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Using metal nanostructures to form hydrocarbons from carbon dioxide, water and sunlight

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Based on experimental results, we propose a mechanism that allows the use of metal nanostructures to synthesize hydrocarbons and carbohydrates from carbon dioxide, water and sunlight. When sunlight impinges on cobalt nanostructures in a glass chamber, its intensity is greatly enhanced around the tips of the nanostructures through surface plasmon excitations focusing effect, and it then photodissociates the water and carbon dioxide molecules through enhanced photon absorptions of ions around the tips of the nanostructures. The photodissociated molecules in excited states remain on the cobalt nanostructure surfaces and various hydrocarbons and carbohydrates then will be formed around the surfaces at temperatures much lower than 100 °C. *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:10.1063/1.3657847]

I. INTRODUCTION

Solar energy can be a viable alternative energy source if it could be effectively converted and stored in the form of hydrocarbon fuels on a large scale at low cost. Researchers have endeavored to replicate natural photosynthesis by converting carbon dioxide and water to hydrocarbons and carbohydrates.¹⁻⁴ The basic mechanism of these artificial photosynthetic processes is converting the solar energy into electrical energy and then storing the electrical energy in the form of hydrocarbons and carbohydrates. However, the current designs of those devices are complex, and the efficiency is still very low although some progress has been made in attaining a higher photoelectrochemical conversion efficiency for generating hydrocarbons at ultraviolet or short visible wavelengths.¹ Natural photosynthesis through agricultural crops can be applicable to the production of biofuels. However, a dramatic increase in ethanol production may be limited by the fact that grain production for ethanol would compete for limited agricultural land, because the solar energy storage efficiency of natural photosynthesis is generally much less than 10%.⁵

We recently discovered and reported a process to convert water and carbon dioxide into hydrocarbons and carbohydrates on femtosecond-laser-induced metal nanostructures with solar energy.⁶ This technology represents an effective way to (a) replicate the natural process of photosynthesis and (b) store solar energy. We have directly synthesized hydrocarbon compounds with more than two carbons per molecule from carbon dioxide, water, and sunlight at a production rate of more than 10 milliliter (of hydrocarbons and carbohydrates in the solid or liquid phase) per gram of the nanostructured metal per hour (mL/(g×h)), which is significantly higher than the rates in previous studies.¹⁻⁴ However, some experimental conditions, such as maintaining a three-phase (gas/liquid/solid) interface, were not discovered in the previous work. The details of the chemical compositions of the surfaces of the cobalt nanostructures were not clear, and the proposed mechanism lacked experimental support, which are fundamentally important to better understanding this phenomenon and to further control this process for applications. Based on experimental

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results, in this paper, we propose a more comprehensive mechanism for converting carbon dioxide and water to hydrocarbons and carbohydrates with sunlight irradiation on metal nanostructures which may have great potential for manufacturing at low cost on a large scale.

