Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 78 (11) 1797–1807 (2013)
JSCS–4534

UDC 546.264–31+66.094.2+
546.824–31+544.351
Original scientific paper

Investigation of the charge-transfer in photo-excited nanoparticles for CO_2 reduction in non-aqueous media•

NADA M. DIMITRIJEVIĆ*

Chemical Sciences and Engineering Division, and Nanoscience and Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

(Received 26 July, revised 19 September 2013)

Abstract: Photo-induced charge separation in TiO_2 and Cu_2O semiconductor nanoparticles was examined using electron paramagnetic resonance spectroscopy in order to obtain insight into the photocatalytic reduction of CO_2 in non-aqueous media. For dissolution/grafting of CO_2, carboxy-PEG_4-amine was used with poly(ethylene glycol) 200 as the solvent. It was found that the reduction of CO_2 in this system starts at a potential of –0.5 V *vs*. Ag/AgCl, which is significantly more positive than the potential for electrochemical reduction of CO_2 in most organic solvents and water (–2.0 V *vs*. Ag/AgCl). The electron transfer from excited nanoparticles to CO_2 is governed by both thermodynamic and kinetic parameters, namely by the redox potential of conduction band electrons and adsorption/binding of CO_2 on the surface of the nanoparticles.

Keywords: carbon dioxide reduction, photocatalysis, titanium dioxide, cuprous oxide.

INTRODUCTION

Carbon dioxide produced by consuming fossil fuels is regarded as the most significant source of greenhouse gases.[1] Reducing the accumulation of CO_2 in the atmosphere is one of the current major scientific and social challenges. Although the chemical industry currently uses CO_2 as an inexpensive, non-flammable and non-toxic C_1 resource, the processes are conducted at relatively high pressures, at elevated temperatures and in the presence of catalysts.[2–6] Thus, there is a need for the development of facile and inexpensive methods to convert CO_2 to usable materials under mild conditions (temperature and pressure). Using solar light as an energy source and inexpensive semiconductor nanoparticles as photocatalysts is a promising approach for the photochemical transformation of

* Correspondence to E-mail: Dimitrijevic@anl.gov
• Dedicated to late Dr. Olga Mićić, the greatest teacher of Physical Chemistry.
doi: 10.2298/JSC130726093D

CO_2 into fuels: CO, CH_4, and CH_3OH. Each of these fuels could be burned to produce CO_2 and then regenerated by photochemical reduction. Alternatively, CO could be used as a starting material in the water gas shift reaction to generate hydrogen from water. In all these cases, energy would be produced in a CO_2 neutral fashion avoiding a net production of CO_2. While most semiconductor-assisted photocatalytic reductions of CO_2 were realized in aqueous solution,[7–10] the yields were relatively low not only because of the low solubility of carbon dioxide in water, but also because adsorbed/dissociated water on the surface of nanoparticles competes with adsorbed CO_2 for the photogenerated electrons.[11] Different strategies in improving CO_2 sequestration are currently being pursued. Several groups[12–14] have developed reversible CO_2 capture utilizing a strong nitrogen-containing base in conjunction with a proton donor. Meanwhile, amidophosphoranes were also proved to be capable of capturing one equivalent of CO_2 through the insertion of CO_2 into a P–N bond, resulting in the generation of carbamatophosphoranes.[15] Very recently, Brennecke and co-workers[16] designed an ionic liquid (IL) comprising an amino-functionalized anion and a long-chain alkyl phosphonium cation to capture CO_2, while Liu[17] *et al*. employed poly(ethylene glycol) (PEG) solution with amino acid salts. In both cases almost equimolar absorption of CO_2 (1 mol CO_2 per mol of IL, or per mol of amino acid in PEG) was obtained.

In this work, the non-aqueous solvent PEG 200 was combined with short-chain amine group salts to increase CO_2 dissolution, and semiconductor nanoparticles were employed to initiate light-induced CO_2 reduction. For these studies, electron paramagnetic resonance (EPR) spectroscopy was used as a tool for examining the initial photo-induced charge separation and transfer in the presence of dissolved/grafted CO_2.

