Synthesis and Characterization of a Ternary Nanocomposite Based on CdSe Decorated Graphene-TiO₂ and its Application in the Quantitative Analysis of Alcohol with Reduction of CO₂

Asghar Ali*, Md Rokon Dowla Biswas**, Yonrapach Areerob**,
Dinh Cung Tien Nguyen**, and Won-Chun Oh**†

**University of Chitral, Chitral, Khyber Pakhtunkhwa, Pakistan*

***Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 31962, Korea*

(Received May 1, 2018; Revised May 20, 2018; Accepted May 21, 2018)

ABSTRACT

In this work, photocatalytic CO₂ reduction over a CdSe-graphene-TiO₂ nanocomposite has been studied. The obtained material was successfully fabricated via ultrasonic technique. The physical properties of the as-synthesized materials were characterized by some physical techniques. The TiO₂ and CdSe dispersed graphene nanocomposite showed excellent results of strong reduction rates of CO₂ compared to the results of bare TiO₂ and binary CdSe-graphene. An outstanding point of the combination of CdSe-TiO₂ and graphene appeared in the form of great photocatalytic reduction capability of CO₂. The photocatalytic activity of the as-fabricated composite was tested by surveying for the photoreduction of CO₂ to alcohol under UV and visible light irradiation, and the obtained results imply that the as-prepared CdSe-graphene-TiO₂ nanocomposite is promising to become a potential candidate for the photocatalytic CO₂ reduction.

Key words : CO₂ reduction, CdSe-graphene-TiO₂, Photocatalytic activity

1. Introduction

The decline in fossil resources and growing concerns about CO₂ emissions are now a major global challenge.^{1,2)} Carbon dioxide (CO₂), the main and most abundant green-house gas, and CO₂ levels in atmospheric are higher than in the past decade.^{3,4)} The increase in the level of atmospheric carbon dioxide (CO₂) caused serious concerns about global warming.⁵⁻⁸⁾ Therefore, it is an urgent need to convert CO₂ into useful energy products. A converting CO₂ to useful products is not only potential way to control the greenhouse effect, but also a very convenient way of decreasing fuel consumption to solve the energy problem.⁹⁻¹³⁾ Artificial photosynthesis (photocatalysis and photo electrocatalysis) is an innovative technology to convert CO₂ into valuable chemicals.^{14,15)} Solar fuel production by CO₂ photocatalytic conversion provides a best way for carbon cycling and fulfill the deficiency of energy demand and controlling increasing CO₂ levels.^{16,17)} A researcher focuses on a semiconductor-based photocatalytic reduction of CO₂ with H₂O to renewable hydrocarbon fuels by solar energy.¹⁸⁾ Among many kinds of semiconductor, titanium dioxide TiO₂ is the outstanding materials due to unique properties (e.g. cheap, nontoxic, and abundant n-type semiconductor), and most used in photocatalysis, photodegradation of organic dyes in a variety of

applications.^{19,20)} CH₃OH is a primary product of semiconductor-based material for CO₂ reduction,^{21,22)} but the main drawbacks of TiO₂ are its large band gap (3.2 eV) and fast recombination of photogenerated charge carriers which effected the catalytic capacity.²³⁾ To decrease these barriers and enhance the photocatalytic efficiency of photocatalysts, the TiO₂ doped with either anions or cations,²⁴⁻²⁷⁾ surface coupling with metals or semiconductors, such as CdSe,²⁸⁻³⁰⁾ CdS^{31,32)} and CdTe^{33,34)} and enhancing the structure of photocatalysts to open their surface area, porosity or reactive facets.^{35,36)} In recent decades, the application of an ultrasound-based sonochemical process as an advanced oxidation process has gained more attention in terms of the purification of polluted effluents because of its high efficiency and an easy operation. During this process, ultrasound waves lead to a quick growth and collapse of bubbles within the solution, which results in an extremely high temperature and pressure in the bubbles. The use of ultrasound to degrade dye pollutants consumes large amounts of energy, and a complete mineralization of the organic pollutants rarely occurs from the application of sonolysis alone.³⁷⁾ Graphene has unique electrochemical properties such as large theoretical specific area, excellent electron mobility, and high transparency. Graphene oxide (GO) has been used to couple with various photocatalysts to enhance the efficiency of photocatalytic activity.³⁸⁻⁴⁸⁾ Metal oxides coupled with graphene enhance visible light absorption and improve the efficiency of charge splitting, which is important for the CO₂ reduction of visible photocatalyst absorption.^{47,51)} In this paper, a new

†Corresponding author : Won-Chun Oh

E-mail : wc_oh@hanseo.ac.kr

Tel : +82-41-660-1337 Fax : +82-41-688-3352

CdSe-graphene-TiO₂ materials were fabricated by ultra-sonication techniques. The photocatalytic CO₂ reduction was then conducted UV and visible light irradiation.

2. Experimental Procedure

2.1. Materials

Ethanol (C₂H₅OH, 95%), selenium powder (Se, 99%), sodium sulfite (Na₂SO₃·7H₂O, 95%) were purchased from Duskan Pure Chemicals Co. Ltd., Korea. Cadmium acetate dihydrate ((CH₃COO)₂Cd, 98%) was purchased from Daejung Chemicals Co. Ltd., Korea. Titanium (IV) oxide (TiO₂, anatase, and nano power, 99.7%) used as a titanium source was purchased from Sigma-Aldrich Co. (USA).

