Surface-Plasmon-Enhanced Carbon Dioxide Activation and Conversion

Hui Song,[a,b] **Jinhua Ye**[a,b,*]
[a]*Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo 060-0814, Japan.*
[b]*International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
**Corresponding author: Fax number: +81-29-860-4958, E-mail address: Jinhua.YE@nims.go.jp*

Abstract: Photocatalytic reduction of CO_2 is attractive for the production of valuable fuels and mitigating the influence of greenhouse gas emission. However, the extreme inertness of CO_2 and the sluggish kinetics of photo-excited charge carrires transfer process greatly limit the conversion efficiency. Herein, we report that the plasmonic coupling effect profoundly enhance the efficiency of CO_2 reduction through dry reforming of methane reaction,reducing activation energies for CO_2 reduction ~30% below thermal activation energies. This work provides a new pathway towards the efficient plasmon-enhanced chemical reactions via reducing the activation energies by utilizing solar energy.

Keywords: CO_2 conversion, plasmonic coupling effect, activation energy.

1. Introduction

Photocatalytic CO_2 reduction on semiconductors offer a promising and attractive route to take the advantage of abundant solar energy and recycle CO_2 resource.[1] However, the extreme inertness of CO_2 ($\Delta_f G^0$= -396 kJ mol^{-1}) and the sluggish kinetics of multiple e^-/H^+ transfer process result in low energy conversion efficiency.[2] Dry reforming of methane (DRM) reaction can reduce CO_2 by utilizing CH_4 to produce industrially important syngas (H_2 and CO).[3] However, this reaction requires operating temperatures of 1100-1300 K to activate the reactants and achieve high equilibrium conversion of CO_2 and CH_4 to syngas, which waste a lot of heat energy and shorten catalyst lifetime via sintering deterioration and carbon deposition.[4] Great efforts have been devoted to improve CO_2 conversion efficiency in DRM at lower temperatures over past few years, but most of the reported ways were limited and few strategies were reported to directly reduce the activation energies of DRM reaction. Recently, it has been reported that plasmonic metallic nanostructures can efficiently drive chemical reactions with photo-excited charge carriers to overcome activation barriers.[5,6] Plasmonic nanostructures of metals (such as Ag, Au, Cu, Pd, Pt and Rh) exhibit strong light absorption through an excitation of localized surface plasmon resonances (LSPR). Interestingly, LSPR excitation produces a large number of energetic electrons (hot electrons) at the nanostructured surfaces that can transfer to adsorbates and promote reaction rates. Herein, we report that the plasmonic coupling effect of Pt and Au NPs can significantly reduce activation energies and enhance reaction rates of CO_2 reduction in DRM reaction. Under low-intensity light (300~800 nm, ~0.6 W cm^{-2}) irradiation, the activation energies for CO_2 reduction are reduced ~30% below thermal activation energies and the reaction rate is 2.4 times higher than that of the thermal-catalytic reaction rate at 673 K.

2. Experimental (or Theoretical)

Pt and Au nanoparticles different loadings were loaded on SiO_2 (BET surface area, 436 m^2 g^{-1}) by impregnation and precipitation method. The catalysts were characterized with XRD, XPS, HAADF-STEM, HR-TEM and in situ DRIFTS measurements. The electromagnetic fields distributed around plasmonic Pt and Au nanoparticles were conducted using finite-difference time-domain (FDTD) methods (FullWAVE, Synopsys'RSoft). The catalytic test was performed under atmospheric pressure in a fixed-bed reactor system. The catalysts were *in-situ* reduced in DRM reaction for one hour. After the catalytic reactions were carried out for one hour, the effluent gas streams were analyzed using gas chromatograph (GC) equipped with a thermal conductivity (TCD) and a flame ionization detector (FID) to gain the relative amounts of CO_2, CH_4, CO and H_2.

