted seawater-1 (PSW-1) and polluted seawater-2 (PSW-2) is shown in Figures 2a and 2b respectively. The corresponding production of methanol in the respective medium is shown in Figure 3a and 3b. Generally carbon modification can reduces the band gap energy [16,39,40], and consequently will enhance the photocatalytic reduction of CO_2. The doping of metal redistributes the charges formed by the light irradiation [17,41,42] and therefore the doping of Cu will reduce the recombination of electron and hole by acting as an electron trapper [43]. Apart from this, prompt excitation of an electron from

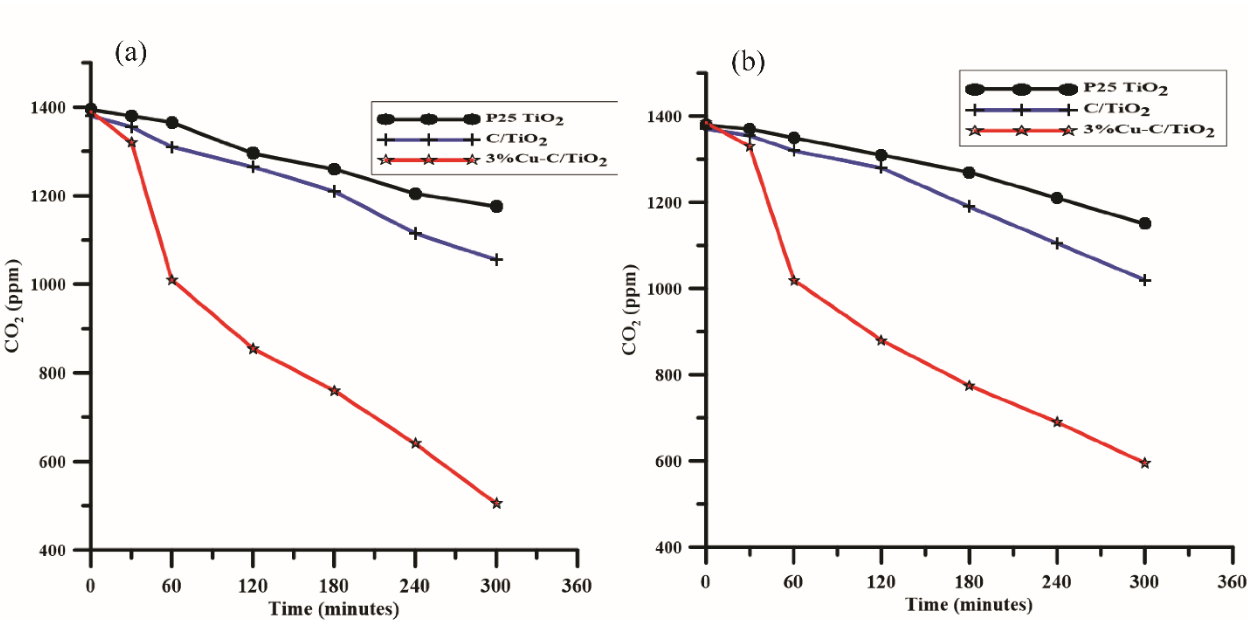

Figure 2: Time dependence on the photocatalytic reduction of CO_2 under UV light (a); PSW-1, (b); PSW-2.