2.2. Preparation of CdSe composite

In a typical procedure, 1.5 g Na₂SO₃ and 0.3 g Se powder were added to 40 mL distilled water. After vigorous stirring for 1 h at 90°C to form the transparent dispersion, 0.05 g Cd(CH₃COO)₂ and 5 mL NH₄OH were dropped into the above dispersion and stirring continued for 1 h. At the end of that second hour of stirring, the prepared solution was sonicated for 2 h. The mixture was filtered through Whatman filter paper (Φ = 110 mm). The product was washed with distilled water 3 times and with 95% ethanol twice. After drying under a vacuum at 100°C for 8 h, the material was synthesized.

2.3. Preparation of CdSe-graphene-TiO₂ composite

Separately, 300 mg graphene oxide, which was dispersed in 20 mL EG using an ultrasonication (250W) for 30 min and the mixture of ethanol : H₂O : titanium (IV) n-butoxide = 35 : 15 : 4 (by mass ratio) were added drop by drop to the above CdSe dispersion to obtain the final dispersion. The obtained dispersion was subjected to hydrothermal treatment at 100°C for 10 h and then naturally reduced to ambient temperature. The mixture was filtered through Whatman filter paper (Φ = 110 mm). The product was washed with distilled water 3 times and with 95% ethanol twice. After drying under a vacuum at 105°C for 24 h before heat treatment at 500°C for 2 h, the materials were prepared.

2.4. Characterization of sonocatalysts

An X-ray diffraction (XRD, Shimadzu XD-D1) was made using monochromatic high-intensity CuKα radiation (λ = 1.5406 Å). Nitrogen adsorption/desorption isotherm studies were investigated using a Micromeritics ASAP 2020 M+C operating at 77 K. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) method. The morphology, shape, structure, size, and distribution of the nanoparticles of the products were investigated using SEM (JSM-5600 JEOL, Japan) and TEM analysis. The EDS analysis was used to test the element mapping of the as-fabricated materials (attached to the SEM analysis). The XPS analysis was observed using a

VG Scientific ESCALAB250 XPS system equipped with a monochromated AlKα X-ray source (hν = 1,486.6 eV) with charge compensation. A UV-vis diffuse reflectance spectra (DRS) analysis was obtained by UV-vis spectrophotometry (Neosys-2000) by using BaSO₄ as a reference at room temperature. The analysis was converted from reflection to absorbance by the Kubelka-Munk method. The Raman spectra were achieved by spectrometry (Jasco Model NRS-3100) with an excitation laser wavelength of 532.06 nm.

2.5. Photocatalytic reduction of CO₂

The photocatalytic capacity of CO₂ reduction was investigated using CdSe-graphene, CdSe-graphene-TiO₂ as a photocatalysts. In this experiment, 150 mg of the photocatalyst was dissolved in a 100 ml NaHCO₃ 0.04 M and continuously stirred, extremely high purity CO₂ was filtered through the reactor for 30 minutes to remove O₂, then the suspension solution was magnetic stirred and then irradiated to visible light by a metal halide (500W, SOLAREEDGE700, Perfect Light, China). The distance between the light source and reaction vessel was maintained as 10 cm and the temperature within the reactor was maintained at 10°C by placing a continuous water loop in a jacket around the reactor. The photocatalytic efficiency was tested within 2 days and in each 12 h interval the reactor could cool down naturally for CH₃OH desorption from the catalyst. The obtained solution was centrifuged and analyzed by GC. Further the chromic acid test for alcohols was also introduced to the samples. For example, into the 10 ml sample 0.1 M CrO₃ was put and stirred for 15 min. after that centrifuge the sample and find their concentration peak with the help of UV spectrophotometer.

3. Results and Discussion

The information of crystal structure and composition of CdSe-graphene-TiO₂ via facile ultra-sonication techniques

Fig. 1. XRD pattern of CdSe, graphene-TiO₂ and CdSe-graphene-TiO₂.

were synthesized by power XRD measurement. Fig. 1 depicts the XRD patterns of CdSe-graphene, graphene-TiO₂ and CdSe-graphene-TiO₂. Fig. 1 shows that TiO₂ is the anatase structure. In graphene-TiO₂ composite, the results of XRD diffraction peaks around 2θ of 25.48, 37.8, 48.0 and 53.7, which can be indexed to the characteristic peaks (101), (004), (200) and (105) [JCPDS PDF#00-21-1272], respectively. For characterization of crystallinity of CdSe and CdSe-graphene-TiO₂, the XRD diffraction peaks appeared at 25.3, 42.1 and 50 belongs to the diffractions of (111), (220) and (311) (JCPDS Card #77-2307). There is no graphene peak in the obtained composites due to the low content.⁵²⁾ XRD patterns exhibited a decrease of TiO₂ intensity peaks in CdSe-graphene-TiO₂ (2θ) at 25.1, 37.0, 37.7, 38.5, 48.0,

53.8, 55.0 and 62.6, [JCPDS PDF#00-65-2891] respectively. Moreover Fig. 1 shows that some Cd peaks is also present around 2θ of 32, 35.2 and 38.3, which can be assigned to the characteristic peaks (002), (001), and (101) [JCPDS PDF#00-21-1272].

The elemental microanalysis and element weight % of the ultrasonication assisted CdSe, CdSe-graphene-TiO₂ and graphene-TiO₂ nanocomposites were characterized by EDX analysis as shown in the Fig. 2(a-c). The spectra show that the C, O, Ti, Cd and Se are major elements for the CdSe-graphene-TiO₂ nanocomposites. From EDX data, C elemental peak shows evidence of graphene sheet. The Ti and O elemental peaks are the precursor material. And high diffraction Ti peaks appear at 4.54 and 4.98 keV, while Cd and

Fig. 2. EDX spectra of the (a) CdSe, (b) CdSe-graphene-TiO₂ and (c) graphene-TiO₂.

