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The Detection of Volatile Organic Compounds (VOCs) Emissions by Using Photoacoustic Method- A Case Study of Formaldehyde

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I. Introduction

Building materials such as wood based materials, adhesive, paints, varnish, and vinyl floorings are important sources of volatile organic compounds (VOCs). Taiwan is located in subtropical and tropical zone where the climate is typically hot and humid for the whole year. Therefore, they have been used widely as interior building material. However, there are several hundred different pollutants in ambient indoor environment. Formaldehyde is often considered as one of the most dangerous toxins that can be found in living space.

None of VOCs (such as formaldehyde) detected methods fulfilled the requirements for an ideal detection technique. The application of several different approaches in formaldehyde emission measurements gives reasonable amount of information to make conclusions concerning formaldehyde emissions and abatement possibilities[7]. The originality photoacoustic (PA) system employed was designed for simultaneous response, low electronic, and high sensitivity. In order to facilitate their identification without a molecule specific separation step preceding the PA measurement, and to reduce the interference of water absorption the IR characteristic region should be selected for the utility of this experiment design.

II. Experimental

Photoacoustic is a calorimetric method, in which the optical energy absorbed in a gaseous species is directly measured through the heating produced in the medium. The small local temperature variation in the gas is associated to a pressure variation. When the deposited optical energy is modulated, a periodic heating is produced, thus generating a modulation of the sample pressure. This results in an acoustic wave, which can be detected using a sensitive miniature microphone. Therefore, the PA effect can be divided into five steps (Figure 1):

The absorbed energy is converted into acoustic energy that is cause the atoms

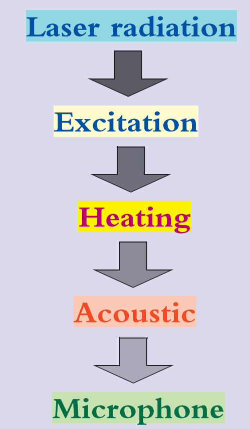


Figure 1. The photoacoustic basic theory

in the gas molecule to vibrate. Therefore, as the light is chopped, the heated gas expands and causes a pressure rise which will alternately increase or decrease the sound pressure levels. The magnitude of the sound pressure signal that results is described by the equation:

$$\text{Sound pressure level} ? \frac{? \left(\frac{C_p}{C_v} ? 1\right) ? m I_0}{?_a}$$

σ = a constant coefficient,
C_p 、 C_v =the heat capacity of the gas at constant pressure and constant volume,
m = the gas concentration,
I_o = the intensity of light,
ν_o = the light chopper frequency.

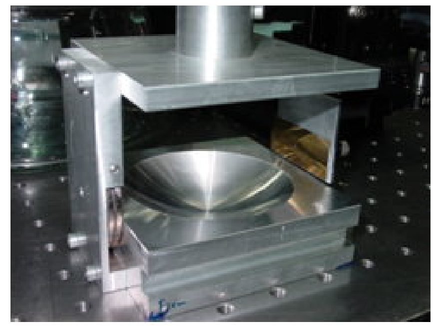
III. Materials and Methods

Photoacoustic systems

The photoacoustic system designed to compose of the equipments and procedures which can be divided into four units part shown in Figure 2: (1) Light source - the optical parametric oscillator laser (OPO) (2) Multipass acoustically open photoacoustic detector (MOPAD) (3) Desiccator chamber and (4) Lock-in amplifier analysis system.

Multi-pass acoustically open photoacoustic detector (MOPAD)

The MOPAD consists of two optical mirrors and acoustic reflectors. The two parallel gold coated optical mirrors reflected the laser beam with a designated path. A microphone sensor was located at the center of the plane carved out by the laser beam (Figure 3).



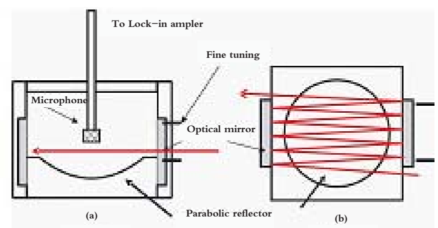


Figure 3. Schematic views of the MOPAD detector: (a) the plane of the drawing is normal to the plane of the optical mirrors and contains the acoustic axis; (b) View of MOPAD showing the path of the multiple passes of the laser beam inside the detector.