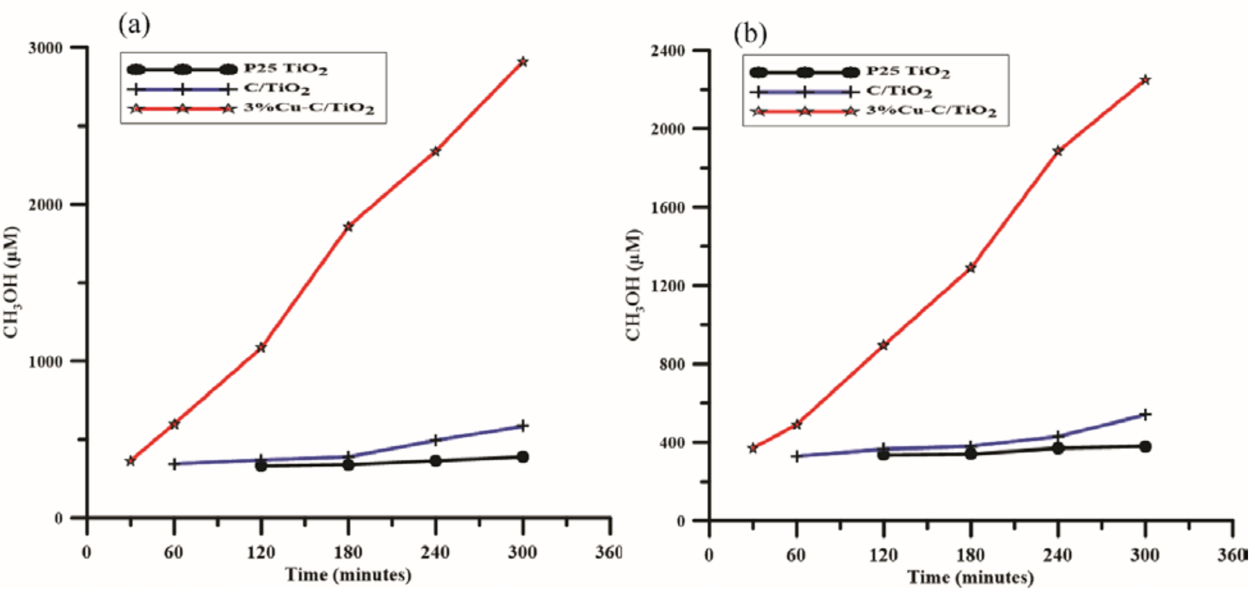

Figure 3: Time dependence on the photocatalytic production of CH_3OH under UV light (a); PSW-1, (b); PSW-2

the valence band to the conduction band will facilitate the separation of electron and hole [44]. This is shown by the results which prove the better photoactivity of C/TiO_2 compared to the P25 TiO_2.

The production of methanol in the matrix of oxygen-depleted water was fairly interest. The observed level of methane in the PSW-2 system was 4.09µM and the concentration was quite high compared to the 0.4µM in the PSW-1 system. When the system is de-aerating the level of the oxygen will go down further, which may effectively increase the activity of methanogens and the production of methanol in the PSW-2 system will be lower than PSW-1. The production of methanol in the case of oxygen-depleted water was low which can be mainly attributed to the competition of methanogenic bacteria over methanol production [35]

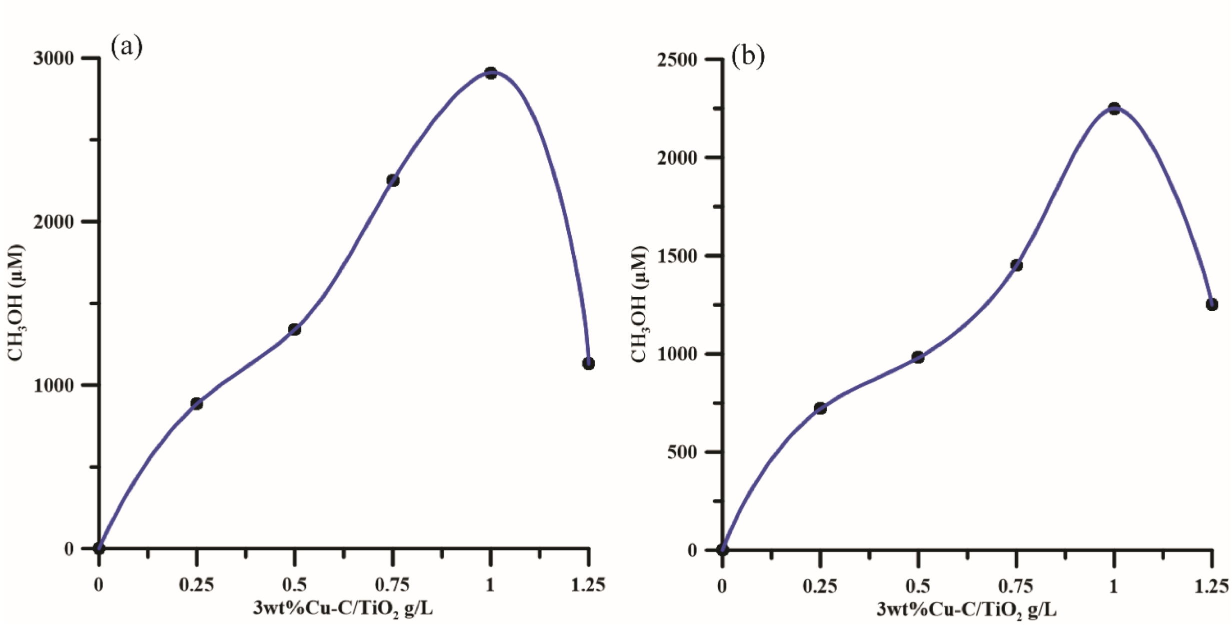

Figure 4: The effect of dosage of 3wt% Cu-C/TiO_2 after 5h irradiation of UV (a); PSW-1, (b); PSW-2

To prove the production of methanol was due to the photocatalytic reduction, a different set of blank experiments were performed. The photocatalytic reduction experiment was carried out with UV light and without TiO_2 and the other one was without UV and with TiO_2. The observed changes of reduction in CO_2 and production of methanol are shown in Figures 4a and 4b, respectively. In the case of the first experiment, there was not significant decline of CO_2. However, in the second set, there was a small change in the initial 30 minutes ascribing the adsorption of CO_2 into the photocatalyst. In both experiments production of methanol was not observed.