II. PHOTOSYNTHESIS FROM CARBON DIOXIDE, WATER AND SUNLIGHT ON COBALT NANOSTRUCTURES

In the experiments using the simple setup shown in Figure 1, we placed a thin layer of nanostructured Co microparticles with femtosecond laser irradiations⁷ at the bottom of a glass chamber. The microparticles were then covered by distilled water with a depth of about 1 mm so that a very shallow water layer can be maintained when the dew returns back to the nanostructured surfaces as shown in Figure 1, and the glass chamber was filled with CO₂ at a pressure up to about 5 atm, this three-phase experimental condition is found to be essential for the hydrocarbon formation. In the laboratory, a light source was used to simulate sunlight at 100 mW/cm² and irradiate the nanostructured Co microparticles in the sealed container at room temperature. After about 6 hours of irradiation, the solution became turbid and light brown, and a layer of oil- or wax-like substance accumulated on its surface. Using proton nuclear magnetic resonance (¹H NMR) and gas chromatography with mass spectrometry and with thermal conductivity detector (GC-MS and GC-TCD) techniques, we analyzed the produced compounds and found that H₂, CO (carbon monoxide), and CH₄ (methane) were formed in the gas in the glass chamber. Analysis of the solution after irradiation showed that alcohols were synthesized in the water. The analysis of the accumulated oil- or wax-like material on the water surface indicated that various types of hydrocarbon bonds were present, including alkanes (C–C), olefins (C=C), alcohols (C–O–H), and branched paraffins. To demonstrate the feasibility of this process, we have also harvested some oil/wax-like hydrocarbons and carbohydrates obtained with this device in natural sunlight, and shown that these compounds readily undergo combustion (Figure 1). For the comparison of the photosynthesized hydrocarbon fuels with typical gasoline and petroleum, chemical contents are also shown in Figure 1. The photosynthesized hydrocarbon fuel can be used easily for applications or storage at low cost. We also discovered that when the CO₂ pressure in the glass container is higher, the efficiency of the solar energy storage increases. We did not observe any obvious degradation of the Co nanostructures after more than ten uses in the experiments if the light intensity is lower than about 400 mW/cm², which is about four times that of the sunlight.

III. THE SURFACE CHEMICAL COMPOSITIONS OF THE METAL NANOSTRUCTURES

In our previous work,⁶ using the energy-dispersive x-ray (EDX) spectrum with a scanning electronic spectroscopy (SEM) machine, we could not detect any oxidations on the cobalt nanostructures because the EDX is not sensitive to the chemical analysis for the surface layer within a few nanometers. To analyze the surface chemical compositions of the Co surfaces, we studied three controlled samples by x-ray photoelectron spectroscopy (XPS). As in Figure 2, spectrum 1 represents Co particles without the nano-flakes structure, and both the displacement binding energy and the relative intensity are consistent with the literature.^{8–13} For this sample, the Co₂p_{3/2} and Co₂p_{1/2} peaks indicate the main compound of the surface oxide layer is Co₃O₄. After irradiation by femtosecond laser, nano-flakes structure formed on the surface of Co particles and the Co peaks shift to a higher binding energy, which is shown as spectrum 2 in Figure 2. The peak shift from Co₂p_{3/2} to Co₂p reveals that CoO is the main compound in the oxide layer. Spectrum 3 shows the oxide layer after several days' artificial photosynthesis reaction. The structures of spectrum 3 remain the same as those in spectrum 2, which indicates that the oxide layer does not change, even during long time artificial photosynthesis.

With a transmission electron microscope (TEM), we have observed the CoO layer of the cobalt nano-flakes (as shown in the SEM in Figure 3) on a cobalt microparticle surface. As shown in the TEM in Figure 3, the gray part on the edge of the nanostructures (about 1 nm thickness) shows the CoO layer which has less condensed structure than the cobalt metal inside the nanostructures. The