3. Results and discussion

The HAADF-STEM image (Figure 1a) of Pt-Au/SiO_2 shows that Pt NPs with an average diameter of about 2.0 nm and Au NPs with size about 30 nm dispersed on SiO_2. The catalytic activities of the catalysts in DRM reaction with light irradiation (300 nm<λ<800 nm) at the same reaction temperature (673 K) are shown in Figure 1b. Clearly, without light illumination, the thermal-catalytic activities of Pt-Au/SiO_2 and Pt/SiO_2 were almost the same, while the Au/SiO_2 showed almost no performance in DRM reaction. However, the reaction rates of Pt/SiO_2, Pt-Au/SiO_2 and Au/SiO_2 were all improved under irradiation of light. The reaction rates of Pt/SiO_2 and Pt-Au/SiO_2 exhibited a nearly linear dependence on the light intensity. The linear dependence of catalytic activity on the light intensity agrees well with the mechanism of photo-induced reactions driven by hot electrons. The linear dependence also provides an indication that the localized heating, which usually induce an exponential dependence, is negligible in these reactions.

In order to demonstrate the observed photo-enhancement activities resulting from LSPR coupling effect of Pt and Au NPs, the impact of different irradiation wavelength on the catalytic activities of Pt-Au/SiO_2 and Pt/SiO_2 were performed. Pt-Au/SiO_2 also showed a broad absorption and two peaks locating at 275 and 520 nm (Figure 1c), combining the SPR absorption characteristics of both Pt/SiO_2 and Au/SiO_2. The dependencies of the apparent quantum efficiency (AQE) of Pt-Au/SiO_2 and Pt/SiO_2 on the wavelength of irradiation showed the similar trend to the light absorption spectra of Pt-Au/SiO_2 and Pt/SiO_2, respectively (Figure 1c). Thus, it can be concluded that the observed activity enhancement was induced by the excitation of hot carrier. In addition, the AQE of Pt-Au/SiO_2 at the wavelength of 520 nm were higher than those at the other four wavelengths and higher than that of Pt/SiO_2 at 520 nm, indicating that surface plasmon and catalytic activity of Pt/SiO_2 were significantly enhanced by introducing Au NPs.

To understand the mechanism of DRM reaction under light irradiation, the reaction kinetics test on Pt-Au/SiO_2 and Pt/SiO_2 in light and dark were carried out. Figure 1d shows Arrhenius-type plots for the CO_2 conversion rate *versus* temperature. The apparent activation energy (E_a) of Pt/SiO_2 (243.52±11.31 kJ mol^{-1}) and Pt-Au/SiO_2 (241.34±10.56 kJ mol^{-1}) are similar under dark condition. Intriguingly, the E_a over Pt/SiO_2 and Pt-Au/SiO_2 decreased to 189.23±9.39 and 170.69±10.28 kJ mol^{-1} under light illumination, respectively. These changes in E_a suggested that the coupling LSPR effect changed the energetics of DRM reaction.