3.2 The Reaction Pathway

The detailed photocatalytic CO_2 reduction mechanism has been reported in our previous study [13]. The mechanism was elucidated by the adsorption of CO_2 on doped Cu. The H- atom which is already adsorbed on the metallic Cu surface attacks the C-atom of the adsorbed CO_2 and will help the formation of the formate intermediate. Further attack of H-atoms on C-O bond of formate will lead to the formation of a formaldehyde type intermediate. To end, H-atoms formed on TiO_2 will change the structure of formaldehyde type to methoxy intermediate followed by the formation of methanol. Mostly, 6H radical is involving in the reduction of CO_2 to methanol.

$$CO_2 + 6H^{\bullet} \rightarrow CH_3OH \tag{1}$$

The transformation procedure is not just restricted to the CO_2 species, the carbonate and bicarbonate species are additionally including, the accompanying steps has been included.

$$H_2CO_3 + e^- \rightarrow HCOO^{\bullet} + OH^- \tag{2}$$

$$HCO_3^- + H_2O + e^- \rightarrow HCOO^{\bullet} + 2OH^- \tag{3}$$

$$HCOO^{\bullet} + e^- \rightarrow HCOO^- \tag{4}$$

$$HCOO^- + H^+ \rightarrow HCOOH \tag{5}$$

In the final step, the formic acid is reduced to methanol.

$$HCOOH + 3H_2O + 4e^- \rightarrow CH_3OH + 4OH^- \tag{6}$$

3.3 The effect of copper doping

By trapping the electron, copper serves as an excellent inhibitor for the recombination of an electron-hole pair of the photocatalyst, consequently, it will enhance its photoactivity [13, 43, 45]. Based on the thermodynamic aspects, the capturing of an electron by a metal ion (either Cu^+ or Cu^{2+}) within the surface of the semiconductor

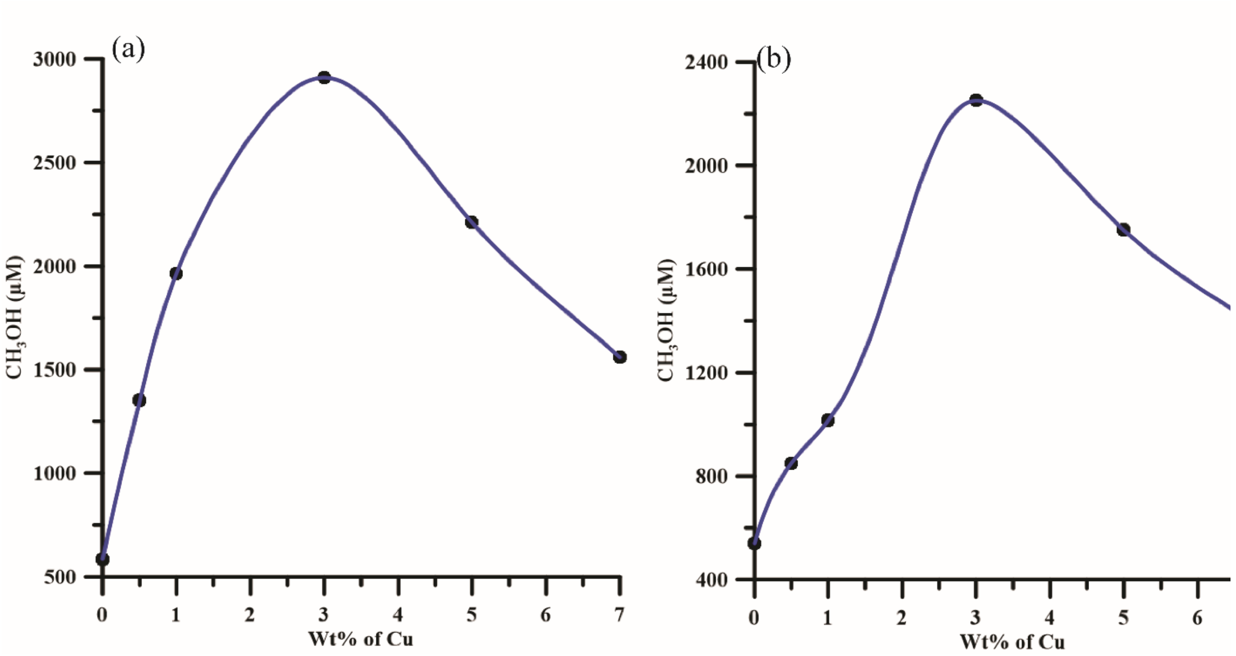

Figure 5: The effect of Cu loading on methanol yield after 5 h irradiation of UV (a); PSW-1, (b); PSW-2

photocatalyst is achievable due to the reduction potential of the metal ion being more positive than conduction band edge of TiO_2 (~ -0.2V) [46]. As a result, Cu will effectively suppress the recombination of electron-hole pairs and enhance the photocatalytic reduction. Furthermore, an unfilled 3d shell in the Cu^{2+} makes easy trapping of an electron on the surface of $CuSO_4$ [45]. Trapping a part of an electron on the conduction band could facilitate the reduction of Cu^{2+} to Cu^+ species. The presence of H^+ and or O_2 in the system could consume the trapped electron and it will re-oxidize Cu^+ to Cu^{2+} [13]. Due to this sequential cycle, the recombination of the electron-hole pair will be effectively declined.