IV. Results

The photoacoustic spectra were taken by scanning the OPO (2796cm^{-1} ~ 2806cm^{-1}) through a wavelength range where formaldehyde absorbs (Figure 4). The moisture absorption lines could overlap most of the formaldehyde lines at 2801.5 cm^{-1} and 2082.9 cm^{-1}. However, PA methods could detect the amounts of formaldehyde and negligible water vapor effect in the ambient. A spectral feature of formaldehyde, centered at 2805 cm^{-1} and free of water-interference, was used to evaluate the sensitivity of our technique for detecting formaldehyde

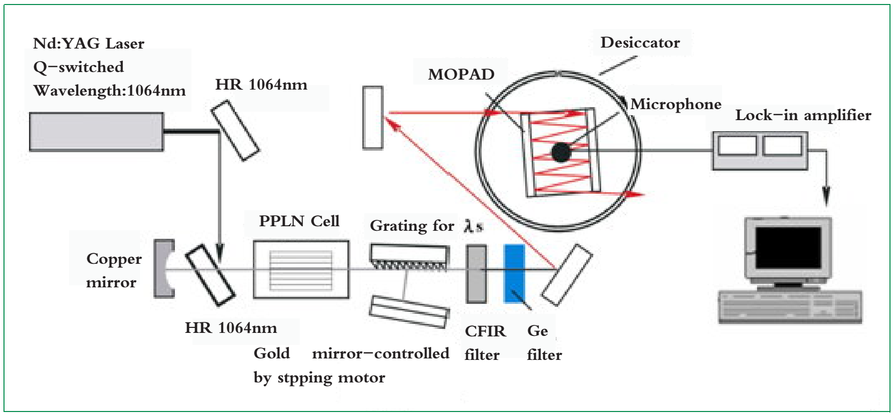


Figure 2. Schematic illustration of the OPO-MOPAD measurement setup with the desiccator test cell.

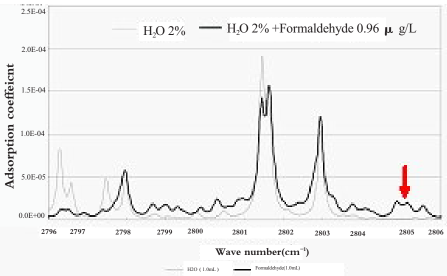
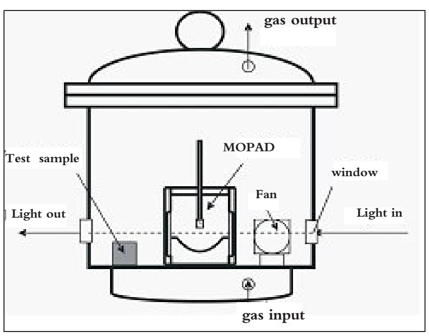


Figure 4. The comparison of spectra ($2796 cm^{-1}$ ~ $2806\ cm^{-1}$) calculated for formaldehyde and moisture in ambient laboratory air.

Calibration of the equipment was performed at $2805\ cm^{-1}$ using the modified standard formaldehyde (0.05~1.5mg/mL) that were tested to draw the calibration curve (Figure 5).



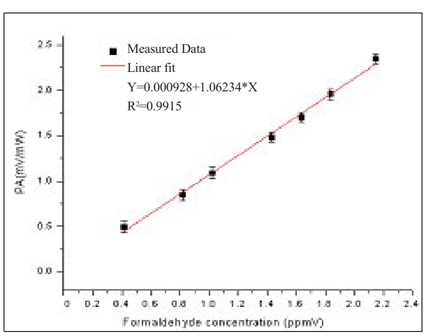
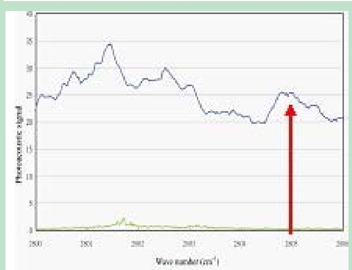
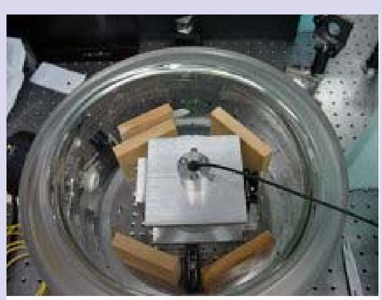


Figure 5. Potoacoustic methods calibration curve measured for formaldehyde between 0.05~1.5mg/mL.