Se elemental peak appear at 3.2, 3.9, 11.4 and 12.5 keV, respectively.⁵³⁾

Figure 3 presented the SEM images of the CdSe, CdSe-graphene and CdSe-graphene-TiO₂ with different magnification. From the Fig. 3(a) to (b), CdSe particles and TiO₂ particles were roughly dispersed and these particles highly grow on the surface graphene. From Fig. 3(c-d), it depicted that spherical-shaped CdSe particles are anchored on the graphene surface. The plate-like structure of graphene shows the existence of oxygen functionalities on the surface

of graphene. Owing to a Van der Waals interaction, graphene sheets turn to graphitic structure therefore the attachment of nanoparticles on the graphene sheets is helpful to overcome these interactions.⁵⁴⁾ Fig. 3(e-f) displays the CdSe-graphene-TiO₂ nanocomposites which clearly exhibits the difference point of the binary and ternary materials. After combination of TiO₂, the brighter spot arises in the ternary composite shown that the CdSe-graphene-TiO₂ particles were successful and of proper distribution pattern. TEM images were taken for furthermore analysis and pro-

Fig. 3. SEM images of the (a-b) CdSe, (c-d) CdSe-graphene, and (e-f) CdSe-graphene-TiO₂.

Fig. 4. TEM images of CdSe-graphene-TiO₂ (a) 50 nm and (b) 100 nm.

vide the clear morphology and shape of the CdSe-graphene-TiO₂ nanocomposites. Fig. 4(a) and (b) shows the different magnification of the CdSe-graphene-TiO₂ nanocomposites. From the Fig. 4(a-b), it clearly seen that the spherical CdSe were existed with dark in color and highly agglomerated structure is anchored onto the surface of the graphene sheets. On the other hand, graphene nanosheets covered with TiO₂ particles attached unevenly to the surface of graphene sheets and almost in the circular form. The average size of the TiO₂ particles approximately is 6 to 10 nm. During ultrasonic assisted synthesis of CdSe-graphene-TiO₂, graphene sheet is prevented with partial agglomeration and TiO₂ nanoparticles are remain on the CdSe nanosheets and graphene.⁵⁵⁾

The chemical states of the components elements of the CdSe-graphene-TiO₂ nanocomposites were analyzed by XPS. Fig. 5(a) presented the XPS survey spectrum indicated peaks corresponding to Se, Cd, Ti, O and C components exhibited the formation of CdSe-graphene-TiO₂ nanocomposites. Fig. 5(b) has clearly shown that C 1s has a strong peak located between 285 to 290 eV. These values of binding energies have the C-C at 284.8 eV, C-O at 286 eV and C=O at ~ 289 eV corresponding to each functional group. This consequence shows that some partial oxygen functional groups contain in studied nanocomposites.⁵⁶⁾ Fig. 5(c) shows the O 1s peak located at 532.5 eV assigned to C-O and C=O groups. After the heat treatment, the O 1s region may be overlapped by other chemical species peaks.^{57,58)} The present of C-OH group can be proven by a peak at 534.7 eV.⁵⁷⁾ Fig. 5(d) illustrates the Ti_{2p} peaks, which located different energy position (460.4 eV and 466.5 eV), which indicates that the Ti⁺⁴ oxidation state.⁵⁹⁾ Fig. 5(e) and (f) shows the binding energies positions of Cd_{3d3/2} and Cd_{3d5/2} located at 407 eV and 413 eV. And, Se_{3d} core level peak was confirm at 55.2 eV. The CdSe sample proves the present of Cd⁺² and Se⁻² ions.⁶⁰⁾

Further the Raman spectroscopy used for the study of structural properties of the CdSe-graphene-TiO₂. Fig. 6 pro-

vides detail about GO and nanocomposites. It has observed that the peak around the 220 cm⁻¹ waves can be assigned CdSe phase.^{61,62)} The peaks around to 200 cm⁻¹ to 300 cm⁻¹ and 410 cm⁻¹ show the presence of the Se⁰ and anatase TiO₂.^{63,64)} The characteristic D band appears at 1354 cm⁻¹ and G bands appear at 1590 cm⁻¹, which are corresponding to the vibration of carbon atoms in disorder or defect sites and in plane vibration of sp² and sp³ bonded carbon atoms, respectively.⁶⁵⁾ The nature of the defects can be determined from the intensity ratio of the corresponding D to G band. Moreover, the calculated I_D/I_G was found to be ~ 1.07 eV. The intensity ratio I_D/I_G ratio helps to evaluate the defects of CdSe-graphene-TiO₂ samples where a higher ratio Shown more defects.