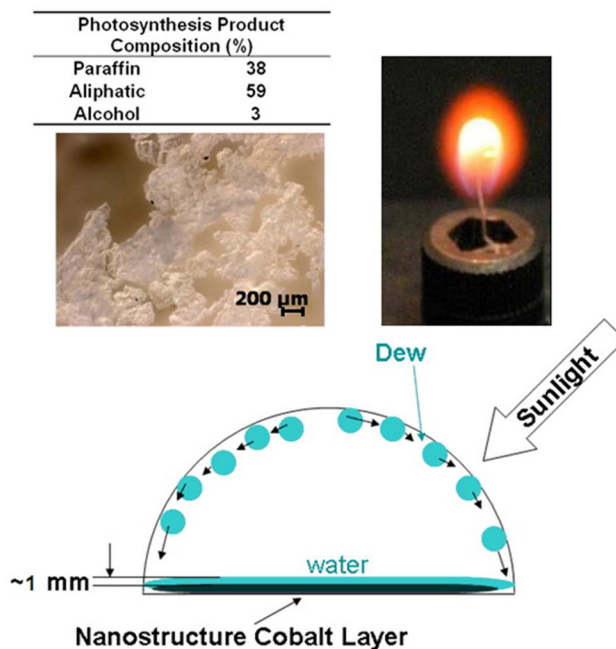


FIG. 1. The cross section of a glass chamber of an experimental setup for artificial photosynthesis with nanostructures. After sunlight irradiation on nanostructured Co microparticles immersed in water with CO_2 in the sealed glass chamber, a thin layer of oil- or wax-like material forms on the water surface. The curved wall of the glass chamber easily permits flow of the dew of water and hydrocarbons back toward the nanostructured cobalt. The optical microscopy image shows the oil/wax like hydrocarbons. The table shows the chemical contents in the water solution and the oil/wax like hydrocarbons. The flame in the optical image shows the oil/wax like compounds readily undergo combustion.

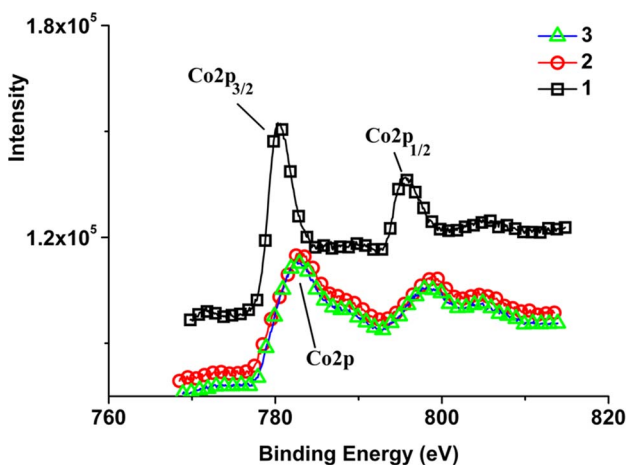


FIG. 2. X-ray photoelectron spectroscopy (XPS) spectra of Co measured in a high-resolution scan mode. Spectrum 1 represents Co particles without nano-flakes structure, the $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ peaks indicate the main compound of the surface oxide layer is Co_3O_4 . Spectrum 2 shows after irradiation by femtosecond laser in water, CoO becomes the main compound of the oxide layer as the peak shifts from $\text{Co}2p_{3/2}$ to $\text{Co}2p$. Spectrum 3 shows the CoO layer does not change after several days' artificial photosynthesis reaction.

photosynthesis processes do not obviously influence the thickness of the CoO layer and we did not find obvious formation of Co_3O_4 on the cobalt surface after the photosynthesis processes.

When the femtosecond laser interacts with the Co micro-particles dispersed in water,⁷ after some laser pulse irradiations the Co_3O_4 layer is ablated away, the underlying cobalt metal is melted to form a thin layer of CoO on the cobalt nanostructures. The CoO layer may prevent the cobalt

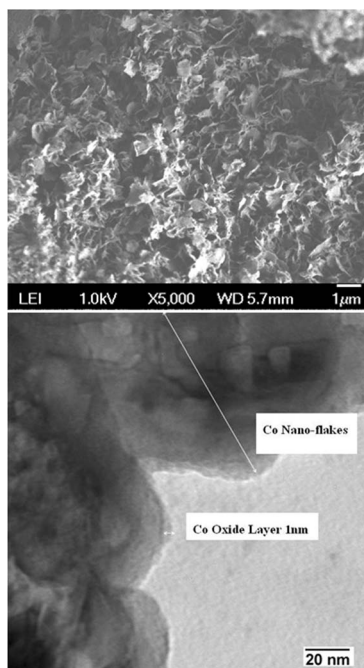


FIG. 3. The scanning electron microscopy (SEM) (upper) image and the transmission electron microscopy (TEM) (lower) image of the surface of a nanoflaked Co particle. On the edge of the TEM image of the nano-flakes, the gray part (thickness about one or two nanometers) shows the CoO layer which has less condensed structure than cobalt metal inside the particles.

from further oxidation in the photosynthesis processes. The observation of the surface-enhanced Raman spectra (SERS) signal with these cobalt nanostructures suggests the thin layer of CoO does not prevent the interactions between light and the metals for the photosynthesis.