Formaldehyde emission of the wood based composited materials

The initial and subsequent formaldehyde emissions from the products were determined by testing MDF and LVL at 22°C, RH 60% from formaldehyde collected in the desiccator chamber with analysis by photoacoustic method. the concentrations of formaldehyde in LVL (9.2 mg/L) and MDF (0.185 mg/L) were recorded by the photoacoustic method (Figure 6).





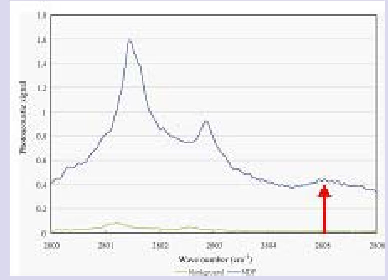


Figure 6. Measured photoacoustic spectrum of (a)LVL and (b)MDF formaldehyde emission in ambient laboratory air.

Formaldehyde adsorption of the bamboo charcoals

The bamboo charcoals were derived by the variation of activation temperature. Therefore the surface chemistry of charcoal affects the adsorption capacity significantly while the texture characteristics of surface area and pore volume play a minor role in formaldehyde adsorption. The results from Figure 7, the photoacoustic indicated that the adsorptive capacity of bamboo charcoal and initial 1.8 ppmV formaldehyde decreased to 0.2 ppmV.

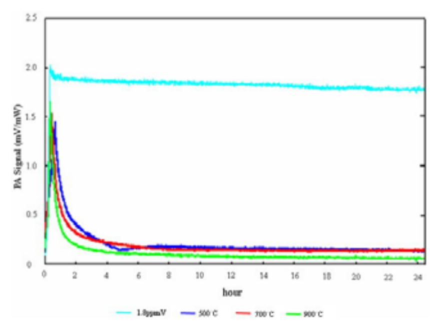


Figure 7. The formaldehyde adsorption history obtain the various charcoalization bamboo charcoals in the small chamber under ambient air.

V. Conclusions

The high sensitivity of photoacoustic detection and the ability to make measurements in real time allow the characterization of materials and the monitoring of trace gases in a realistic environment. It is an effective method for evaluating the reduction performance of adsorption charcoal and the quantitatively evaluation can be measured simultaneity. This study was successful in designing a highly sensitivity and excellent selectivity method in detecting formaldehyde emission from

MDF and LVL were accomplished. Furthermore, we demonstrated its sensitivity with trace detection of formaldehyde and the use of the apparatus for time-resolved measurement of the gas adsorption in bamboo charcoal.

In future research, the photoacoustic system will be improved to solve more complex problems, such as monitoring the indoor air quality associated with VOCs.

VI. Acknowledgements

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Profile of Old Architecture Rescue Center

Photo/text April Hueimin Lu
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1.About Old Architecture Rescue Center

Carved beams and painted columns are so beautiful and present exquisite crafts' aesthetics in every detail in the arts of eastern architecture which is far contrast to the western. Although traditional arts of architecture still surprise many foreigners, it stays in an inferior situation and gradually loses its importance under the impact of modern industry and technology. Therefore, owing to acknowledge the important task of cultural heritage preservation, Old Architecture Rescue Center (OARC) of NPUST (http: //oarc.npust.edu.tw/) was established and preserves about one thousand pieces of architectural elements with exquisite ornaments of old Xinhuei temple constructed in 1926 and dismantled in 2005 (Fig. 1~2).

Fig.1 Old Architecture Rescue Center (outside)

Fig.2 Artifacts preserved in Old Architecture Rescue Center

In order to transmit the cultural beauty and techniques and to educate next generations' traditional arts, the center proceeded several projects, such as digital archive of NSC, international symposiums with workshops on emergency conservation and exploit added value of digital archives to produce innovative commodities. The center functions as a university museum as well as a research center for conservation of historical architecture and a center of innovative design. In 2008, the left structural frame (Jia-shan) of the central bay of back was reconstructed in OARC .

2.The Purposes of OARC

The purposes of OARC are to preserve and transmit Taiwanese architectural techniques and arts. Its four main functions are research, conservation, education, and production . It was also founded for nurturing architects, conservators, designers, and craftsmen as well as a territory to educate and provide creative origins.

(1) Research and Archive

One of missions of OARC is to set up a standard process for hetero conservation of temple architecture and its related arts in terms of research and archive from dismantling, recording, classifying, coding, and measuring to restorations. The preservation of cultural heritage , especially, Taiwanese traditional architecture and arts are the major field of research.