EXPERIMENTAL

Materials

All chemicals were of analytical grade and used as received, without further purification. Poly(ethylene glycol) 200 was purchased from J. T. Baker, carboxy-PEG_4-amine, $C_{11}H_{23}O_6N$, abbreviated in the text as $CA(PEG)_4$, from Thermo Scientific, tetra(*n*-butyl)ammonium hexafluorophosphate, Bu_4NPF_6, from Aldrich, anatase nanoparticles (d = 20 nm) from SkySpring, and Cu_2O colloidal nanoparticle (d = 30 nm) solution in ethanol from Aldrich. Research-grade carbon dioxide, 99.999 % (Airgas), was passed consecutively through two hydrocarbon traps (Supelco) to remove even trace amounts of impurities.

Instrumentation

X-Band continuous wave EPR experiments were conducted on a Bruker Elexsys E580 spectrometer equipped with an Oxford CF935 helium flow cryostat with an ITC-5025 temperature controller. The EPR spectra of the photogenerated charges were recorded at cryogenic temperatures from 4.5 to 77 K. The g factors were calibrated for homogeneity and accuracy by comparison with a coal standard, g = 2.00285±0.00005. Simulations were performed using Bruker SimFonia, version 1.25. Samples in the EPR cavity were illuminated

using a 300-W Xe lamp (ILC) with water as the cut-off IR filter. Cyclic voltammetry measurements were performed with a three-component system containing a glassy carbon working electrode, Pt as the counter electrode, and Ag/AgCl as the reference electrode, using a BAS-100B/W (Bioanalytical Systems, USA) workstation with a single compartment closed quartz cell. Absorption spectra were recorded on a Shimadzu UV-1601 spectrophotometer.

RESULTS AND DISCUSSION

Electrocatalytic reduction of CO_2 in non-aqueous media has recently gathered increased interest,[18] while semiconductor-assisted photocatalytic reduction is mainly focused on metal oxides in aqueous media. In photocatalytic processes, semiconductor metal oxide nanoparticles are used as light-harvesting materials. Nanocrystalline semiconductors are capable of coupling single photon events to the accumulation of multiple redox equivalents (photogenerated electrons) that participate in catalytic reduction of CO_2. The semiconductors Cu_2O (p-type), because of its favorable electronic properties for CO_2 reduction, Fig. 1, and TiO_2, because of its proven ability to convert carbon dioxide to methane in the presence of proton donors,[7–11] were chosen as photocatalysts of interest. The low yield of methane production in aqueous solutions is due to the competition of water and

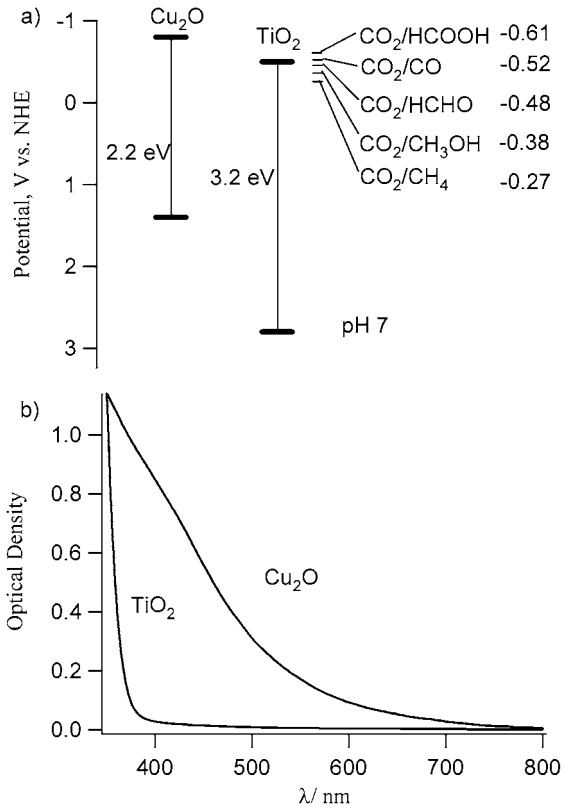

Fig. 1. a) Schematic presentation of the band positions and band gap energies and b) absorption spectra of Cu_2O and TiO_2 semiconductor nanoparticles. Optical pathlength: 0.5 cm.

carbon dioxide for the photogenerated electrons combined with the low solubility of carbon dioxide in water. Thus, the highest yields were achieved using a CO_2/water vapor (2:1) combination.[11] The redox potentials of CO_2 reduction products in aqueous solution are also indicated in Fig. 1a. In the absence of proton donors (as in non-aqueous solvents), the major product is carbon monoxide.