The increase of the weight percentage Cu doping to an optimum level can generally increase the production of methanol, by forming the more active sites on the photocatalytic surface. It is clearly observed in Figures 5a and 5b, that the production of methanol is increased until the doping percentage was optimized at 3wt % of Cu-C/TiO_2 and then starts to decline. This is mainly attributed to the shielding of the photoactive sites on the TiO_2 surface [47,48].

3.4 The effect of catalyst dosage

The effect of the amount of photocatalyst dose on the photocatalytic reduction of CO_2 to methanol was investigated by varying the amount of photocatalyst ranging from 0 to 1.25 g/L under irradiation of UV light. Figures 6a and 6b illustrate the photocatalytic production of methanol in the PSW-1 and PSW-2 samples, respectively after 5 hours irradiation of UV light. The production of methanol was gradually increased up to 1 g/L of 3%Cu-C/TiO_2. When the dosage of the photocatalyst is increased in the medium, the total number of active sites on the photocatalyst surface also increases [49]. Which increases the number of electrons that can be used for the photocatalytic reduction of CO_2 to methanol. Over 1g/L of 3%Cu-C/TiO_2 the concentration of methanol lowered which is likely due to the turbidity of the suspension which reduces the penetration of the light [50,51]. Subsequently, all photocatalyst particles were not uniformly exposed to incident light [43] and thereby the production of methanol was decreased. In addition, the higher dosage may also create a promising condition for surface agglomeration and will lower the active sites, which in turn decreases the methanol yield [52].

3.5 Photocatalytic Reduction of CO_2 under natural sunlight

It is quite interesting to investigate the photocatalytic reduction of CO_2 to methanol using C/TiO_2 and 3%Cu-C/TiO_2 under natural sunlight. The observed photocatalytic reduction of CO_2 is shown in Figures 7a and 7b and the corresponding production of methanol is illustrated in

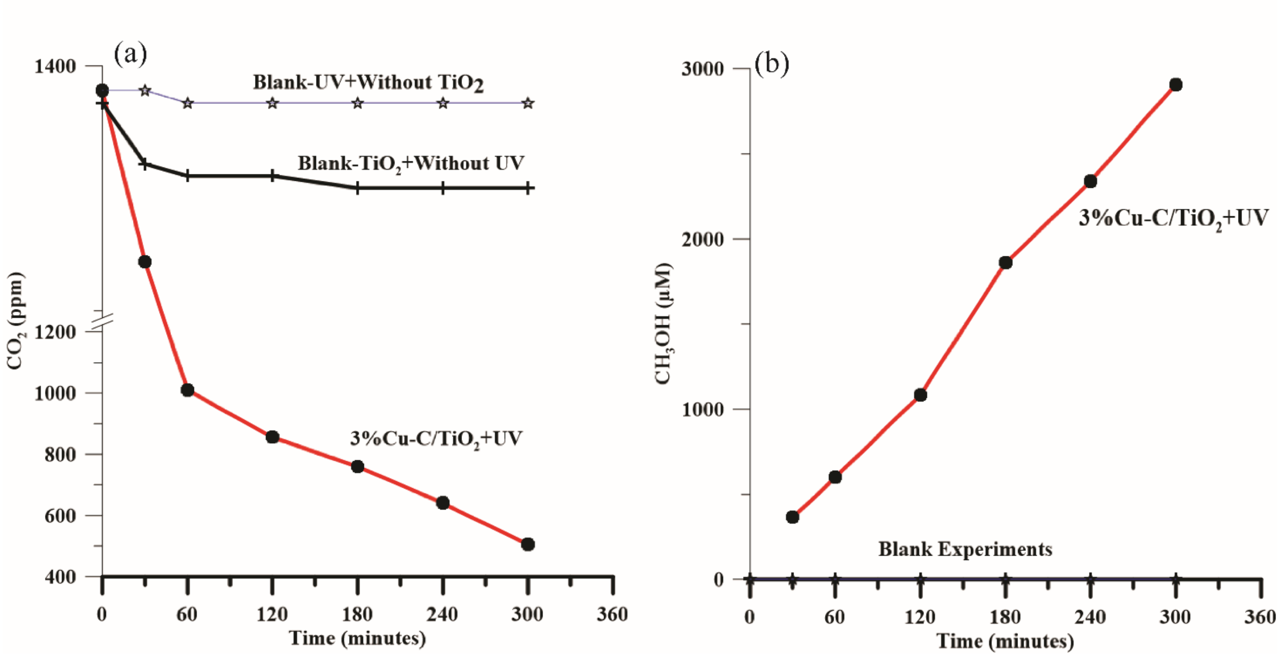

Figure 6: Blank experiment (a); reduction of CO_2 at various conditions, (b); production of methanol at various conditions.