In the year of 2007/03-2008/02, OARC participated National Digital Archives Program of NSC to proceed 2D digital archives under the project of "Digital archives of museum of rural arts". Afterwards, for the following three years, OARC continues to proceed 2D archives and research 3D digital technology. The website of http: //oarc.npust.edu.tw shows the results of one year of funding and three years of self supports on digital archives of a traditional temple and its related projects.

At present, OARC preserves about 1000 pieces of architectural elements and finish the digital archive- the retrieval system of 200 structural elements of left frame of back hall with descriptions .

(2)Conservation and Restoration

OARC occasionally holds international symposiums and workshops on theory and practice of traditional temple architecture and arts, such as timber structure, wood polychrome, fresco, wood carving, and clay sculpture. It is to transmit those precious traditional techniques and advocate adequate techniques for cultural heritage preservation and restoration.

(3)Education and Exhibition

The center is not only a shelter for these dismantle elements, but also a "learning by doing" workshop. It opens periodically extension courses on timber structure as well as conservation of architectural decorations. To integrate the extensional course of timber structural reconstruction on the left frame of back hall, the architectural exquisite techniques and aesthetics can be presented for public to invoke more attentions for the beauty of arts crafts and construct a learning environment for arts and humanities. The integrated function of archive, reconstruction, and education with exhibition is one of distinguished features of the center.

(4) Creation and Production

From preservation of cultural heritage to creation of innovative cultural products is a necessary process to promote the beauty and value of those architectural elements. Some prototypes of innovative commodities are developed, such as 1/4 model, 3d animation of temple reconstruction, carving artifacts, and etc. Those prototypes of innovative commodities has ever participated international Licensing EXPO(Fig.3~4).

Fig3 2009 International Licensing Expo (Delivery before exhibition in Taipei)

Fig4 OARC, 2009 International Licensing Expo in Las Vegas, USA.

3.List of recent projects

(1) List of recent projects of OARC

2010 Extension on digital archives of traditional temple architecture: creative production and educational extension on piling up Do timber structure (NSC)

2010 Environmental planning of settlements after Morak typhoon (CEPD)

2009 1.Innovative products of piling up Do timber temple structure of old Xinhuei temple , "Licensing International Expo" in Las Vegas, USA (NSC)

2.Innovative Products of piling up Do timber temple structure of old Xinhuei temple, " ACE Fair in Kuangzhong, Korea" (NSC)

2009 Cultural heritage conservation technology: research and application of 3D scanning techniques on traditional temple architecture and art (NSC)

2008 Timber structure extension courses (CLA)

2008 International Symposium and workshop on Emergency Conservation (CCA)

2007 Park of Rural cultural extension and education (COA)

2007 Digital Archive of rural arts museum(NSC)

2007 Preservation and rehabilitations of old Architecture - sustainable development of rural Taiwan (CEPD)

2006 Preservation of temple culture - a study on Temple architectural ornament of Xinhuei Gong, Pingtung

4.Digital archives and its application of old Xinhuei temple (4 NSC Projects)

4.1 Digital Archives of Piling up Dou timber structure

This project is to digitally preserve all the structural members decomposed from an old temple through classification, coding, and digitalization with 2D and 3D techniques to vividly display to the public. Besides, with convenient interface of retrieval system, the public can understand the techniques and beauty of a temple to promote the preservation consciousness and enhance the artistic appreciation level of public.

The recording for digital archive of old Xinhuei temple architecture includes three different scales of digital scanning - whole, object, and detail. The whole scale digital preservation is to 3D scan whole temple before being dismantled . The 3D animation of temple before its deconstruction is shown in the website (http://oarc.npust.edu.tw/Xinhuei/movie.aspx).

The object scale of digitalization is the main task for the project of "Digital archives ". Two hundreds' components are digitalized. They are structural members of Piling up Dou timber structural system of traditional temple architecture. For some refined artifacts, such as climbing squash tube, lion seat, and Mazu mud sculpture (now is destroyed) are 3D scanned to preserve its 3D dimensional data for later applications .