IV. MOLECULAR PHOTODISSOCIATIONS WITH METAL NANOSTRUCTURES

To directly investigate the functions of metal nanostructures in the photosynthesis, we have simply sealed water and the nanostructured Co microparticles in a glass container for irradiation with the same light source as in Figure 1 and at room temperature. The gas in the container after the irradiation was analyzed with GC-TCD. We found that a small amount of hydrogen gas was formed. We also performed the same irradiation of carbon dioxide and nanostructured Co microparticles sealed in the glass container, and a similar amount of carbon monoxide gas was formed. Thus these experiments show the existence of the dissociation processes of H_2O and CO_2 . If using Co microparticles without nanostructures, we did not find any formation of hydrogen or carbon monoxide under the conditions described above. The fact that the nanostructured Co surface enhanced the photodissociation is of importance for the hydrocarbon synthesis. When the photodissociated water molecules (containing hydrogen atoms at excited states) and the photodissociated carbon dioxide molecules (containing carbon monoxide molecules (CO) at excited states) formed in the photodissociation coexist around the Co surface, various hydrocarbons will be synthesized with Co atoms or ions as a catalyst.

As an additional control, we used nanostructured silver surfaces by coating nanostructures with silver¹⁴ to perform photodissociation experiments similar to the ones on Co described above. We obtained the same photodissociation of water and CO_2 . However, when using the nanostructured silver to perform the experiment in Figure 1, we did not observe measurable amounts of hydrocarbons or carbohydrates.

Further direct observation of the surface-enhanced Raman spectra (SERS) signal (Figure 4) of the carbon monoxide (CO) formed on cobalt nanostructures also supports the photodissociation of CO_2 . For the SERS measurements, both untreated and femtosecond laser nanostructured cobalt

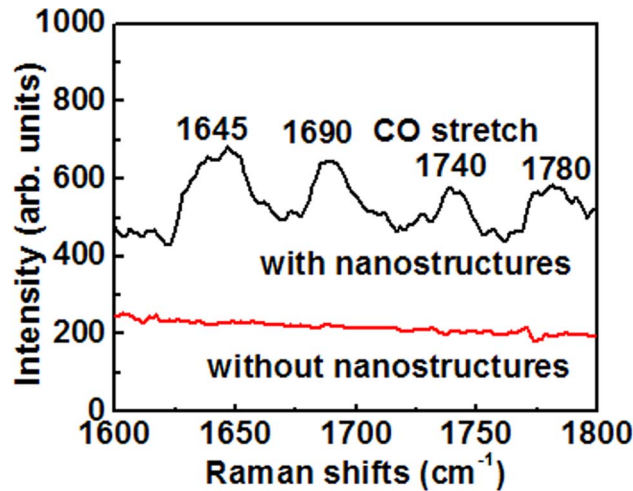


FIG. 4. The surface-enhanced Raman spectra (SERS) of carbon monoxide (CO) formed from CO₂ by photodissociation on cobalt nanostructures.

microparticles were put into separate glass containers with CO₂ gas. The Raman-scattering measurements were conducted on a portable system with a resolution of about 10 cm⁻¹, equipped with a semiconductor laser providing an excitation wavelength of 785 nm. Figure 4 shows the Raman spectra obtained from the surfaces of cobalt microparticles with and without nanostructures after light irradiation. There is no visible Raman scattering signal from the untreated microparticles. However, Raman peaks can be clearly observed when using nanostructured particles. Some of the peaks are related to CO vibrations, such as the peak at 1740 cm⁻¹ assigned to the stretching vibration of a CO molecule. The data in Figure 4 show that CO₂ gas is photodissociated into CO on the surfaces of the cobalt nanostructures and that the CO molecules can be detected with SERS.