In order to increase the solubility of CO_2, 10 mM carboxy-PEG_4-amine, $CA(PEG)_4$ in PEG 200 solvent was used. The choice of $CA(PEG)_4$ was based on its high solubility in PEG 200 and because the amine group can effectively graft CO_2. It was shown previously that amino and amine groups capture CO_2 *via* the sequestration formation of the carbamic acid or carbamate pathways in a high yield.[17] In order to gain insight into the photocatalytic reduction of CO_2 in non-aqueous media, photo-induced charge formation, separation and transfer in semiconductor nanoparticles were examined in $CA(PEG)_4$/PEG 200 solution saturated with N_2 or CO_2.

CO_2 in non-aqueous amine solution

The ability of $CA(PEG)_4$ dissolved in PEG 200 to sequester CO_2 efficiently was demonstrated using cyclic voltammetry. The voltammograms of the solutions saturated with N_2 and CO_2 are presented in Fig. 2a, from which it can be seen that the reversible one-electron redox process of $CA(PEG)_4$ with $E_{1/2}$ = = –0.84 V *vs*. Ag/AgCl occurred in the absence of CO_2. At the same time, when solution was bubbled with CO_2, a quasi-reversible electron transfer occurred. Moreover, the reduction of amine-grafted CO_2 starts at a potential of –0.5 V, while the electrochemical reduction of CO_2 occurs at rather negative potentials (more negative than –2 V) at low temperatures in most organic solvents. In the absence of $CA(PEG)_4$, no significant changes in the voltammograms of PEG 200 with and without CO_2 could be observed, Fig. 2b, showing that CO_2 does not dissolve in PEG 200 very efficiently, and confirming that the $–NH_2$ group is essential for the dissolving/grafting of CO_2.

Not only the increased solubility, but also the measured relatively positive potential for CO_2 reduction in this system made it the medium of choice for further studies and possible applications.

Light-induced charge transfer

The photo-excitation of TiO_2 (anatase) with energies greater than its band gap (3.2 eV) results in the formation of conduction band electrons and valence band holes (charge carriers):

$$TiO_2 \xrightarrow{h\nu} (e^- + h^+)TiO_2 \quad (1)$$

EPR spectroscopy has been widely used to examine paramagnetic species in illuminated titania, starting with the seminal work of Howe and Gratzel.[19] At cryo-