Figure 7(a-b) shows the UV-visible diffuse reflectance spectra of CdSe, TiO₂ and CdSe-graphene-TiO₂. As shown in Fig. 7, an increase of absorbance toward the visible region 550 nm was observed with the ternary compound. And, it clearly shows the homogenous distribution of the nanoparticles with increase of the absorbance. After the anchoring of CdSe on graphene, the absorption region shifts to the visible light region.⁶⁶⁾ From Fig. 8(a-b), shown that after the synthesis of a composite (TiO₂ and CdSe-TiO₂) with graphene, a threshold wavelength was extended to 405 and 797 nm and band gap energies were 3.4 and 2.6 eV estimated by using the Kubelka-Munk theory, respectively.^{67,68)} The reason of the variation of band gap energies of as-prepared composites may possibly be introduction of CdSe and TiO₂ particles on the graphene sheet surface or partial agglomeration, which may affect the optical property of nanocomposites.^{69,70)} The decreasing Eg of the CdSe-graphene-TiO₂ nanocomposite can be attributed to both the inherent light absorption capacity of carbon materials and the electron transitions between carbon of graphene and metal oxide (CdSe and TiO₂) phase.^{71,72)}

The photocatalytic capacity of the as-synthesized CdSe-graphene-TiO₂ material was tested by surveying the photocatalytic reduction of CO₂ under UV-visible and visible light

Fig. 5. XPS results of the CdSe-graphene-TiO₂ nanocomposite (a) survey scan spectra (b) C_{1s} (c) O_{1s} (d) Ti_{2p} (e) Cd_{3d} and (f) Se_{3d}.

irradiation (in the region of 300 ~ 450 nm). Using alcohol oxidation method with CrO₃ four types of sample were synthesized. Fig. 9 exhibited the photocatalytic capacity of the photocatalytic reduction of CO₂ four different samples. Fig. 9(a) shows the reduction effect of CO₂-dissolved water samples, and Fig. 9(b) is the corresponding reduction effect for

commercial carbonated water without additional CO₂, showing reaction rate with different reaction conditions with photocatalyst. With increasing time, the photocatalytic efficiency increases. Fig. 9 shows that the amount of alcohol increases with the time of light irradiation.

Fig. 6. Raman spectra of CdSe-graphene-TiO₂ nanocomposites.

To find the methanol concentration in CdSe-graphene-TiO₂ nanocomposites, CrO₃ use as an oxides agent. During experiment methanol was oxides and the result the CrO₃ oxidation form change to reduce form then the color of the sample was change. CH₃OH can follow indirectly on the CrO₃, increasing methanol concentration the color of CrO₃ were changed.

Further for conformation chromic acid test result, CdSe-graphene-TiO₂ were also evaluated by gas-chromatography (GC). Photocatalytic reaction time is up to 48 h and, after

Fig. 7. Diffuse reflectance spectra (DRS) of (a) CdSe, CdSe-graphene-TiO₂ (b) TiO₂.

12 h, liquid product is manually taken for GC analysis. A series of test were conducted for the confirmation of CH₃OH, 1st control experiment was conducted in dark with catalysts, and 2nd experiment was conducted under light radiation but no catalysts, both results shown no CH₃OH were detected. These control experiments show that both irradiation and

Fig. 8. Diffuse reflectance spectra (DRS) obtained from Kubelka-Munk transformation function versus photon energy (a) TiO₂ and (b) CdSe-graphene-TiO₂.

Fig. 9. (a) Photocatalytic reduction of CO_2 with carbonated water without CO_2 gas under visible light and (b) photocatalytic reduction of CO_2 with water dissolve with CO_2 gas under UV light.

light catalysts are important factors for the uptake of CO_2 for CH_3OH formation.

The photocatalytic efficiency of the CdSe-graphene- TiO_2 composites with different time interval was evaluated in term of photoreduction of CO_2 to CH_3OH under visible and UV light irradiation. Fig. 10(a-b) shows the effect of methanol yield. The results show that the photocatalytic CO_2 reduction of CdSe-graphene- TiO_2 under UV light were found to be higher than that visible light. The methanol yield for CdSe-graphene- TiO_2 (12 h), CdSe-graphene- TiO_2 (24 h), CdSe-graphene- TiO_2 (36 h) and CdSe-graphene- TiO_2 (28 h) under visible light are 0.12, 0.44, 0.49 and 0.69 $\mu\text{mol g}^{-1}\text{h}^{-1}$, and methanol yield for CdSe-graphene- TiO_2 (12 h), CdSe-graphene- TiO_2 (24 h), CdSe-graphene- TiO_2 (36 h) and CdSe-graphene- TiO_2 (48 h) under UV light are 0.36, 0.54, 0.71 and 1.12 $\mu\text{mol g}^{-1}\text{h}^{-1}$, respectively. Graphene oxide plays the role of an electron acceptor, photosensitizer, and the adsorbent to efficiently enhance the photodegradation of organic dyes.

Fig. 10. The methanol yield in the photo reduction of CO_2 under (a) visible light irradiation and (b) UV light irradiation using CdSe-graphene- TiO_2 nanocomposites as photocatalysts.

The presence of the high density of oxygen-containing functional groups, such as hydroxyl groups, epoxy, and carboxyl at the edge or on the large surface area of graphene oxide provides the more space for ionic/electro interaction between dye molecules and the aromatic rings of graphene oxide sheets, and from that, the better absorptivity can be achieved.⁷³⁻⁷⁶⁾

4. Conclusions

In conclusion, we profitably prepared CdSe-graphene- TiO_2 nanocomposites by facial ultrasonic method. SEM and TEM results indicated that the TiO_2 particles were uniformly dispersed on the surface graphene sheets supported by CdSe. TiO_2 and CdSe- TiO_2 are in anatase structure with size approximately 6 to 10 nm. The samples were tested under UV-visible and visible light irradiation to convert CO_2 to CH_3OH , the experimental results shown excellent light

absorption and enhanced photocatalytic efficiency for CO₂ reduction under both UV-visible and visible light irradiation. The maximum CH₃OH yield 1.12 μmolg⁻¹h⁻¹ was achieved under UV-visible light irradiation. This work reveals that CdSe-graphene-TiO₂ could be used as a promising candidate for CO₂ reduction.