4.2 the Website (http://oarc.npust.edu.tw) (Lu, 2008a,)

The preparation period is to set up the coding system of temple architecture and design the description form for each structural member. Each structure member, can be called an artifact, too, is the main object for digitalization. Setting up an idea of place and time for taking photos and control its quality is the first crucial step of digitalization. After collecting those digital contents, I design the structure of website according to the logics of the construction system of a temple. The retrieval system in the web for researchers and public are according to 1) all components, 2) key words, 3) codes of members, 4) names of members, 5) types of ornaments

For one year project, 200 structural members accompanied with 1200 photos are archived, including 28 decorative members of carving or refined painting and 7 fresco paintings. Each member has at least six photos (front, back, left, right, up, and down) with a format of 500 × 500psi and 200dpi to demonstrate its form, color, and ornament as detail as possible. Besides, each decorative member has seventeen items of description. They are 1)Serial Number, 2)Code, 3) Hall, 4)Purlin-Frame, 5)Name, 6)Scale, 7)Material, 8)Functional description, 9) Mortise-Socket, 10)Ornament, 11)Ornament in detail, 12) Theme/Type, 13)Contents of theme, 14)Technique and Color, 15)Damage, 16)Condition, 17)Craftsman, Researcher (collect, photo, description, and drawing), Restorer.

4.3 The prospect about Digital Archive of OARC

OARC has demonstrated a digital archive system for preserving traditional temple architecture in web and finished digital archives of 200 structural objects. Besides, it also develops the way of application of innovative added value of traditional architecture by developing prototypes of creative commodities in realities. Furthermore, OARC also participate international Licensing Expos to promote Taiwanese creativity and beauty and set up a web network. Both for digital contents and added value of digital archives, I have tried to exploit traditional architecture as a unique element with social, cultural and educational purposes. The question that academic data can be applied to market and have commercial effect is still unknown. However, this is expected to make the beauty and knowledge of traditional architecture residing in the heart of common people and in turn promote the public consciousness of cultural heritage preservation. Finally, there are still a lot challenges in the future, including developing markets for mass productions, setting up a reasonable licensing mechanism, and developing compromise mechanism to adjust different perceptions between academics and industries to reach consensus.

5.Related Projects - Cultural Heritage and Environment Conservation

Old architecture rescue center not only concern temple architecture, it also concern other kinds of cultural heritage and its environment conservation. For example, the aboriginal architecture and settlements, hakka architecture and settlement. In the year of 2010, one research project on the conservation of aboriginal settlements after Morak typhoon disaster and the other project on old hakka architecture are to be proceeded. This is an attitude that any study or any actions are deserved to be taken which is helpful for cultural heritage conservation, then OARC will undertake it and would like to share the research results with public.

6. Future Prospect

The Future goal of OARC is to accumulate researches and professional information on cultural heritage conservation, restoration, and reuse on historical architecture and set up a platform for information exchange to be a place for extension on cultural heritage and its related fields.

Preparation Mico/Nano Composite Particles and Their Applications for Dye-Sensitized Solar Cells

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1. Introduction

According to a prediction by "BP Statistical Review of World Energy, June 2009," global petroleum reserves may be sufficient to meet the consumption requirements only for another 1.708 trillion tonnes. With increasing concerns about energy demands and the global warming, the development of cheap and accessible renewable energy productions has received the substantial attention. Among the alternative energy resources, the solar energy is more notable because of its low environmental impact. Therefore, the research on photovoltaic has attracted considerable interest. Particularly, the dye-sensitized solar cell (DSSC) proposed by O'Regan and Gratzel [1,2] has attracted substantial interest since 1991. Recently, several methods have been utilized to modify the structure of the working electrode (TiO_2 electrode) to improve the performance of the DSSC [3-12]. The studies cited were concerned with only the increase in travel rate of the electrons. Less attention was paid to reduce the recombination of charges in the dye or electrolyte. Using a chemical reduction method, Su et al. prepared Au nanoparticles, which were fabricated layer-by-layer onto the working electrode as a Schottky barrier in the cell of a water-based DSSC [18], so the DSSC proposed herein is probably thought of as being in some way analogous to the McFarland and Tang's photovoltaic device with a gold layer sandwiched between the dye molecule layer and the TiO_2 semiconductor layer [29].

In this study, extending the method of Chou et al. [12], the TiO_2/Au (or TiO_2/Ag) composite particles were prepared using the dry coating process in a Mechanofusion system. A layer of TiO_2/Au (or TiO_2/Ag) composite particles (Fig. 1) was then fabricated for use in a new type of DSSC to enhance its power conversion efficiency. Aside from this, the results presented in this are cited from Chou et al. [30].