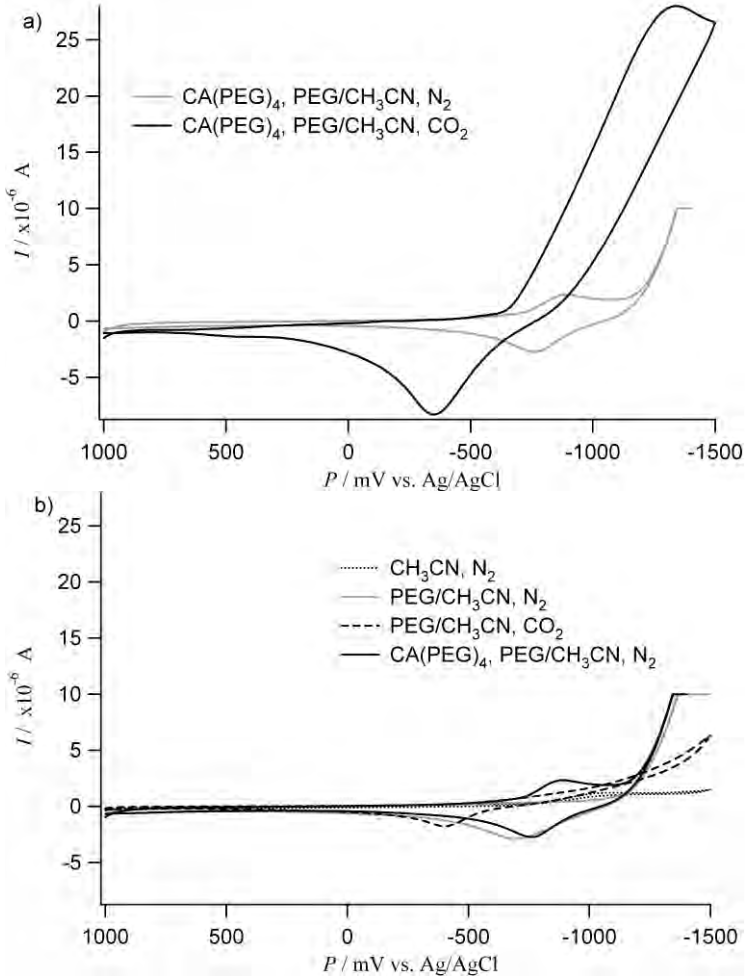

Fig. 2. Cyclic voltammograms of a) PEG 200 solutions containing 10 mM carboxy-PEG_4--amine, $CA(PEG)_4$, and 20 vol. % acetonitrile, saturated with N_2 and CO_2; b) solutions without $CA(PEG)_4$ measured as a control under the same conditions. All solutions contain 5 mM Bu_4NPF_6 as a redox relay. Glassy carbon as working, Pt as auxiliary and Ag/AgCl as reference electrodes were used. Scan rate 20 mV s^{-1}.

genic temperatures, photogenerated charge carriers localize in the interior of TiO_2 nanoparticles or migrate to the surface where they localize at surface trap sites. The signals associated with the trapped electrons are those due to lattice $(Ti^{3+})_{latt}$, sharp signal at $g_{\perp} = 1.990$ and $g_{||} = 1.961$, and surface $(Ti^{3+})_{surf}$ centers, broad signal with $g = 1.924$, Fig. 3a. The observed signals are characteristic of the electron in the Ti 3d orbital of the anatase lattice and surface.[20] Simultaneously, no signal due to the oxygen-centered radical, $(Ti^{4+}O^{\bullet})_{surf}$, *i.e.* holes, was observed. The observed signal with $g = 2.001$ is due to the reaction of

photogenerated holes with carboxy-PEG_4-amine. The 6-line spectrum with the intensity ratios of 1:2:3:3:2:1 presented in Fig. 3b corresponds to $CH_3CH_2^{\bullet}$ radicals,[21] and is the result of C–O bond scission.[22] The efficient scavenging of holes by carboxy-PEG_4-amine is facilitated by the strong binding of carboxyl groups on TiO_2.[23]