REFERENCES

1. M. Aresta, A. Dibenedetto, and A. Angelini, "Catalysis for the Valorization of Exhaust Carbon: from CO₂ to Chemicals, Materials, and Fuels. Technological Use of CO₂," *Chem. Rev.*, **114** [3] 1709-42 (2014).
2. S. C. Roy, O. K. Varghese, M. Paulose, and C. A. Grimes, "Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons," *ACS Nano*, **4** [3] 1259-78 (2010).
3. B. Guo, Y. Geng, B. Franke, H. Hao, Y. Liu, and A. Chiu, "Uncovering China's Transport CO₂ Emission Patterns at the Regional Level," *Energy Policy*, **74** 134-46 (2012).
4. B. C. O'Neill and M. Oppenheimer, "Dangerous Climate Impacts and the Kyoto Protocol," *Science*, **296** [5575] 1971-72 (2002).
5. S. Solomon, G.-K. Plattner, R. Knutti, and P. Friedlingstein, "Irreversible Climate Change due to Carbon Dioxide Emissions," *Proc. Natl. Acad. Sci. U. S. A.*, **106** [6] 1704-9 (2009).
6. D. Lüthi, M. L. Floch, B. Bereiter, T. Blunier, J.-M. Barnola, U. Siegenthaler, D. Raynaud, J. Jouzel, H. Fischer, K. Kawamura, and T. F. Stocker, "High-Resolution Carbon Dioxide Concentration Record 650,000-800,000 Years before Present," *Nature*, **453** 379-82 (2008).
7. S. Kiatphuengporn, M. Chareonpanich, and J. Limtrakul, "Effect of Unimodal and Bimodal MCM-41 Mesoporous Silica Supports on Activity of Fe-Cu Catalysts for CO₂ Hydrogenation," *Chem. Eng. J.*, **240** 527-33 (2014).
8. W. Donphaia, K. Faungnawakij, M. Chareonpanich, and J. Limtrakul, "Effect of Ni-CNTs/Mesoporous Silica Composite Catalysts on Carbon Dioxide Reforming of Methane," *Appl. Catal., A*, **475** 16-26 (2014).
9. S. N. Habisreutinger, L. Schmidt-Mende, and J. K. Stolarczyk, "Photocatalytic Reduction of CO₂ on TiO₂ and Other Semiconductors," *Angew. Chem., Int. Ed.*, **52** [29] 7372-408 (2013).
10. A. Dhakshinamoorthy, S. Navalon, A. Corma, and H. Garcia, "Photocatalytic CO₂ Reduction by TiO₂ and Related Titanium Containing Solids," *Energy Environ. Sci.*, **5** [11] 9217-33 (2012).
11. H. Shi, G. Chen, C. Zhang, and Z. Zou, "Polymeric g-C₃N₄ Coupled with NaNbO₃ Nanowires toward Enhanced Photocatalytic Reduction of CO₂ into Renewable Fuel," *ACS Catal.*, **4** [10] 3637-43 (2014).
12. V. Kumar, N. Labhsetwar, S. Meshram, and S. Rayalu, "Functionalized Fly Ash Based Alumino-Silicates for Capture of Carbon Dioxide," *Energy Fuels*, **25** [10] 4854-61 (2011).
13. K. Huang, C. L. Sun, and Z. J. Shi, "Transition-Metal-Catalyzed C-C Bond Formation through the Fixation of Carbon Dioxide," *Chem. Soc. Rev.*, **4** [5] 2435-52 (2011).
14. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, and C. P. Kubiak, "Photochemical and Photoelectrochemical Reduction of CO₂," *Annu. Rev. Phys. Chem.*, **63** 541-69 (2012).
15. O. K. Varghese, M. Paulose, T. J. LaTempa, and C. A. Grimes, "High-Rate Solar Photocatalytic Conversion of CO₂ and Water Vapor to Hydrocarbon Fuels," *Nano Lett.*, **9** [2] 731-37 (2009).
16. S. Wang and X. C. Wang, "Photocatalytic CO₂ Reduction by CdS Promoted with a Zeolitic Imidazolate Framework," *Appl. Catal., B*, **162** 494-500 (2015).
17. T. Inoue, A. Fujishima, S. Konishi, and K. Honda, "Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders," *Nature*, **277** 637-38 (1979).
18. P. W. Huo, Z. Y. Lu, X. L. Liu, X. Gao, J. M. Pan, D. Wu, J. Ying, H. M. Li, and Y. S. Yan, "Preparation Molecular/Ions Imprinted Photocatalysts of La³⁺@POPD/TiO₂/Fly-Ash Cenospheres: Preferential Photodegradation of TCs Antibiotics," *Chem. Eng. J.*, **198-199** 73-80 (2012).
19. X. Nie, G. Y. Li, P. K. Wong, H. J. Zhao, and T. C. An, "Synthesis and Characterization of N-Doped Carbonaceous/TiO₂ Composite Photoanodes for Visible-Light Photoelectrocatalytic Inactivation of Escherichia Coli K-12," *Catal. Today*, **230** 67-73 (2014).
20. J. C. S. Wu, H.-M. Lin, and C.-L. Lai, "Photo Reduction of CO₂ to Methanol Using Optical-Fiber Photoreactor," *Appl. Catal., A*, **296** [2] 194 -200 (2005).
21. Q. D. Truong, T.H. Le, J.-Y. Liu, C.-C. Chung, and Y.-C. Ling, "Synthesis of TiO₂ Nanoparticles Using Novel Titanium Oxalate Complex towards Visible Light-Driven Photocatalytic Reduction of CO₂ to CH₃OH," *Appl. Catal., A*, **437-438** 28-35 (2012).
22. W. N. Wang, W. An, B. Ramalingam, S. Mukherjee, D. M. Niedzwiedzki, S. Gangopadhyay, and P. Biswas, "Size and Structure Matter: Enhanced CO₂ Photoreduction Efficiency by Size-Resolved Ultrafine Pt Nanoparticles on TiO₂ Single Crystals," *J. Am. Chem. Soc.*, **134** [27] 11276 (2012).
23. X. Chen, S. Shen, L. Guo, and S. S. Mao, "Semiconductor-Based Photocatalytic Hydrogen Generation," *Chem. Rev.*, **110** [11] 6503-70 (2010).
24. T. Tachikawa, M. Fujitsuka, and T. Majima, "Mechanistic Insight into the TiO₂ Photocatalytic Reactions: Design of New Photocatalysts," *J. Phys. Chem. C*, **111** [14] 5259-75 (2007).
25. Y. Huang, W. K. Ho, S. C. Lee, L. Z. Zhang, G. S. Li, and J. C. Yu, "Effect of Carbon Doping on the Mesoporous Structure of Nanocrystalline Titanium Dioxide and its Solar-Light-Driven Photocatalytic Degradation of NO_x," *Langmuir*, **24** [7] 3510-16 (2008).
26. X. F. Yang, J. Chen, L. Gong, M. M. Wu, and J. C. Yu, "Cross-Medial Arrays of Ta-Doped Rutile Titania," *J. Am. Chem. Soc.*, **131** [34] 12048-49 (2009).
27. D. N. Tafen, R. Long, and O. V. Prezhdo, "Dimensionality of Nanoscale TiO₂ Determines the Mechanism of Photo-induced Electron Injection from a CdSe Nanoparticle," *Nano Lett.*, **14** [4] 1790-96 (2014).
28. Y. Hassan, C. H. Chuang, Y. Kobayashi, N. Coombs, S. Gorantla, G. A. Botton, M. A. Winnik, C. Burda, and G. D.