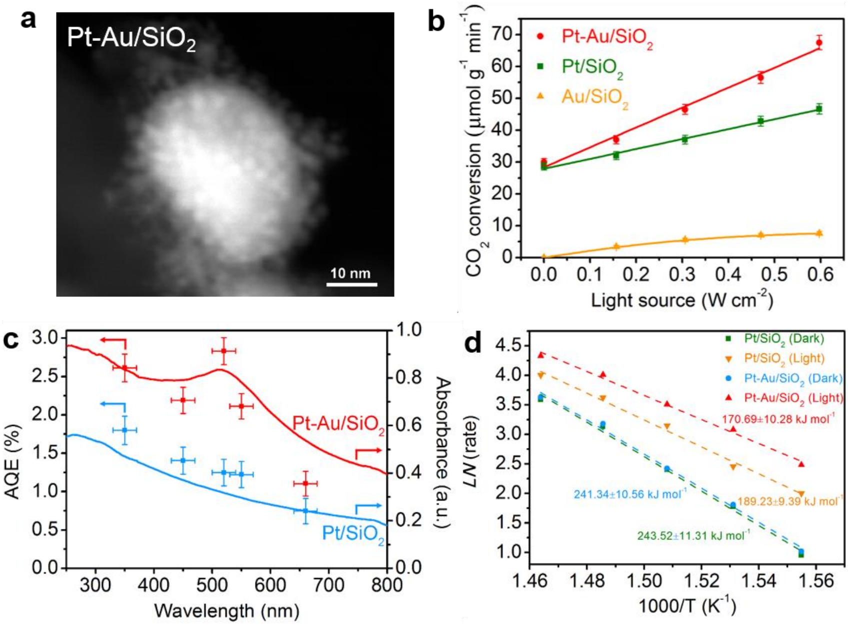

Figure 1. (a) HAADF-STEM images of Pt/SiO_2 and Pt-Au/SiO_2; b) UV-vis absorption spectra of Pt-Au/SiO_2, Pt/SiO_2 and Au/SiO_2; (c) effects of light intensity on the activities of the catalysts in DRM reaction; (d) UV-vis absorption spectra and AQE values of Pt-Au/SiO_2 and Pt/SiO_2 without or with light irradiation of different wavelength ranges.

In order to reveal the underlying mechanism, FDTD methods were conducted to calculate the intensity of electric near-field of catalysts. Figure 2 shows the electric fields distributions of the Pt-Au/SiO_2, Pt/SiO_2 and Au/SiO_2 under light excitation of 350 and 530 nm. The intensities of electric fields on Pt-Au/SiO_2 at the

350 and 530 wavelengths were significantly higher than those of Pt/SiO_2 and Au/SiO_2 (Figure 2c and f), respectively, which could be explained by the strong near-field coupling between Pt and Au NPs. The generated strong electric fields yield high concentrations of hot electrons at the surface of the Pt and Au NPs. These electrons tend to be more energetic under thermal excitation (673 K) and might play a vital role in activating chemical bonds in chemical transformations.

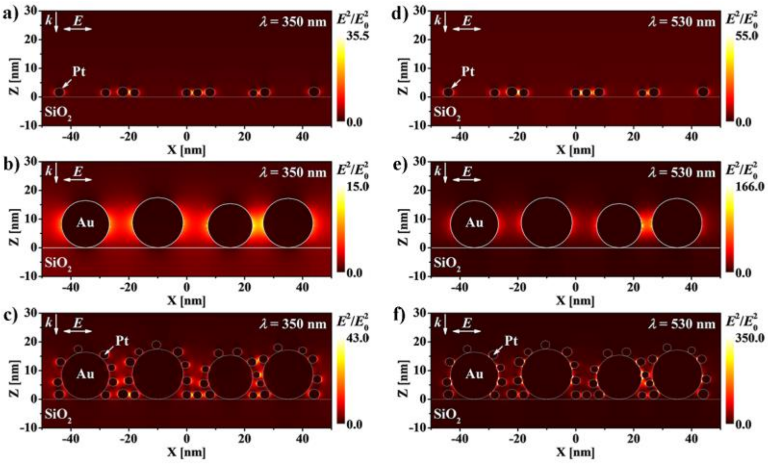

Figure 2. Spatial distribution of the enhancement of electric field intensity at the wavelength of 350 and 530 nm, from FDTD simulation of (a and d) Pt/SiO_2, (b and e) Au/SiO_2, and (c and f) Pt-Au/SiO_2.

.