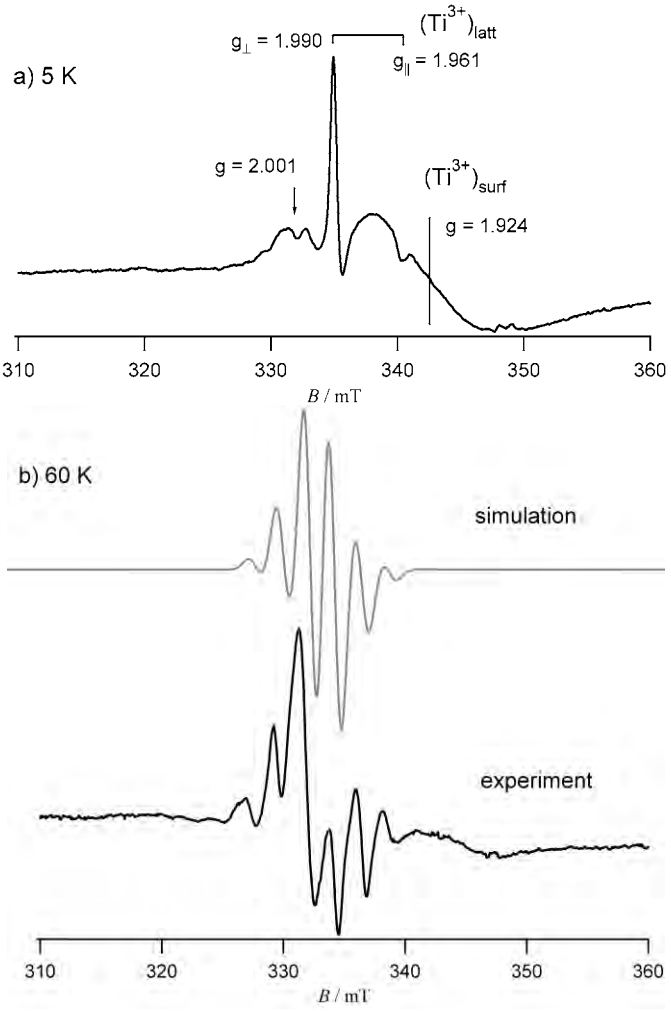

Fig. 3. EPR Spectra of TiO_2 in a solution of 10 mM carboxy-PEG_4-amine in PEG 200 measured under UV illumination at a) 5 K, power, 2 mW, modulation amplitude, 0.5 mT and b) 60 K, power, 0.2 mW, modulation amplitude, 0.3 mT. The gray line presents the simulated spectrum. The conditions of EPR measurements were adjusted to better resolve the signal from the $CH_3CH_2\cdot$ radical.

By increasing the temperature from 5 to 77 K, the electrons from the interior of the TiO_2 nanoparticle had enough energy to detrap and move to the surface where they localize at mid-gap states. The decrease of the signal for lattice-trapped and the increase of the signal that corresponds to the surface-trapped electrons, can be seen for a solution saturated with N_2, Fig. 4a.

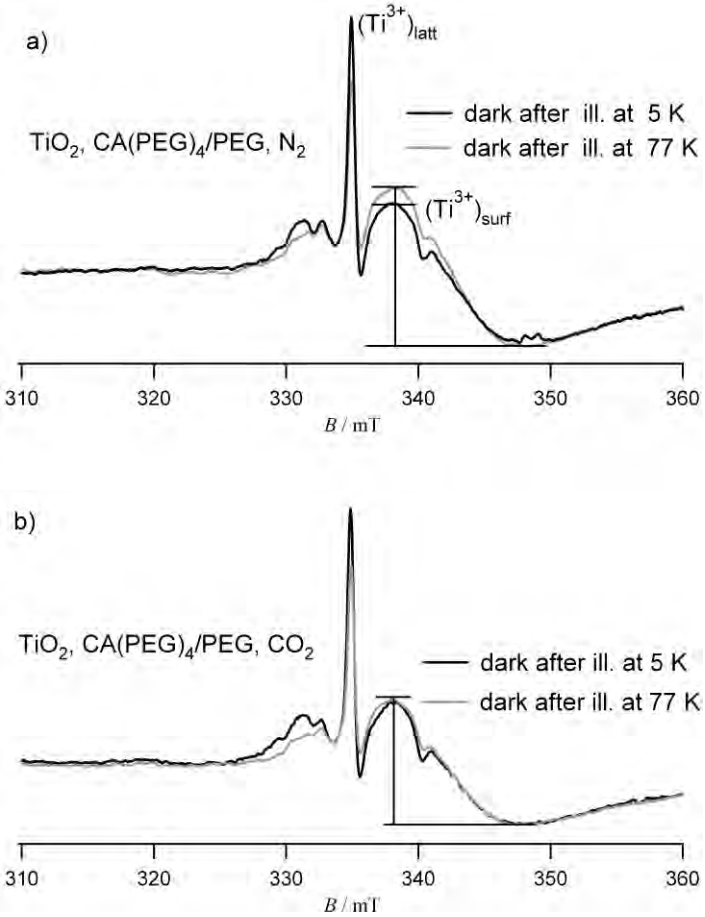

Fig. 4. EPR Spectra measured in the dark (at 5 K) after illumination at 5 and 77 K of a PEG 200 solution containing 10 mM carboxy-PEG_4-amine, $CA(PEG)_4$, and TiO_2 saturated with a) N_2 and b) CO_2. Power, 2 mW, modulation amplitude, 0.5 mT.

On the other hand, dissolved CO_2 acts as an electron acceptor, Eq. (2). The R–CO_2 in equations represents grafted CO_2, most probably carbamate:[17]

$$e^{-}(TiO_2) + R - CO_2 \rightarrow R - CO_2^{-} \quad (2)$$

It was found that at the elevated temperature of 77 K, detrapped lattice electrons do not localize on the surface, rather they react with CO_2, Fig. 4b. Con-

sequently, no increase in the signal due to the surface-trapped electrons that were present at 5 K accompanies the decrease in the signal of the lattice-trapped electron. This means that *i*) the energy of mid-gap surface trapped electrons is below the redox potential for CO_2 reduction and *ii*) only conduction band electrons can react with CO_2. Although the driving force for CO_2 reduction with TiO_2 conduction band electrons is not high (Fig. 1), the efficient scavenging of photogenerated holes by $CA(PEG)_4$ enables a relatively high yield of the reduction reaction.