- Scholes, "Synthesis and Optical Properties of Linker-Free TiO_2/CdSe Nanorods," *J. Phys. Chem. C*, **118** [6] 3347-58 (2014).
29. L. L. Su, J. Lv, H. E. Wang, L. J. Liu, G. Q. Xu, D. M. Wang, Z. X. Zheng, and Y. C. Wu, "Improved Visible Light Photocatalytic Activity of CdSe Modified TiO_2 Nanotube Arrays with Different Intertube Spaces," *Catal. Lett.*, **144** [4] 553-60 (2014).
 30. B. Jiang, X. L. Yang, X. Li, D. Q. Zhang, J. Zhu, and G. S. Li, "Core-Shell Structure CdS/TiO_2 for Enhanced Visible-Light-Driven Photocatalytic Organic Pollutants Degradation," *J. Sol-Gel Sci. Technol.*, **66** [3] 504-11 (2013).
 31. H. M. Choi, I. A. Ji, and J. H. Bang, "Quantum Dot Solar Cells Prepared Using Electrophoretic Deposition," *Bull. Korean Chem. Soc.*, **34** [3] 713-14 (2013).
 32. Q. Y. Wang, X. C. Yang, L. N. Chi, and M. M. Cui, "Photoelectrochemical Performance of CdTe Sensitized TiO_2 Nanotube Array photoelectrodes," *Electrochim. Acta*, **91** 330-36 (2013).
 33. J. Q. Zhang, J. Y. Yang, M. Liu, G. Li, W. X. Li, S. Gao, and Y. B. Luo, "Fabrication of CdTe Quantum Dots sensitized TiO_2 Nanorod-Array-Film Photoanodes via the Route of Electrochemical Atomic Layer Deposition," *J. Electrochem. Soc.*, **161** [1] 55-8 (2014).
 34. H. J. Wang, F. Q. Sun, Y. Zhang, L. S. Li, H. Y. Chen, Q. S. Wu, and J. C. Yu, "Photochemical Growth of Nanoporous SnO_2 at the Air-Water Interface and its High Photocatalytic Activity," *J. Mater. Chem.*, **20** [27] 5641-45 (2010).
 35. G. S. Li, D. Q. Zhang, and J. C. Yu, "Ordered Mesoporous BiVO_4 through Nanocasting: A Superior Visible Light-Driven Photocatalyst," *Chem. Mater.*, **20** [12] 3983-92 (2008).
 36. Y. Areerob, J. Y. Cho, W. K. Jang, and W. C. Oh, "Enhanced Sonocatalytic Degradation of Organic Dyes from Aqueous Solutions by Novel Synthesis of Mesoporous Fe_3O_4 -Graphene/ ZnO/SiO_2 Nanocomposites," *Ultrason. Sonochem.*, **41** 267-78 (2018).
 37. I. V. Lightcap, T. H. Kosel, and P. V. Kamat, "Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide," *Nano Lett.*, **10** [2] 577-83 (2010).
 38. G. Williams, B. Seger, and P. V. Kamat, " TiO_2 -Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide," *ACS Nano*, **2** [7] 1487-91 (2008).
 39. H. Zhang, X. J. Lv, Y. M. Li, Y. Wang, and J. H. Li, " P_{25} -Graphene Composite as a High Performance Photocatalyst," *ACS Nano*, **4** [1] 380-86 (2010).
 40. Y. H. Ng, A. Iwase, A. Kudo, and R. Amal, "Reducing Graphene Oxide on a Visible-Light BiVO_4 Photocatalyst for an Enhanced Photoelectrochemical Water Splitting," *J. Phys. Chem. Lett.*, **1** [17] 2607-12 (2010).
 41. Y. H. Ng, A. Iwase, N. J. Bell, A. Kudo, and R. Amal, "Semiconductor/Reduced Graphene Oxide Nanocomposites Derived from Photocatalytic Reactions," *Catal. Today*, **164** [1] 353-57 (2011).
 42. H. T. Hu, X. B. Wang, F. M. Liu, J. C. Wang, and C. H. Xu, "Rapid Microwave-Assisted Synthesis of Graphene Nanosheets-Zinc Sulfide Nanocomposites: Optical and Photocatalytic Properties," *Synth. Met.*, **161** [5-6] 404-10 (2011).