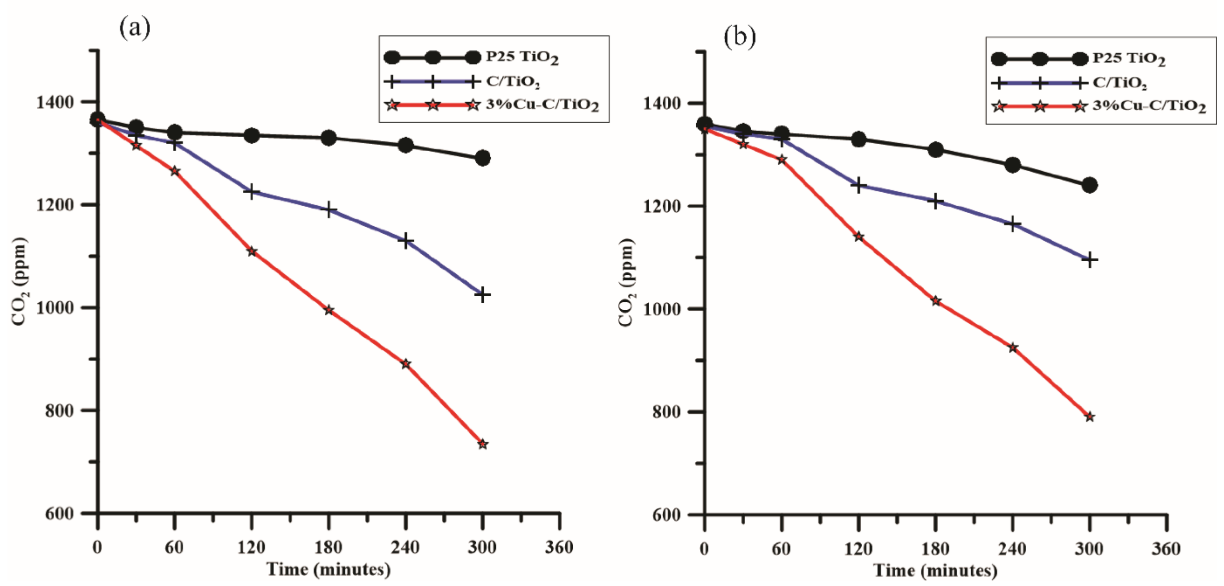

Figure 7: Time dependence on the photocatalytic reduction of CO_2 under sunlight (a); PSW-1, (b); PSW-2

Figure 8a and 8b. There was a slight decline of CO_2 when P25 was the photocatalyst. This is mainly ascribed to the adsorption of CO_2 onto the photocatalytic surface. However, a significant photocatalytic reduction was observed when the photocatalysts C/TiO_2 and 3%Cu-C/TiO_2 were used. The addition of a dopant modifies the electronic structure of TiO_2 by lowering its band gap either by increasing the valence band and/or by decreasing the conduction band energy shifting its absorbance into the visible light region [53]. The maximum photocatalytic reduction was noted using the optimum 3%Cu-C/TiO_2.

The production of methanol by photocatalytic reduction of CO_2 under visible light was observed when C/TiO_2 and 3%Cu-C/TiO_2 were used. However, the absorbance

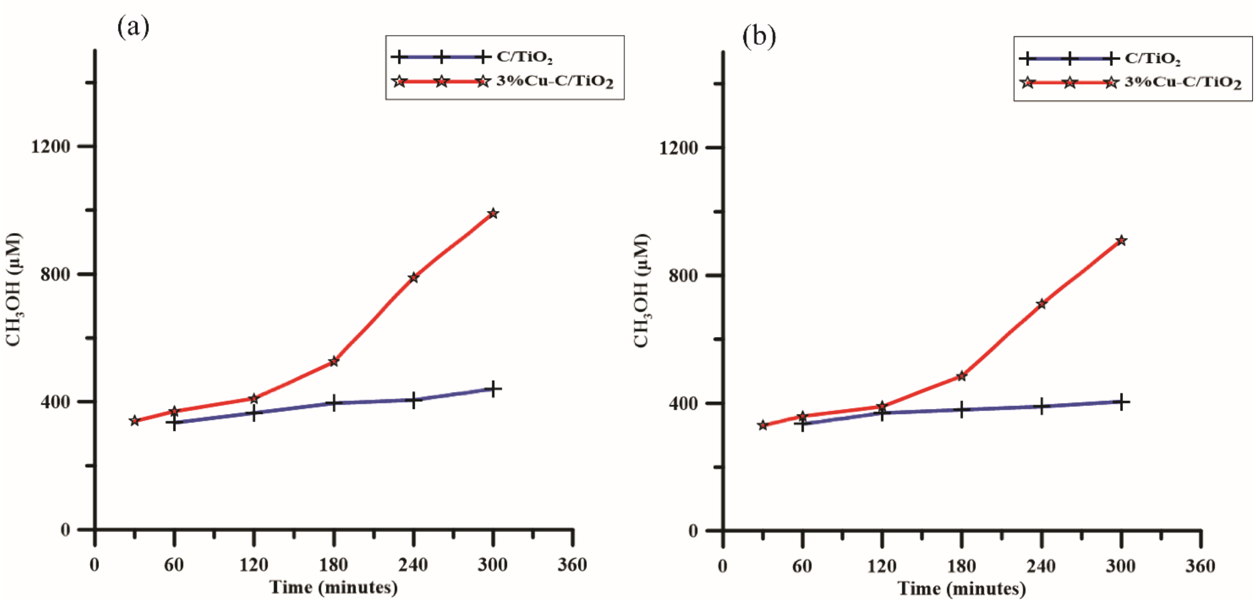

Figure 8: Time dependence on the photocatalytic production of CH_3OH under sunlight (a); PSW-1, (b); PSW-2.