V. DISCUSSION

In the experiment we discovered that for the hydrocarbon formation, the thickness of the water above the cobalt particles has to be as thin as possible to maintain a three-phase condition when the sunlight irradiates cobalt particles. Gas (CO₂, water vapor and photodissociated molecules), liquid (water with dissolved CO₂) and solid (nanostructured Co catalyst) are involved in the reactions in the hydrocarbon and carbohydrate formations. This observation is in agreement with the recent research result that a three phase interface increases the reaction rate of the CO₂.^{15,16}

The observation of SERS also supports the concept that the nano-focusing effect occurs with the nanostructures^{17,18} although there is a CoO oxide layer on the Co nanostructure surface. SERS can be explained by the electromagnetic (EM) enhancement.¹⁸⁻²⁰ The simplest expression that describes the EM enhancement is the electric field at a small spherical particle,

$$E_{local} = \frac{E_0}{\varepsilon(\omega) + 2} \quad (1)$$

where E_{local} is the local electric field due to the polarization of the particle, ω is the frequency of the incident light, $\varepsilon(\omega)$ is the dielectric constant of the small metal at the frequency ω , and E_0 is the electric field of the incident light. According to this equation, the local electric field will approach infinity when the dielectric constant approaches -2, but the small imaginary part of the dielectric constant keeps the EM enhancement finite. For particles smaller than 100 nm, the resonant frequency of this plasmon effect depends on the metal material, size and shape of the particles.^{17,21} The EM enhancement factor ($\frac{E_{local}}{E_0}$) can be larger than 10².²⁰ The EM enhancement occurs since the local field described by Equation (1) oscillates at the frequency of the incident light as a dipolar optical radiation source and can interact with molecules near the surface at a distance d , which lead to a distance dependence of the SERS signal intensity. If the d is less than 3 nm, the decrease

of the SERS signal intensity is not significant for metal structures tens of nanometers in size.^{17,18} Therefore, the SERS of the nanostructured cobalt also show that the very thin CoO layer found on the surface of the Co nanostructure surface does not obstruct the surface plasmon effect necessary for the electromagnetic field enhancement. The photon energy of incident light is too small to be absorbed for dissociating water and carbon dioxide. The high intensity of the light may result in two-photon or multiple-photon absorptions. The enhancement factor can be more than 10^8 for a two-photon absorption process which is proportional to the fourth power of the local electric field, E_{local}^4 . The enhanced light may directly disassociate water and carbon dioxide molecules, then hydrocarbons and carbohydrates form on the nanostructure surfaces from the disassociation.

The energy band gap of CoO is around 2.5 eV;²² the CoO layer may be excited with the one or two-photon absorption processes. CO and H₂ can be produced by dissociating CO₂ and water molecules in a cobalt complexes system under visible light irradiation via mono-electronic or polyelectronic processes.²³ The layer of CoO could act as a photosensitizer which will absorb visible light^{22,24} and then provide energy for molecules and electrons to be excited. Since Co(II) ion is an efficient and specific catalyst of CO₂ and water splitting²³ as well as a good catalyst for the formation of hydrocarbons and carbohydrates,²⁵ the formation of hydrocarbons and carbohydrates will follow or be concurrent with the dissociation process of CO₂ and water around the tip of nanostructure. Co ions on the nanostructure surface act as catalyst for dissociating CO₂ and water and forming hydrocarbons and carbohydrates. The Co nanostructures enhance the light intensity around the tip, which leads the artificial photosynthesis process because of the high concentration of dissociated CO₂ and water molecules around the tips.