 43. T. N. Lambert, C. A. Chavez, N. S. Bell, C. M. Washburn, D. R. Wheeler, and M. T. Brumbach, "Large Area Mosaic Films of Graphene-Titania: Self-Assembly at the Liquid-Air Interface and Photo-Responsive Behavior," *Nanoscale*, **3** [1] 188-91 (2011).
 44. Y. P. Zhang and C. X. Pan, " TiO_2 /Graphene Composite from Thermal Reaction of Graphene Oxide and its Photocatalytic Activity in Visible Light," *J. Mater. Sci.*, **46** [8] 2622-26 (2011).
 45. B. J. Li and H. Q. Cao, " $\text{ZnO}/\text{Graphene}$ Composite with Enhanced Performance for the Removal of Dye from Water," *J. Mater. Chem.*, **21** 3346-49 (2011).
 46. O. V. Prezhdo, P. V. Kamat, and G. C. Schatz, "Virtual Issue: Graphene and Functionalized Graphene," *J. Phys. Chem. C*, **115** [8] 3195-97 (2011).
 47. V. Kamat, "Graphene-Based Nanoassemblies for Energy Conversion," *J. Phys. Chem. Lett.*, **2** [3] 242-51 (2011).
 48. X. Lv, W. Fu, C. Hu, Y. Chen, and W. Zhou, "Photocatalytic Reduction of CO_2 with H_2O over a Graphene-Modified $\text{NiO}_{x-1}\text{Ta}_2\text{O}_5$ Composite Photocatalyst: Coupling Yields of Methanol and Hydrogen," *RSC Adv.*, **3** [6] 1753-57 (2013).
 49. X. An, K. Li, and J. Tan, " $\text{Cu}_2\text{O}/\text{Reduced Graphene Oxide}$ Composites for the Photocatalytic Conversion of CO_2 ," *ChemSusChem*, **7** [4] 1086-93 (2014).
 50. J. Yu, J. Jin, B. Cheng, and M. Jaroniec, "A Noble Metal-Free Reduced Graphene Oxide-CdS Nanorod Composite for the Enhanced Visible-Light Photocatalytic Reduction of CO_2 to Solar Fuel," *J. Mater. Chem. A*, **2** [10] 3407-16 (2014).
 51. K. Ullah, S. Ye, S.-B. Jo, L. Zhu, K.-Y. Cho, and W.-C. Oh, "Optical and Photocatalytic Properties of Novel Heterogeneous PtSe_2 -Graphene/ TiO_2 Nanocomposites Synthesized via Ultrasonic Assisted Techniques," *Ultrason. Sonochem.*, **21** [5] 1849-1857 (2014).
 52. T. Ghosh, J.-H. Lee, Z.-D. Meng, K. Ullah, C.-Y. Park, V. Nikam, and W.-C. Oh, "Graphene Oxide Based CdSe Photocatalysts: Synthesis, Characterization and Comparative Photocatalytic Efficiency of Rhodamine B and Industrial Dye," *Mater. Res. Bull.*, **48** [3] 1268-74 (2013).
 53. T. Ghosh, K. Y. Cho, K. Ullah, V. Nikam, C. Y. Park, Z.-D. Meng, and W.-C. Oh, "High Photonic Effect of Organic Dye Degradation of Cd-Graphene- TiO_2 Particles," *J. Ind. Eng. Chem.*, **19** [3] 797-805 (2013).
 54. L. Zhu, M. Teo, P. C. Wong, K. C. Wong, I. Narita, F. Ernst, K. A. R. Mitchell, and S. A. Campbell, "Synthesis, Characterization of a CoSe_2 Catalyst for the Oxygen Reduction Reaction," *Appl. Catal., A*, **386** [1-2] 157-65 (2010).
 55. L. Zhu, G. Trisha, C. Y. Park, Z. D. Meng, and W.-C. Oh, "Enhanced Sonocatalytic Degradation of Rhodamine B by Graphene- TiO_2 Composites Synthesized by an Ultrasonic-Assisted Method," *Chin. J. Catal.*, **33** [7-8] 1276-83 (2012).
 56. K. Ullah, S. Ye, L. Zhu, S. B. Jo, W. K. Jang, K. Y. Cho, and W.-C. Oh, "Noble Metal Doped Graphene Nanocomposites and its Study of Photocatalytic Hydrogen Evolution," *Solid State Sci.*, **31** 91-8 (2014).