of P25 TiO_2 was limited to the UV region [13], consequently there was no production of methanol detected. The modification of the photocatalyst, TiO_2 with C and Cu greatly enhanced the ability of the photocatalyst to absorb light in the visible region. As discussed in the previous section, the maximum yield of methanol was noted for the PSW-1 sample when the optimized 3% Cu-C/TiO_2 was used as the photocatalyst. It reflects the ability of Cu metal to re-distribute the photogenerated electron and hole by capturing an electron and for the selective photocatalytic reduction of CO_2 to methanol. The observed results open the way to explore environmental application in the visible region in order to make a better green environment.

4 Conclusions

Photocatalytic reduction of the CO_2 present in polluted seawater to methanol using C/TiO_2 and Cu-C/TiO_2 has been carried out under both UV and natural sunlight. Under the present experimental conditions, the optimum dosage was 1g/L and the ideal doping was 3 wt % of Cu. Both carbon modification and copper doping enhance the ability of the photocatalyst to absorb light in the visible region. This is mainly due to the lowering of the bandgap by carbon modification and the suppression of electron and hole recombination by copper, acting as an electron trapper. Due to the environmental condition, PSW-1 system act as the dominant medium for the production of methanol over the PSW-2 system. This is attributed the amplified activity of methanogens at PSW-2 over the methanol production, while in PSW-1, the oxygen depletion was not observed and methanol production was maximum.

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References

[1] Hansen J., Sato M., Russell G., Kharecha P., Climate sensitivity, sea level and atmospheric carbon dioxide, Philos. T. In Roy. Soc. A, 2013,371, 20120294.
[2] Barros V.R., Field C.B., Dokken D.J., Mastrandrea M.D., Mach K.J., Bilir T.E., Chatterjee M., Ebi K.L., Estrada Y.O., Genova R.C., Girma B., Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part B: Regional Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2014
[3] Thornton P.E., Doney S.C., Lindsay K., Moore J.K., Mahowald N., Randerson J.T., Fung I., Lamarque J.F., Feddema J.J., Lee Y.H., Carbon-nitrogen interactions regulate climate-carbon cycle feedbacks: results from an atmosphere-ocean general circulation model, Biogeosciences, 2009, 6(10), 2099-2120.

[4] Tripati A.K., Roberts C.D., Eagle, R.A., Coupling of CO_2 and ice sheet stability over major climate transitions of the last 20 million years, science, 2009, 326(5958), 1394-1397.

[5] Sahir M.H., Qureshi A.H., Specific concerns of Pakistan in the context of energy security issues and geopolitics of the region, Energ Policy, 2007, 35(4), 2031-2037.

[6] Al-Iriani M.A., Energy–GDP relationship revisited: an example from GCC countries using panel causality, Energ Policy, 2006, 34(17), 3342-3350.

[7] Soytas U., Sari R., Ewing B.T., Energy consumption, income, and carbon emissions in the United States, Ecol Econ, 2007, 62(3), 482-489.

[8] Niu S., Ding Y., Niu Y., Li Y., Luo G., Economic growth, energy conservation and emissions reduction: A comparative analysis based on panel data for 8 Asian-Pacific countries, Energ Policy, 2011, 39(4), 2121-2131.

[9] Arouri M.E.H., Youssef A.B., M'henni H., Rault C., Energy consumption, economic growth and CO_2 emissions in Middle East and North African countries, Energ Policy, 2012, 45, 342-349.

[10] Tans P., An accounting of the observed increase in oceanic and atmospheric CO_2 and the outlook for the future, Oceanography, 2009, 22(4), 26-35.

[11] Canadell J.G., Le Quéré C., Raupach M.R., Field C.B., Buitenhuis E.T., Ciais P., Conway T.J., Gillett N.P., Houghton R.A., Marland G., Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks, Proceedings of the national academy of sciences, 2007, 104(47), 18866-18870.

[12] Denman K.L., Brasseur G.P., Chidthaisong A., Ciais P., Cox P.M., Dickinson R.E., Hauglustaine D.A., Heinze C., Holland E.A., Jacob D.J., Lohmann U., Couplings between changes in the climate system and biogeochemistry. In Climate change 2007: The physical science basis, Cambridge University Press, 2007.