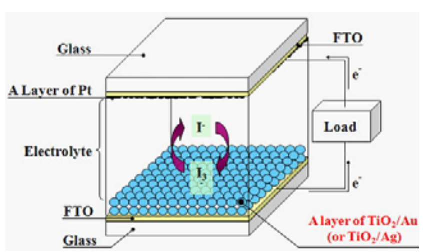

Fig.1. Schematic of the dye-sensitized solar cell with a TiO_2/Au (or TiO_2/Ag) thin-film electrode.

2. Abstract

This study investigated the applicability of TiO_2/Au (or TiO_2/Ag) composite particles, which probably have the plasmon resonance effect, on FTO-glass substrate of the working electrode of a DSSC. The dry particle coating technique was utilized to coat the surfaces of TiO_2 particle with nano-sized Au (or Ag) powder particles. A layer of TiO_2/Au (or TiO_2/Ag) composite particles was deposited on the FTO-glass substrate of the working electrode, and it was then sintered in a high-temperature furnace. The working electrode covered with a TiO_2/Au (or TiO_2/Ag) thin film was kept immersed in a solution of N-719 (Ruthenium) dye for 12 h. Further, a thin film of platinum was deposited on the FTO-glass substrate of the counter electrode. Finally, the DSSC was assembled, and the short-circuit photocurrent; the open-circuit photovoltage, and the power conversion efficiency η of DSSC were measured using a home-made I-V measurement system. This study also examined the effects of the mass ratio of TiO_2 to Au (or Ag), and the duration of dry coating on the η of the DSSC. If the duration of dry coating is adequate, the η of the DSSC with TiO_2/Au (or TiO_2/Ag) composite particles increased with increase in the percentage of Au (or Ag) in the composite particles. Most importantly, this study shows that the power conversion efficiency η of the DSSC with a film of TiO_2/Au (or TiO_2/Ag) on the working electrode always exceeds that of the con-

ventional DSSC due to presence of the Schottky barrier, which is probably created in the TiO_2/Au (or TiO_2/Ag) composite particle.

3. Experimental apparatus and procedure

The steps involved were (1) preparing the TiO_2/Au (or TiO_2/Ag) composite particles (Table 1), and measuring their characteristics; (2) preparing the working electrode (Table 2), and measuring its surface properties; (3) assembling the DSSC by placing the copper conductive tape, mounting the working electrode and the counter electrode, and charging the electrolyte in the cell, and (4) making I-V measurements of the DSSC at an energy intensity of 100 mW/cm^2.

A digital multimeter (Keithley 2400) was utilized to measure the open-circuit photovoltage and short-circuit photocurrent of the DSSC. A solar simulator with a 150 W xenon lamp and a light intensity of 100 mW/cm^2, were employed to illuminate the DSSC. In addition, the power conversion efficiency η of the DSSC was determined by

$$\eta\ (\%) = \frac{V_{oc} I_{sc} EF}{P_{in} S} \times 100 \qquad (1)$$

In Eq. (1), V_{oc}, I_{sc}, S, and P_{in} represent the open-circuit photovoltage, the short-circuit photocurrent, the area of thin film on the working electrode (1 cm^2), and the incident light power (100 mW/cm^2), respectively. Further, the fill factor FF is given by

$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}} \qquad (2)$$

In Eq. (2), V_{max} and I_{max} represent the voltage and the current at the maximum output power point, respectively.

Table 1 Test conditions of preparing composite particles.

	Host particle	Guest particle	Mass ratio of TiO_2 to metal powder (g:g)	Time of dry coating (min)	Rotation speed of rotating chamber (rpm)
P1	TiO_2	Au	10:0.1	30	6000
P2			10:0.2		
P3			10:0.1	45	
P4			10:0.2		
P5			10:0.4		
P6			10:0.8		
P7		Ag	10:0.1		
P8			10:0.2		
P9			10:0.4		
P10			10:0.8		

Table 2 Test conditions of preparing the working electrode.