The conduction band electrons of cuprous oxide (Cu_2O) have a more negative potential than those of TiO_2; thus, the thermodynamic parameters favor reduction of CO_2. However, Cu^+ is a non-paramagnetic ion and light-induced charge separation and transfer cannot be detected by EPR directly. As the Cu_2O nanoparticles used in this study did not have a protective ligand on their surface, a slow oxidation of bare nanoparticles occurred in air, resulting in the formation of thin layer of copper oxide (CuO) on the surface. This was confirmed by EPR spectra measured in the dark before illumination, Fig. 5. The spectra show hyperfine structure that is characteristic of Cu^{2+} (I = 3/2). In both cases (N_2 *vs*. CO_2 saturated solutions), the values of $g_{||}$ and $g_{\perp}$ satisfy the relation $g_{||} > g_{\perp} > g_e$ = = 2.0023 (g_e represents the g-tensor of free electron), indicating that the Cu^{2+} were coordinated by six ligand atoms in an axially distorted octahedron, that is characteristic of copper ions in CuO. However, the values for parallel and normal component differ, $g_{||}$ = 2.256 and $g_{\perp}$ = 2.036 for N_2, and $g_{||}$ = 2.276 and $g_{\perp}$ = 2.038 for CO_2, which suggests that CO_2 adsorbs/binds strongly to the surface of CuO,

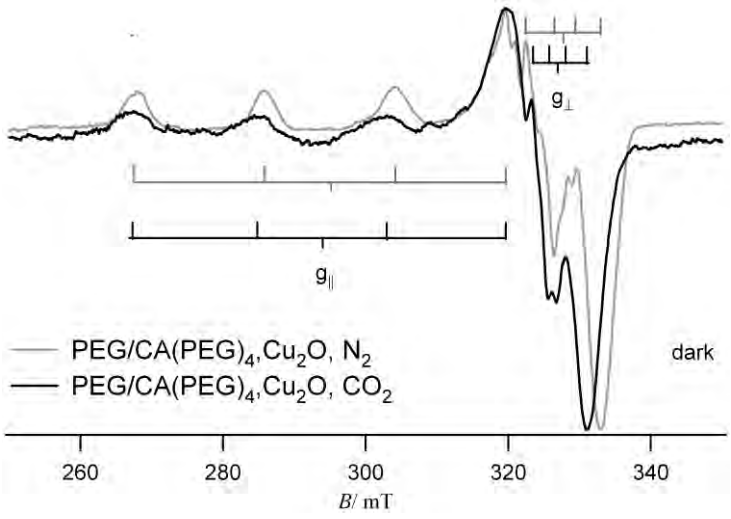

Fig. 5. EPR Spectra measured at 5 K in the dark of Cu_2O/CuO in PEG solution containing 10 mM carboxy-PEG_4-amine, $CA(PEG)_4$, saturated with N_2 or CO_2. Power, 2 m; modulation amplitude, 1 mT.

not only to carboxy-PEG_4-amine, affecting the hyperfine structure of surface Cu^{2+}. The binding of CO_2 onto Cu_2O/CuO was previously observed in aqueous solutions.[24]

Under illumination with visible light (λ > 400 nm), an increase in the concentration of Cu^{2+} was observed in the presence of CO_2, Fig. 6, due to electron transfer:

$$\begin{gathered} Cu_2O \xrightarrow{h\nu} (e^- + h^+)Cu_2O \\ (e^-)Cu_2O + R-CO_2 \rightarrow Cu^+OCu^{2+} + R-CO_2^- \end{gathered} \quad (3)$$

In the absence of CO_2, no change in the signal associated with Cu^{2+} was observed (Fig. 6a) because of the fast recombination of the photogenerated electrons and holes. The redox potential of valence band holes of Cu_2O is not