[13] Kavil Y.N., Shaban Y.A., Al Farawati R.K., Orif M.I., Zobidi M., Khan S.U., Photocatalytic conversion of CO_2 into methanol over Cu-C/TiO_2 nanoparticles under UV light and natural sunlight, J. Photochem. Photobiol A: Chem., 2017, 347, 244-253.

[14] Henderson M.A., A surface science perspective on TiO2 photocatalysis. Surf. Sci. Rep., 2011, 66(6-7), 185-297.

[15] Lee Y.S., Kim S.J., Venkateswaran P., Jang J.S., Kim H., Kim J.G., Anion co-doped Titania for solar photocatalytic degradation of dyes, Carbon. Lett., 2008, 9(2), 131-136.

[16] Khan S.U., Al-Shahry M., Ingler W.B., Efficient photochemical water splitting by a chemically modified n-TiO_2, science, 2002, 297(5590), 2243-2245.

[17] Anpo M., Yamashita H., Ichihashi Y., Fujii Y., Honda M., Photocatalytic reduction of CO_2 with H_2O on titanium oxides anchored within micropores of zeolites: effects of the structure of the active sites and the addition of Pt, J. Phys. Chem. B, 1997, 101(14), 2632-2636.

[18] Al-Azri Z.H., Chen W.T., Chan A., Jovic V., Ina T., Idriss H., Waterhouse G.I., The roles of metal co-catalysts and reaction media in photocatalytic hydrogen production: Performance evaluation of M/TiO_2 photocatalysts (M= Pd, Pt, Au) in different alcohol–water mixtures, J. Catal., 2015, 329, 355-367.

[19] Chen H., Shao Y., Xu Z., Wan H., Wan Y., Zheng S., Zhu D., Effective catalytic reduction of Cr (VI) over TiO_2 nanotube supported Pd catalysts, Appl. Catal. B-Environ., 2011, 105(3), 255-262.

[20] Choi W., Termin A., Hoffmann, M.R., The role of metal ion dopants in quantum-sized TiO_2: correlation between photo reactivity and charge carrier recombination dynamics, J. Phys. Chem., 1994, 98(51), 13669-13679.

[21] Asahi R.Y.O.J.I., Morikawa T.A.K.E.S.H.I., Ohwaki T., Aoki K., Taga, Y., Visible-light photocatalysis in nitrogen-doped titanium oxides, science, 2001, 293(5528), 269-271.

[22] Umebayashi T., Yamaki T., Itoh H., Asai K., Band gap narrowing of titanium dioxide by sulfur doping, Appl. Phys. Lett., 2002, 81(3), 454-456.

[23] Kukovecz Á., Kordás K., Kiss, J., Kónya, Z., Atomic scale characterization and surface chemistry of metal modified titanate nanotubes and nanowires, Surf. Sci. Rep., 2016, 71(3), 473-546.

[24] László B., Baán K., Varga E., Oszkó A., Erdőhelyi A., Kónya Z., Kiss J., Photo-induced reactions in the CO_2-methane system on titanate nanotubes modified with Au and Rh nanoparticles, Appl. Catal. B-Environ., 2016, 199, 473-484.

[25] Xu C., Killmeyer R., Gray M.L., Khan S.U., Photocatalytic effect of carbon-modified n-TiO_2 nanoparticles under visible light illumination, Appl. Catal. B-Environ., 2006, 64(3), 312-317.

[26] Shaban Y.A., Khan, S.U., Visible light active carbon modified n-TiO_2 for efficient hydrogen production by photoelectrochemical splitting of water, Int. J. Hydrog. Energy., 2008, 33(4), 1118-1126.

[27] Shaban Y.A., El Sayed M.A., El Maradny A.A., Al Farawati R.K., Al Zobidi, M.I., Photocatalytic degradation of phenol in natural seawater using visible light active carbon modified (CM)-n-TiO_2 nanoparticles under UV light and natural sunlight illuminations, Chemosphere, 2013, 91(3), 307-313.

[28] Shaban Y.A., El Sayed M.A., El Maradny A.A., Al Farawati R.K., Al Zobidi M.I., Khan S.U., Photocatalytic removal of polychlorinated biphenyls (PCBs) using carbon-modified titanium oxide nanoparticles, Appl. Surf. Sci., 2016, 365, 108-113.

[29] Shaban Y.A., Solar light-induced photodegradation of chrysene in seawater in the presence of carbon-modified n-TiO_2 nanoparticles, Arab. J. Chem., (in press), DOI: https://doi.org/10.1016/j.arabjc.2018.01.007.

[30] Yamashita H., Nishiguchi H., Kamada N., Anpo M., Teraoka Y., Hatano H., Ehara S., Kikui K., Palmisano L., Sclafani A., Schiavello, M., Photocatalytic reduction of CO_2 with H_2O on TiO_2 and Cu/TiO_2 catalysts, Res. Chem. Intermed., 1994, 20(8), 815-823.

[31] Adachi K., Ohta K., Mizuno, T., Photocatalytic reduction of carbon dioxide to hydrocarbon using copper-loaded titanium dioxide, Sol. Energy, 1994, 53(2), 187-190.