	First layer				Second layer		
	Particles in the colloid	Sintering temperature (°c)	Sintering time (hr.)		Dye	Time of dipping in the dye (hr.)	Average thickness of film on substrate (μm)
F1	P1	450	1		N719	12	9.18
F2	P2						8.98
F3	P3						9.21
F4	P4						8.11
F5	P5						8.07
F6	P6						8.10
F7	P7						8.13
F8	P8						8.05
F9	P9						7.98
F10	P10						8.11
F11	TiO_2						7.96

4. Results and discussion

Table 3 presents the V_{oc}, I_{sc}, FF, and η of the DSSC in tests D1-D11. In this investigation, an FTO-glass substrate coated with a thin film of platinum was used as the counter electrode of the DSSC. At a fixed mass ratio of TiO_2 to Au and a fixed rotation speed of the rotating chamber, the power conversion efficiency η increases with increase in duration of dry coating. For example, at a fixed mass ratio of TiO_2 to Au (10:0.1), and a fixed rotation speed of the rotating chamber (6000 rpm), the η increases from 0.77% (in test D1) to 0.90% (in test D3) as the duration of dry coating increases from 30 to 45 min. This variation is probably due to the fact that a longer duration of the coating corresponds to a more uniform and extensive dispersion of Au powder on the TiO_2 surface.

If the duration of dry coating is adequate, the η increases with increase in the percentage of Au in the TiO_2/Au composite particles. For instance, at a fixed duration of dry coating (45 min), and a fixed rotation speed of the rotating chamber (6000 rpm), the η increases from 0.90% (in test D3) to 1.37% (in test D4) as the mass ratio of TiO_2 to Au changes from 10:0.1 to 10:0.2. In contrast, at a fixed the duration of dry coating (30 min), and a fixed rotation speed of the rotating chamber (6000 rpm), the η decreases from 0.77%(in test D1) to 0.73% (in test D2) as the mass ratio of TiO_2 to Au changes from 10:0.1 to 10:0.2.

Most interestingly, at a fixed duration of dry coating (45 min), and a fixed rotation speed of the rotating chamber (6000 rpm), as the mass ratio of TiO_2 to Au (or Ag) changes from 10:0.1 to 10:0.8, the η of the DSSC with TiO_2/Au composite particles increases from 0.90% (in test D3) to 1.57% (in test D6), and the power conversion efficiency η of the DSSC with TiO_2/Ag composite particles increases from 0.73% (in test D7) to 0.93% (in test D10). These results are probably due to the following facts. (1) The nano-sized Au (or Ag) particles are photoexcited due to the plasmon resonance, and the photoexcited electrons are transferred from Au (or Ag) particles to the conduction band of TiO_2 [29, 31-32]; (2) The larger percentage of nano-sized Au (or Ag) in the TiO_2/Au (TiO_2/Ag) composite particles corresponds to a better status of the plasmon-induced photoelectron chemistry in the visible region.

For the same test conditions, the η of DSSC with TiO_2/Au composite particles always exceeds that of DSSC with TiO_2/Ag composite particles. For example, at a duration of dry coating (45 min), a rotation speed of the rotating chamber (6000 rpm), and the mass ratio of TiO_2 to nano-sized metal (10:0.2), the power efficiencies in test D4 (TiO_2/Au) and test D8 (TiO_2/Ag) are 1.37% and 0.77%, respectively. This result is probably due to the following facts. (1) The work function of Au (5.1 eV) substantially exceeds that of Ag (4.26 eV); (2) a larger work function corresponds to a bigger barrier of Schottky, which causes a smaller dark current. Therefore, the Isc of DSSC with TiO_2/Au composite particles exceeds that of DSSC with TiO_2/Ag composite particles.

Most importantly, the η of the DSSC with a layer of TiO_2/Au (or TiO_2/Ag) composite particles exceeds that of the conventional DSSC in test D11. Even in test D1 (with the dry coating of 30 min, rotation speed of 6000 rpm, and TiO_2:Au=10:0.1), the power efficiencies in test D1 (0.77%) exceeds that of the conventional DSSC in test D11 (0.71%). This difference is probably due to the fact that the Schottky barrier, established in the TiO_2/Au (or TiO_2/Ag) composite particle, obstructs the recombination of charges in the dye (or electrolyte).

Table 3 VOC, ISC, FF, and η of DSSCs.

