Synthesis and Characterization of a Ternary Nanocomposite Based on CdSe Decorated Graphene-TiO$_2$ and its Application in the Quantitative Analysis of Alcohol with Reduction of CO$_2$


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ABSTRACT

In this work, photocatalytic CO$_2$ reduction over a CdSe-graphene-TiO$_2$ 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 TiO$_2$ and CdSe dispersed graphene nanocomposite showed excellent results of strong reduction rates of CO$_2$ compared to the results of bare TiO$_2$ and binary CdSe-graphene. An outstanding point of the combination of CdSe-TiO$_2$ and graphene appeared in the form of great photocatalytic reduction capability of CO$_2$. The photocatalytic activity of the as-fabricated composite was tested by surveying for the photoreduction of CO$_2$ to alcohol under UV and visible light irradiation, and the obtained results imply that the as-prepared CdSe-graphene-TiO$_2$ nanocomposite is promising to become a potential candidate for the photocatalytic CO$_2$ reduction.

Key words : CO$_2$ reduction, CdSe-graphene-TiO$_2$, Photocatalytic activity

1. Introduction

The decline in fossil resources and growing concerns about CO$_2$ emissions are now a major global challenge.$^{12,13}$ Carbon dioxide (CO$_2$), the main and most abundant greenhouse gas, and CO$_2$ levels in atmospheric are higher than in the past decade.$^{5,6}$ The increase in the level of atmospheric carbon dioxide (CO$_2$) caused serious concerns about global warming.$^{50}$ Therefore, it is an urgent need to convert CO$_2$ into useful energy products. A converting CO$_2$ 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.$^{14,15}$ Artificial photosynthesis (photocatalysis and photoelectrocatalysis) is an innovative technology to convert CO$_2$ into valuable chemicals.$^{14,15}$ Solar fuel production by CO$_2$ photocatalytic conversion provides a best way for carbon cycling and fulfill the deficiency of energy demand and controlling increasing CO$_2$ levels.$^{16,17}$ A researcher focuses on a semiconductor-based photocatalytic reduction of CO$_2$ with H$_2$O to renewable hydrocarbon fuels by solar energy.$^{38}$ Among many kinds of semiconductor, titanium dioxide TiO$_2$ 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.$^{39,40}$ CH$_3$OH is a primary product of semiconductor-based material for CO$_2$ reduction,$^{21,22}$ but the main drawbacks of TiO$_2$ are its large band gap (3.2 eV) and fast recombinination of photogenerated charge carriers which effected the catalytic capacity.$^{78}$ To decrease these barriers and enhance the photocatalytic efficiency of photocatalysts, the TiO$_2$ doped with either anions or captions,$^{24,25}$ surface coupling with metals or semiconductors, such as CdSe,$^{26,27}$ 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.$^{38,39}$ Metal oxides coupled with graphene enhance visible light absorption and improve the efficiency of charge splitting, which is important for the CO$_2$ reduction of visible photocatalyst absorption.$^{45,51}$ In this paper, a new
CdSe-graphene-TiO₂ materials were fabricated by ultrasonication 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 90ºC to form the transparent dispersion, 0.05 g were added to 40 mL distilled water. After vigorous stirring, the prepared solution was sonicated 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 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 100ºC 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 100ºC 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 105ºC for 24 h before heat treatment at 500ºC 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 monochromatic AlKα X-ray source (hv = 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, SOLAREDGE700, 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 10ºC 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 CH₄ desorption from the catalyst. The obtained solution was centrifuged and analyzed by GC. Further the chronic 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.](image-url)
were synthesized by power XRD measurement. Fig. 1 depicts the XRD patterns of CdSe-graphene, graphene-TiO$_2$ and CdSe-graphene-TiO$_2$. Fig. 1 shows that TiO$_2$ is the anatase structure. In graphene-TiO$_2$ composite, the results of XRD diffraction peaks around 2$\theta$ 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-TiO$_2$, 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. XRD patterns exhibited a decrease of TiO$_2$ intensity peaks in CdSe-graphene-TiO$_2$ (2$\theta$) 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 2$\theta$ 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-TiO$_2$ and graphene-TiO$_2$ 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-TiO$_2$ 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-TiO$_2$ and (c) graphene-TiO$_2$.](image-url)
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-TiO\(_2\) with different magnification. From the Fig. 3(a) to (b), CdSe particles and TiO\(_2\) 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.\(^{53}\) Fig. 3(e-f) displays the CdSe-graphene-TiO\(_2\) nanocomposites which clearly exhibits the difference point of the binary and ternary materials. After combination of TiO\(_2\), the brighter spot arises in the ternary composite shown that the CdSe-graphene-TiO\(_2\) 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-TiO\(_2\).
vide the clear morphology and shape of the CdSe-graphene-
TiO$_2$ nanocomposites. Fig. 4(a) and (b) shows the different
magnification of the CdSe-graphene-TiO$_2$ 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 TiO$_2$ particles attached unevenly to the surface of
graphene sheets and almost in the circular form. The aver-
age size of the TiO$_2$ particles approximately is 6 to 10 nm.
During ultrasonic assisted synthesis of CdSe-graphene-
TiO$_2$, graphene sheet is prevented with partial agglomera-
tion and TiO$_2$ nanoparticles are remain on the CdSe
nanosheets and graphene.$^{55}$