The speculated mechanism of thermal and photo-thermal catalytic DRM reaction on Pt-Au/SiO_2 can be explained by Figure 3. In the thermal catalytic reactions, CH_4 adsorbed on Pt surface are firstly dissociated to $CH^*_{x(x=0\text{-}3)}$ and H*, then the adsorbed CO_2 react with H* to form COOH* species (Figure 3B.b) and subsequently generate CO* and OH* species (Figure 3B.c). After that, these intermediate species are subjected to a series of reactions to produce CO and H_2 (Figure 3B.h and i). For the photo-thermal reactions, the DRM reaction over Pt-Au/SiO_2 was also supposed to proceed via the thermally activated process (673 K). Under UV-visible light irradiation, the LSPR of Pt and Au are excited and the electric field intensities at Pt and Au NPs surface are significantly enhanced due to the presence of plasmonic coupling effect of Pt and Au. The hot electrons can overcome the activation energy barrier and transfer to the LUMO of the adsorbed CO_2 and CH_4 molecules (Figure 2A and 2B.e), then decay back to the metal. As a result, the energy originating from energetic carriers can deposit to C=O and C-H bonds, resulting in weakening the C=O and C-H bonds and promoting DRM reaction rates.

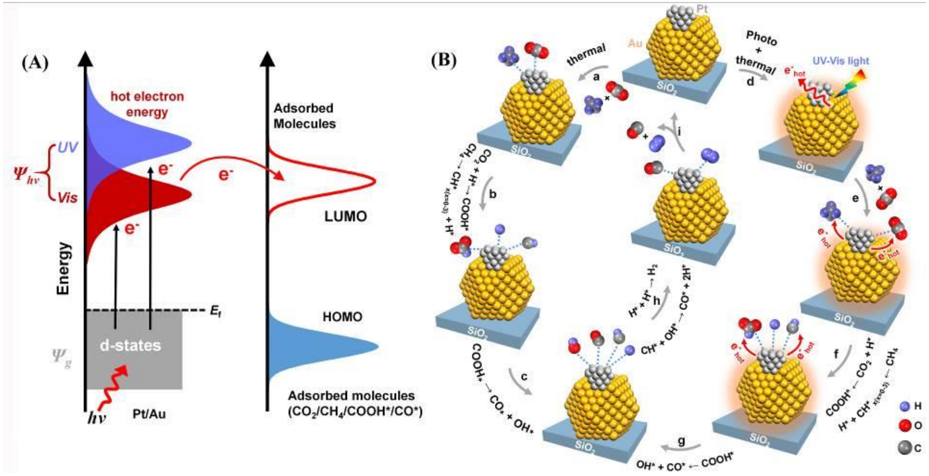

Figure 3. (A) Schematic of energy transfer from phot-excited plasmon states to molecular states. (B) Proposed mechanism for DRM reaction on Pt-Au/SiO_2 in the dark or under UV-visible light illumination.

4. Conclusions

In conclusion, we have demonstrated the coupling of Pt and Au LSPR effect for efficient CO_2 reduction in DRM reaction using UV-vis light illumination. The plasmonic coupling effect reduces the activation energies and changes the energetics of the DRM reaction mechanism, with a reaction rate 2.4 times higher than that of the thermocatalytic reaction rate. Both UV and visible light absorption of Pt-Au/SiO_2 generates stronger electric fields and excites high concentrations of hot electrons via effective coupling LSPR effect of Pt and Au NPs to activate the adsorbed reactants and facilitate the reaction rate. Our findings suggest that it is possible to design more active bimetal plasmonic catalysts through rational combination of plasmonic metal promoter and reaction-selective metal catalyst.

References

1. H. Song, X. Meng, T. Dao, W. Zhou, H. Liu, L. Shi, T. Nagao, T. Kako, J. Ye, ACS Appl. Mater. Interfaces, accepted.
2. X. Meng, L. Liu, S. Ouyang, H. Xu, D. Wang, N. Zhao, J. Ye, *Adv. Mater.* 28, 2016, 6781.
3. H. Liu, X. Meng, T. Dao, H. Zhang, P. Li, K. Chang, T. Wang, M. Li, T Nagao, J. Ye, Angew. Chem. Int. Ed. 54, 2015, 11545.
4. D. Pakhare, J. Spivey,Chem. Soc. Rev. 43, 2014, 7813.
5. P. Christopher, H. Xin, S. Linic, *Nat. Chem.* 3, 2011, 467.
6. U. Aslam, S. Chavez, S. Linic, Nat. Nanotechnol. 12, 2017, 1000.