57. W. Gao, L. B. Alemany, L. Ci, and P. M. Ajayan, "New Insights into the Structure and Reduction of Graphite Oxide," *Nat. Chem.*, **1** 403-8 (2009).
58. D. W. Boukhvalov and M. I. Katsnelson, "Modeling of Graphite Oxide," *J. Am. Chem. Soc.*, **130** [32] 10697-701 (2008).
59. H. K. Jeong, H. J. Noh, J. Y. Kim, M. H. Jin, C. Y. Park, and Y. H. Lee, "X-ray Absorption Spectroscopy of Graphite Oxide," *EPL*, **82** [6] 67004-5 (2008).
60. W. K. Ho and J. C. Yu, "Sonochemical Synthesis of Visible Light Photocatalytic Behavior of CdSe and CdSe/TiO₂ Nanoparticles," *J. Mol. Catal. A: Chem.*, **247** [1-2] 268-74 (2006).
61. H. Lange, M. Artemyev, U. Woggon, and C. Thomsen, "Geometry Dependence of the Phonon Modes in CdSe Nanorods," *Nanotechnology*, **20** [4] 045705 (2009).
62. V. M. Dzhegagan, I. Lokteva, M. Y. Valakh, and O. E. Raevska, "Spectral Features above LO Phonon Frequency in Resonant Raman Scattering Spectra of Small CdSe Nanoparticles," *J. Appl. Phys.*, **106** [8] 084318 (2009).
63. R. C. Wang, Y.-C. Chen, S.-J. Chen, and Y.-M. Chang, "Unusual Functionalization of Reduced Graphene Oxide for Excellent Chemical Surface Enhanced Raman Scattering by Coupling with ZnO," *Carbon*, **70** 215-23 (2014).
64. S. Ameen, H. K. Seo, M. S. Akhtar, and H. S. Shin, "Novel Graphene/Polyaniline Nanocomposites and its Photocatalytic Activity toward the Degradation of Rose Bengal Dye," *Chem. Eng. J.*, **210** 220-28 (2012).
65. Z. Zafar, Z. H. Ni, X. Wu, Z. X. Shi, H. Y. Nan, J. Bai, and L. T. Sun, "Evolution of Raman Spectra in Nitrogen Doped Graphene," *Carbon*, **61** 57-62 (2013).
66. D. Li, H. Haneda, S. Hishita, and N. Ohashi, "Visible-Light-Driven Nitrogen-Doped TiO₂ Photocatalysts: Effect of Nitrogen Precursors on Their Photocatalysis for Decomposition of Gas-Phase Organic Pollutant," *Mater. Sci. Eng., B*, **117** [1] 67-75 (2005).
67. H. Q. Sun, S. B. Wang, H. M. Ang, M. O. Tade, and Q. Li, "Halogen Element Modified Titanium dioxide for Visible Light Photocatalysis," *Chem. Eng. J.*, **162** [15] 437-47 (2010).
68. H. Q. Sun, Y. Bai, W. Q. Jin, and N. P. Xu, "Visible-Light-Driven TiO₂ Catalysts Doped with Low-Concentration Nitrogen Species," *Sol. Energy Mater. Sol. Cells*, **92** [1] 76-83 (2008).
69. R. Rao, R. Podila, R. Tsuchikawa, J. Katoch, D. Tishler, A. Rao, and I. M. Shigami, "Effects of Layer Stacking on the Combination Raman Modes in Graphene," *ACS Nano*, **5** [3] 1594-99 (2011).
70. K. John, D. T. Manolis, D. P. George, N. A. Mariza, S. T. Kostas, G. Soa, B. Kyriakos, K. Christos, O. Michael, and L. Alexis, "Highly Active Catalysts for the Photo Oxidation of Organic Compounds by Deposition of Fullerene onto the MCM-41 Surface," *Appl. Catal., B*, **117-118** 36-48 (2012).
71. D. C. T. Nguyen, K.-Y. Cho, and W.-C. Oh, "Synthesis of Frost-like CuO Combined Graphene-TiO₂ by Self-Assembly Method and its High Photocatalytic Performance," *Appl. Surf. Sci.*, **412** 252-61 (2017).
72. D. C. T. Nguyen, K.-Y. Cho, and W.-C. Oh, "Synthesis of Mesoporous SiO₂/Cu₂O-Graphene Nanocomposites and their Highly Efficient Photocatalytic Performance for Dye Pollutants," *RSC Adv.*, **7** [47] 29284-94 (2017).
73. D. C. T. Nguyen, K.-Y. Cho, and W.-C. Oh, "A Facile Route to Synthesize Ternary Cu₂O Quantum Dot/Graphene-TiO₂ Nanocomposites with an Improved Photocatalytic Effect," *Fullerenes, Nanotubes, Carbon Nanostruct.*, **27** [12] 684-90 (2017).
74. D. C. T. Nguyen and W.-C. Oh, "Ternary Self-Assembly Method of Mesoporous Silica and Cu₂O Combined Graphene Composite by Nonionic Surfactant and Photocatalytic Degradation of Cationic-Anionic Dye Pollutants," *Sep. Purif. Technol.*, **190** 77-89 (2018).
75. D. C. T. Nguyen, K.-Y. Cho, and W.-C. Oh, "New Synthesis of the Ternary Type Bi₂WO₆-GO-TiO₂ Nanocomposites by the Hydrothermal Method for the Improvement of the Photo-Catalytic Effect," *Appl. Chem. Eng.*, **28** 705-13 (2017).
76. D. C. T. Nguyen, J.-H. Woo, K. Y. Cho, C.-H. Jung, W.-C. Oh, "Highly Efficient Visible Light Driven Photocatalytic Activities of the LaCuS₂-Graphene Composite-Decorated Ordered Mesoporous Silica," *Sep. Purif. Technol.*, **205** 11-21 (2018).