The chemical states of the components elements of the
CdSe-graphene-TiO$_2$ 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-TiO$_2$ nano-
composites. 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
energies have the C-C at 284.8 eV, C-O at 286 eV and C=O
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
position (460.4 eV and 466.5 eV), which indicates
the variation of band gap energies of as-prepared compos-
ites may possibly be introduction of CdSe and TiO$_2$
particles on the graphene sheet surface or partial agglomeration,
which may affect the optical property of nanocomposites.$^{58,33}$
The decreasing $E_g$ of the CdSe-graphene-TiO$_2$ nanocom-
posite 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
TiO$_2$) phase.$^{7,12}$

The photocatalytic capacity of the as-synthesized CdSe-
graphene-TiO$_2$ material was tested by surveying the photo-
catalytic reduction of CO$_2$ under UV-visible and visible light
irradiation (in the region of 300 ~ 450 nm). Using alcohol oxidation method with CrO$_3$ four types of sample were synthesized. Fig. 9 exhibited the photocatalytic capacity of the photocatalytic reduction of CO$_2$ four different samples. Fig. 9(a) shows the reduction effect of CO$_2$-dissolved water samples, and Fig. 9(b) is the corresponding reduction effect for commercial carbonated water without additional CO$_2$, 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. 5. XPS results of the CdSe-graphene-TiO$_2$ nanocomposite (a) survey scan spectra (b) C$_1$s (c) O$_1$s (d) Ti$_2p$ (e) Cd$_{3d}$ and (f) Se$_{3d}$. 
\[
\text{CO}_2 + \text{CdSe-graphene-TiO}_2 \rightarrow \text{Alcohol (Under visible light irradiation)} \\
\text{CO}_2 + 2e^- + 2H^+ \rightarrow \text{HCOOH} \\
\text{Alcohol + CrO}_3 \rightarrow \text{Oxidation of alcohol} \\
\text{RCH}_2\text{OH} (1^o \text{ alcohol}) + [O] \rightarrow \text{RCHO (Aldehyde) + [O]} \\
\rightarrow \text{RCOOH (Carboxylic acid)} \\
\text{CrO}_3 + \text{reduction} \rightarrow \text{Cr (III) ion (UV/VIS Spectra response)}
\]

To find the methanol concentration in CdSe-graphene-TiO\textsubscript{2} nanocomposites, CrO\textsubscript{3} use as an oxides agent. During experiment methanol was oxides and the result the CrO\textsubscript{3} oxidation form change to reduce form then the color of the sample was change. CH\textsubscript{3}OH can follow indirectly on the CrO\textsubscript{3}, increasing methanol concentration the color of CrO\textsubscript{3} were changed.

Further for conformation chromic acid test result, CdSe-graphene-TiO\textsubscript{2} were also evaluated by gas-chromatography (GC). Photocatalytic reaction time is up to 48 h and, after 12 h, liquid product is manually taken for GC analysis. A series of test were conducted for the confirmation of CH\textsubscript{3}OH, 1\textsuperscript{st} control experiment was conducted in dark with catalysts, and 2\textsuperscript{nd} experiment was conducted under light radiation but no catalysts, both results shown no CH\textsubscript{3}OH were detected. These control experiments show that both irradiation and

Fig. 6. Raman spectra of CdSe-graphene-TiO\textsubscript{2} nanocomposites.

Fig. 7. Diffuse reflectance spectra (DRS) of (a) CdSe, CdSe-graphene-TiO\textsubscript{2} (b) TiO\textsubscript{2}.

Fig. 8. Diffuse reflectance spectra (DRS) obtained from Kubelka-Munk transformation function versus photon energy (a) TiO\textsubscript{2} and (b) CdSe-graphene-TiO\textsubscript{2}.
light catalysts are important factors for the uptake of CO$_2$ for CH$_3$OH 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$_3$OH 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 µmol g$^{-1}$ 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 µmol g$^{-1}$ h$^{-1}$, respectively. Graphene oxide plays the role of an electron acceptor, photosensitizer, and the adsorbent to efficiently enhance the photodegradation of organic dyes.

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.$^{33-36}$

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$_3$OH, the experimental results shown excellent light
absorption and enhanced photocatalytic efficiency for CO$_2$ reduction under both UV-visible and visible light irradiation. The maximum CH$_3$OH yield 1.12 µmol·g$^{-1}$·hr$^{-1}$ was achieved under UV-visible light irradiation. This work reveals that CdSe-graphene-TiO$_2$ could be used as a promising candidate for CO$_2$ reduction.

REFERENCES