[32] Kavil Y.N., Shaban Y.A., Al Farawati R.K., Orif M.I., Zobidi M., Khan S.U., Efficient Photocatalytic Reduction of CO_2 Present in Seawater into Methanol over Cu/C-Co-Doped TiO_2 Nanocatalyst Under UV and Natural Sunlight, Water Air Soil Poll., 2018, 229(7), 236.

[33] Turki A.J., Metal speciation (Cd, Cu, Pb and Zn) in sediments from Al Shabab Lagoon, Jeddah, Saudi Arabia, Mar. Sci, 2007, 18(1).

[34] El Sayed M.A., Distribution and behavior of dissolved species of nitrogen and phosphorus in two coastal Red Sea lagoons receiving domestic sewage, Mar. Sci, 2002, 13, 47-73.

[35] Orif M.I., Kavil Y.N., Kelassanthodi R., Al-Farawati R., Zobidi, M.I.A., Dissolved methane and oxygen depletion in the two

coastal lagoons, Red Sea. Indian J. Mar. Sci., 2017, 46(7), 1287-1297.

[36] Strickland J.D., Parsons T.R., A practical handbook of seawater analysis, 1972.

[37] Zhan Y.Y., Zhang Y., Li Q.M., Du X.Z., A novel visible spectrophotometric method for the determination of methanol using sodium nitroprusside as spectroscopic probe, J. Chin. Chem. Soc., 2010, 57(2), 230-235.

[38] Blug M., Leker J., Plass L., Günther A., Methanol Generation Economics. In Methanol: The Basic Chemical and Energy Feedstock of the Future, Springer, Berlin, Heidelberg, 2014, 603-618.

[39] Binas V., Venieri D., Kotzias D., Kiriakidis G., Modified TiO2 based photocatalysts for improved air and health quality, J. Materiomics, 2017, 3(1), 3-16.

[40] Wojtoniszak M., Dolat D., Morawski A., Mijowska E., Carbon-modified TiO_2 for photocatalysis, Nanoscale Res. Lett., 2012, 7(1), 235.

[41] Hirano K., Inoue K., Yatsu, T., Photocatalysed reduction of CO_2 in aqueous TiO_2 suspension mixed with copper powder, J. Photochem. Photobiol A: Chem., 1992, 64(2), 255-258.

[42] Janisch R., Gopal P., Spaldin N.A., Transition metal-doped TiO_2 and ZnO—present status of the field, J. Phys. Condens.. Matter., 2005, 17(27), R657.

[43] Tseng I.H., Chang W.C., Wu, J.C., Photoreduction of CO_2 using sol–gel derived titania and titania-supported copper catalysts, Appl. Catal. B-Environ., 2002, 37(1), 37-48.

[44] Uddin M.R., Khan M.R., Rahman M.W., Yousuf A., Cheng C.K., Photocatalytic reduction of CO_2 into methanol over $CuFe_2O_4/TiO_2$ under visible light irradiation, React. Kinet. Mech. Cat., 2015, 116(2), 589-604.

[45] Slamet H.W.N., Purnama E., Riyani K., Gunlazuardi J., Effect of copper species in a photocatalytic synthesis of methanol from carbon dioxide over copper-doped titania catalysts, World. Appl.Sci. J., 2009, 6(1), 112-122.

[46] Chiang K., Amal R., Tran, T., Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide, Adv.Environ. Res., 2002 6(4), 471-485.

[47] Wu J.C., Photocatalytic reduction of greenhouse gas CO_2 to fuel, Catal. Surv. Asia., 2009, 13(1), 30-40.

[48] Kaneco S., Kurimoto H., Ohta K., Mizuno T., Saji A., Photocatalytic reduction of CO_2 using TiO_2 powders in liquid CO_2 medium, J. Photochem. Photobiol A: Chem., 1997, 109(1), 59-63.

[49] Ojemaye M.O., Okoh O.O., Okoh A.I., Performance of $NiFe_2O_4$-SiO_2-TiO_2 Magnetic Photocatalyst for the Effective Photocatalytic Reduction of Cr (VI) in Aqueous Solutions, J. Nanomater., 2017.

[50] Sasirekha N., Basha S.J.S., Shanth, K., Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide, App. Catal. B-Environ., 2006, 62(1), 169-180.

[51] Kočí K., Obalová L., Matějová L., Plachá D., Lacný Z., Jirkovský J., Šolcová O., Effect of TiO_2 particle size on the photocatalytic reduction of CO_2, App. Catal. B-Environ., 2009, 89(3), 494-502.

[52] Yang H.C., Lin H.Y., Chien Y.S., Wu J.C.S., Wu H.H., Mesoporous TiO_2/SBA-15, and Cu/TiO_2/SBA-15 composite photocatalysts for photoreduction of CO_2 to methanol, Catal. Lett., 2009, 131(3-4), 381-387.

[53] Geiss O., Cacho C., Barrero-Moreno J., Kotzias D., Photocatalytic degradation of organic paint constituents-formation of carbonyls, Build. Environ., 2012, 48, 107-112.