Using silver nanostructures, we can photodissociate water and carbon dioxide yet cannot synthesize hydrocarbons or carbohydrates. This is in agreement with the well known fact that silver is not as good a catalyst as Co for the formation of hydrocarbons and carbohydrates, such as in the Fischer–Tropsch process.²⁵ However the chemical reaction process took place at temperatures much lower than 100 °C, which is significantly different from that in processes like Fischer–Tropsch process in which the temperature is much higher than 100 °C. This can be understood by saying that the photodissociated molecules are in excited states for the hydrocarbon synthesis on the Co surfaces, which does not need the activation of the hydrocarbon synthesis reactions with thermal energy. However, the local temperature at the tips of the cobalt nanostructures may be very high due to the interaction between the strong local surface plasmons and the cobalt lattice vibrations. The possible local high temperature may also play a role in the photosynthesis process, which needs further study.

Therefore the above experimental results strongly support the model of a nanostructure-induced artificial photosynthesis illustrated as in Figure 5. When light impinges on the cobalt surface, the light intensity is greatly enhanced around the tips of the nanostructures according to Equation (1), and the water and carbon dioxide molecules are photodissociated (or excited; see Figure 5(a)) through a multiple photon or polyelectronic processes.²³ The products of the photodissociation (or excited molecules) remain on the surface and various hydrocarbons are formed on the nanostructure surfaces (Figure 5(b)). The possible local high temperature at the tips of the nanostructures may also play a role, as mentioned above. The saturation of thickness of the CoO layer explains that that we did not observe any degradation of the Co nanostructures after more than ten uses in the experiments shown in Figure 1. Furthermore, using the SERS signals, we may be able to microscopically monitor chemical reactions on the nanostructured metal surfaces.²⁶ Compared to metal cobalt, the noble metals (like Ag, Au, and Cu) have a smaller imaginary part of the dielectric constant and thus have a stronger EM enhancement resonance according to Equation (1), but the noble metals are not as good as cobalt for hydrocarbon molecular formation. The metal nanostructures of a combination of cobalt with noble metals may further greatly improve the hydrocarbon formation.

VI. SUMMARY

The experimental results support the mechanism that metal nanostructures can be used to synthesize hydrocarbons and carbohydrates from carbon dioxide, water and sunlight. When light impinges on cobalt nanostructures, the light intensity is greatly enhanced around the tips of the

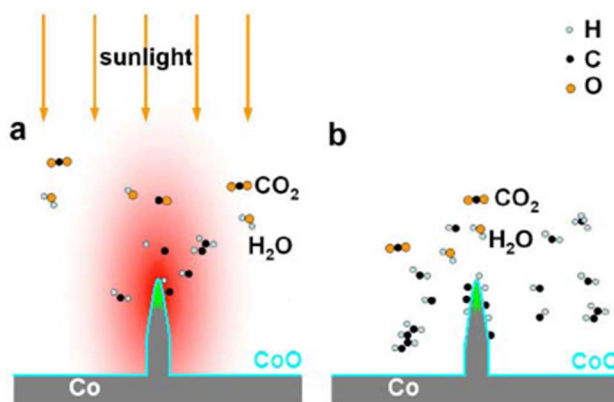


FIG. 5. The artificial photosynthesis mechanism. (a) Incident light becomes intensified around cobalt nanostructures covered with a CoO thin layer. The water and carbon dioxide molecules are photodissociated on the nanostructure surface. (b) The photodissociated molecules remain on the nanostructure surface to form hydrocarbon molecules. The green color at the tips of the cobalt nanostructures in (a) and (b) represents a local high temperature based on the optical absorption of the cobalt. The high local temperature may also play an important role in the artificial photosynthesis.

nanostructures through surface plasmon excitation. Enhanced light then dissociates (or excites) the water and carbon dioxide molecules through a multiple photon process. The products of the photodissociation remain on the surface and various hydrocarbons and carbohydrates then will be formed on the nanostructured cobalt surfaces.

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