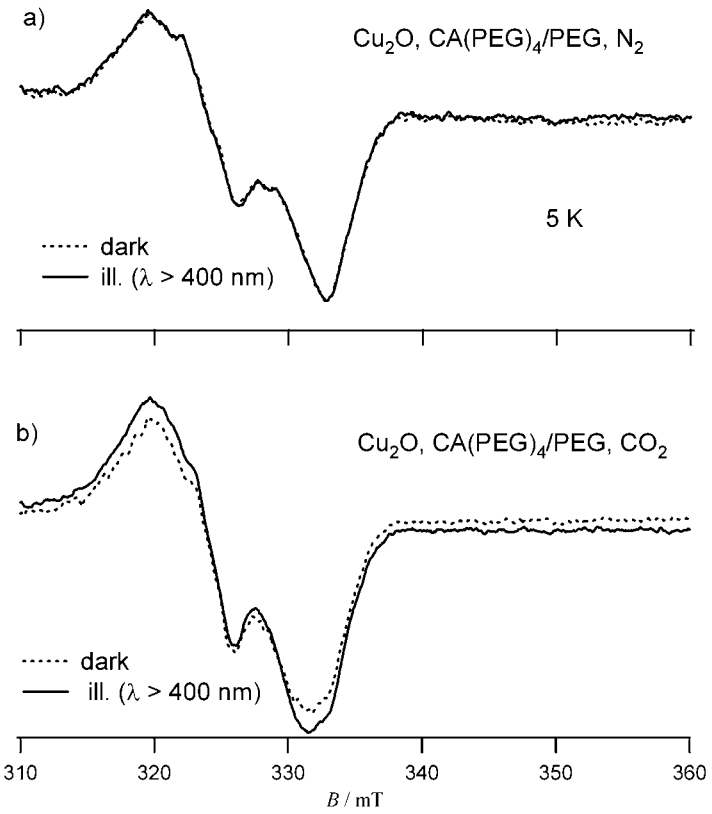

Fig. 6. EPR Spectra measured at 5 K in the dark and under illumination of Cu_2O/CuO in PEG solution containing 10 mM carboxy-PEG_4-amine, $CA(PEG)_4$, saturated with a) N_2 and b) CO_2. The magnetic field was centered on the normal component of the Cu^{2+} signal. Power, 2 mW; modulation amplitude, 1 mT.

positive enough to allow oxidation of carboxy-PEG_4-amine as no signals of organic radicals were observed in this system; thus, recombination of the charges was the favorable process. Therefore, the electron transfer from excited Cu_2O to CO_2 at the extremely low temperature of 5 K was due to the combined effects of the favorable redox potential of Cu_2O conduction band electrons and strong adsorption/binding of CO_2 on the nanoparticles.

CONCLUSION

Carboxy-PEG_4-amine, $C_{11}H_{23}O_6N$, when dissolved in poly(ethylene glycol) 200 efficiently sequesters CO_2. The grafting of CO_2 not only increases its solubility but enables reduction of CO_2 at a significantly more positive potential than the electrochemical reduction of CO_2 in most organic solvents or aqueous solutions. The efficiency of the one-electron transfer from photo-excited TiO_2 and Cu_2O nanoparticles to CO_2 was in the order $Cu_2O > TiO_2$, because of the preferential electronic and surface properties of the cuprous/cupric oxide nanoparticles.

Acknowledgment. This work was supported by the Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

И З В О Д

ИСПИТИВАЊЕ ПРЕНОСА НАЕЛЕКТРИСАЊА У ЕКСЦИТОВАНИМ НАНОЧЕСТИЦАМА ЗА ФОТОКАТАЛИТИЧКУ РЕДУКЦИЈУ CO_2 У НЕВОДЕНОЈ СРЕДИНИ

НАДА М. ДИМИТРИЈЕВИЋ

Chemical Sciences and Engineering Division, and Nanoscience and Technology Division, Argonne National Laboratory 9700 S. Cass Ave., Argonne, IL 60439, USA

Раздвајање наелектрисања у побуђеним CO_2 и Cu_2O полупроводничким наночестицама је испитивано електронском парамагнетном резонантном спектроскопијом да би се добиле информације о фотокаталитичкој редукцији CO_2 у неводеној средини. Да би повећали растворљивост и везивање CO_2 користили смо карбоксил-PEG_4-амин у полиетилен гликолу 200 као растварачу. Нађено је да у том раствору редукција CO_2 почиње на потенцијалу од –0,5 V према Ag/AgCl, што је значајно позитивније него електрохемијска редукција у већини органских растварача и води (–2,0 V према Ag/AgCl). Ефикасност преноса електрона са побуђених наночестица на CO_2 зависи од термодинамичких и кинетичких параметара, наиме зависи и од потенцијала електрона у проводној траци и од адсорпције/везивања CO_2 на површину наночестица.