	Counter electrode	Working electrode	Open-circuit voltage (V)	Short-circuit current (mA)	Fill factor (FF) (%)	η(%)
D1	Platinum film deposited on the FTO	F1	0.65	2.42	49.45	0.77
D2		F2	0.64	2.24	51.71	0.73
D3		F3	0.70	3.24	39.62	0.90
D4		F4	0.65	4.89	43.03	1.37
D5		F5	0.71	5.96	32.79	1.39
D6		F6	0.70	6.18	36.40	1.57
D7		F7	0.82	1.60	54.93	0.73
D8		F8	0.84	1.51	60.51	0.77
D9		F9	0.84	1.74	58.82	0.87
D10		F10	0.82	2.10	54.12	0.93
D11		F11	0.72	1.92	51.52	0.71

As the powder of Au (or Ag) adheres to the surface of TiO_2 particle, the Fermi-level of the TiO_2/Au (or TiO_2/Ag) composite particle is created after the movement of electrons in this compound attains a stable balance. As the electric current flows due to the photo-excitation of the sensitizer and the semiconductor, the conduction and valence bands of TiO_2 particle are bent downward, and their energy levels are lowered. Also, the Fermi-level of the TiO_2/Au (or TiO_2/Ag) composite particle moves downward. Therefore, the Schottky barrier of the TiO_2/Au (or TiO_2/Ag) composite particle is enhanced, and it can reduce the number of electrons going from the semiconductor back to either the dye or the electrolyte.

Although the power conversion efficiency of the DSSC with TiO_2/Au composite particles exceeds that of the DSSC with TiO_2/Ag composite particles (or the conventional DSSC), the VOC of the DSSC with TiO_2/Ag composite particles (0.82 V-0.84 V) is more stable than that of the DSSC with TiO_2/Au composite particles (0.64 V-0.71 V). Also, the V_{OC} of the conventional DSSC (0.72 V) slightly exceeds that of the DSSC with TiO_2/Au composite particles. On the contrary, the short-circuit current (I_{SC}) of the DSSC with TiO_2/Au composite particles exceeds that of the DSSC with TiO_2/Ag composite particles (or the conventional DSSC). These differences are probably attributed to the following facts. (1) V_{OC} is in proportion to the difference between the Femi-level and the Nernst potential of the redox [33]; (2) due to the corrosive property of I^-/I_3^- toward metals [31], the Femi-level of the TiO_2/Au composite particles is interfered, and the Schottky barrier of the TiO_2/Au composite particles is weaken somewhat; (3) the portion of Au stripped from TiO_2/Au composite particles facilitates the conductivity of the electrolyte. In addition, due to the fact that the order of increasing ISC is greater than that of decreasing V_{OC} in the DSSC with TiO_2/Au composite particles, the fill factor (which is in reverse proportion to the product of V_{OC} and I_{SC}) of the conventional DSSC exceeds that of the DSSC with TiO_2/Au composite particles.

For some reason, Ag did not obviously react with triiodide in the electrolyte because the V_{OC} of the DSSC with TiO_2/Ag composite particles stably remains between 0.82 and 0.84 V. Contrarily, the V_{OC} of the DSSC with TiO_2/Au composite particles fluctuates between 0.64 and 0.71 V due to the reaction between triiodide and Au. Therefore, to investigate the reason that Ag do not obviously react with triiodide in the electrolyte must be done in the future. Moreover, to improve the stability of the DSSC with TiO_2/Au (or TiO_2/Ag) composite particles is worthy of ongoing study. One of the possible methods is to employ the electrolyte of $Fe2^+/Fe3^+$ couple [18,31].

Since the V_{OC}, the fill factor and the power conversion efficiency of the DSSC with TiO_2/Ag composite particles exceed those of the conventional DSSC, it is legitimate to infer that the TiO_2/Ag composite particles are able to function as a Schottky barrier in a DSSC. Also, as the mass of Ag in the TiO_2/Ag composite particles increases, the effect of the Schottky barrier is substantially enhanced, and the power conversion efficiency of the DSSC with TiO_2/Au composite particles in test D6 (1.57%) greatly exceeds that of the conventional DSSC in test D11 (0.71%). This inference was also adopted by Su et al. [18] to explain layer-by-layer Au nano-particles as a Schottky barrier in a water-based DSSC. However, to obtain the obvious evidence proving the existence of Schottky barrier in the TiO_2/nano-metal composite particles is an important issue, which is worthy of ongoing study.

5. Conclusion

The power conversion efficiency of the DSSC with a layer of TiO_2/Au (or TiO_2/Ag) composite particles as the Schottky barrier exceeded that of the conventional DSSC. Most importantly, this study supports the application of TiO_2/Au (TiO_2/Ag) composite particles in improving the performance of a DSSC.

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