(Примљено 27. јула, ревидирано 19. септембра 2013)

REFERENCES

1. J. T. Kiehl, K. E. Trenberth, *Bull. Am. Meteorol. Soc*. **78** (1997) 197
2. D. H. Gibson, *Chem. Rev*. **96** (1996) 2063
3. X. Yin, J. R. Moss, *Coord. Chem. Rev*. **181** (1999) 27
4. M. Shi, Y. M. Shen, *Curr. Org. Chem*. **7** (2003) 737
5. S. Zhang, Y. Chen, F. Li, X. Lu, W. Dai, R. Mori, *Catal. Today* **115** (2006) 61
6. J. Huang, T. Ruther, *Aust. J. Chem*. **62** (2009) 298

7. T. Inoue, S. Fujishima, S. Konishi, K. Honda, *Nature* **277 (**1979) 637
8. G. Li, S. Ciston, Z. V. Saponjic, L. Chen, N. M. Dimitrijevic, T. Rajh, K. A. Gray, *J. Catal*. **253** (2008) 105
9. B. Vijayan, N. M. Dimitrijevic, T. Rajh, K. A. Gray, *J. Phys. Chem., C* **114** (2010) 12994
10. K. Mori, H. Yamashita, M. Anpo, *RSC Adv.* **2** (2012) 3165
11. N. M. Dimitrijevic, B. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He, P. Zapol, *J. Am. Chem. Soc*. **133** (2011) 3964
12. a) P. G. Jessop, D. J. Heldebrant, X. W. Li, C. A. Eckert, C. L. Liotta, *Nature* **436** (2005) 1102; b) P. G. Jessop, S. M. Mercera, D. J. Heldebrant, *Energy Environ. Sci*. **5** (2012) 7240
13. a) C. M. Wang, H. M. Luo, D. Jiang, H. R. Li, S. Dai, *Angew. Chem. Int. Ed*. **122** (2010) 6114; b) C. M. Wang, X. Y. Luo, H. M. Luo, D. Jiang, H. R. Li, S. Dai, *Angew. Chem. Int. Ed.* **123** (2011) 5020
14. J. Im, S. Y. Hong, Y. Cheon, J. Lee, J. S. Lee, H. S. Kim, M. Cheong, H. Park, *Energy Environ. Sci*. **4** (2011) 4284
15. L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int. Ed*. **51** (2012) 4714
16. B. F. Goodrich, E. A. Price, W. F. Schneider, J. F. Brennecke, *J. Am. Chem. Soc*. **132** (2010) 2116
17. A.-H. Liu, R. Ma, C. Song, Z.-Z. Yang, A. Yu, Y. Cai, L.-N. He, Y.-N. Zhao, B. Yu, Q.-W. Song, *Angew. Chem. Int. Ed*. **51** (2012) 11306
18. L. L. Snuffin, L. W. Whaley, L. Yu, *J. Electrochem. Soc*. **158** (2011) F115
19. a) R. F. Howe, M. Gratzel, *J. Phys. Chem*. **89** (1985) 4495; b) R. F. Howe, M. Gratzel, *J. Phys. Chem*. **91** (1987) 3906
20. N. M. Dimitrijevic, Z. V. Saponjic, B. M. Rabatic, O. G. Poluektov, T. Rajh, *J. Phys. Chem., C* **111** (2007) 14597
21. R. W. Fessenden, R. H. Schuler, *J. Chem. Phys*. **39** (1963) 2147
22. Y. S. Won, D. Cho, Y. Kim, J. Lee, S. S. Park, *J. Appl. Polym. Sci*. **117** (2010) 2083
23. B. O'Regan, M. Gratzel, *Nature* **353** (1991) 737
24. G. Li, N. M. Dimitrijevic, L. Chen, T. Rajh, K. A. Gray, *J. Phys. Chem., C* **112** (2008) 19040.