Cobalt–Citrate Metal–Organic-Framework UTSA-16 on TiO₂ Nanoparticles

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Abstract. Over the past few decades, the multifunctional material, metal-organic frameworks (MOFs), has been distinguished for their unique properties such as reticular structure, permanent porosities, high surface area, straightforwardly self-assembly and crystalline nature. On a count of these potentialities, the applications of MOFs can be classified into separation, catalysis, sensing, and biomedicine these four fields. In our studies, we will concentrate on the fields of gas storage and separations, water splitting, CO₂ reduction, and White-light emission and so on.

Keywords: metal-organic frameworks (MOFs), UTSA-16, carbon dioxide capture, titanium dioxide, photocatalysis

1. Introduction
Nowadays, one of the urgent global problems for us is the wide use of fossil fuels and environmental pollution. These troubles not only damage human bodies but also rise some energy crises for human beings. For instance, carbon dioxide emissions which have grown dramatically ever recorded in recent decades increase the greenhouse effect [1]. These emissions are primarily resulted from the combustion of fossil fuel, natural gas and coal, which are always from our daily life especially for the developing counties. The industrial development and economic growth usually come...
with environmental concerns that we are supposed to be confronted with the issue of civilization and globalization seriously\(^2\). Therefore, the development of the methodology how to capture and separate carbon dioxide has been extremely significant in order to decrease the environmental impact.

As for the part of capturing carbon dioxide, aqueous alkanol-amine absorbents are very useful to the chemical absorption. Nevertheless, this current technology has some weaknesses during the process of capture as followings. It is necessary to need a higher energy requirement for the regeneration of the solvent for the removal of acidic gases such as carbon dioxide\(^3\). And it is the reason that carbon dioxide can be released only at a high raising temperature due to the strong interactions between carbon dioxide and these absorbents. In addition, the high boiling points of these alkanol-amine absorbents is another reason why this kind of technology cost an enormous number of energy\(^4\). What’s worse, carbon dioxide capture from a post-combustion gas through this technology leads to an energy penalty. Because of the corrosive natural property of the absorbents, they bring the hazard damage to the environment as well.

Among these feasible materials, metal-organic frameworks (MOFs) have emerged as a phenomenal carbon dioxide adsorbent. Metal-organic frameworks are crystalline materials that consist of coordination bonds between transition-metal cations and multidentate organic linkers through strong metal-ligand coordination bonds. The structure of MOFs is characterized by an open framework that can be porous. In addition, due to their unique properties such as reticular structure, crystalline nature, controllable structure, permanent porosities, high surface area, straightforward self-assembly, metal-organic frameworks has attracted increasing attention in the clean energy applications\(^5\). In particular, the properties of permanent porosities and high surface area, such a physical adsorption provides an alternative way to capture and separate carbon dioxide very easily. According to the previous document, the metal-organic frameworks, UTSA-16, which empirical formula is \[ \text{[K(H}_2\text{O})_2\text{Co}_3\text{cit}(\text{Hcit})] \] (with cit = fully dehydroxylated citrate anion (4-) and Hcit = citrate anion (3-)), displays high uptake (160 cm\(^3\) cm\(^{-3}\)) of CO\(_2\) at ambient conditions\(^6\). This MOF also has high separation selectivity and capacity for CO\(_2\) capture applications.

It is very essential to mention that the cobalt−citrate metal−organic framework (UTSA-16) has the property of oxygen-evolution which is able to efficiently electro-catalyzing water oxidation\(^7\). UTSA-16, which we concentrate on in this study, has a three-dimensional anatase-type structure. It was composed of tetrahedral Co(II) atoms linked to tetranuclear cobalt citrate clusters in octahedral geometry. Each potassium ion coordinates two water molecules. Around them, there are two hydroxyl groups belonging to Carboxylic acid groups of the citrate units, which would be present conferring to the site a particularly interesting reactivity.\(^8\)

On the basic of the previous popular paper\(^9\), we can further explore more applications because of the multifunctional MOF materials beyond the traditional organic/inorganic hybrid materials. The multifunctional MOF materials have extremely extensive applications, i.e. gas storage and gas separation, water splitting, carbon dioxide reduction, white-light emission, chemical sensors and so on. And in other word, metal-organic frameworks could be applied in many fields like optical, electric and magnetic materials, catalysis, or biomedicine. In our research, we tend to focus on whether UTSA-16 synthesized with TiO\(_2\) nanoparticles has the dual effect of carbon dioxide capture and water splitting, and the interaction between the MOF and TiO\(_2\) nanoparticles. And thanks to the characteristic of high stability, low cost and non-toxic nature, TiO\(_2\) materials are one of the most widely photocatalysts to date\(^10\). Moreover, we would synthesize a variety of concentrations of Cobalt−citrate metal−organic framework in the experimental section below so as to search the optimum effect within those composites. Since our research is still in progress, in the following discussion I’ll refer to some papers as a comparison.

2. Materials and experiments

2.1. Materials
Cobalt acetate (Co(Ac)₂·4H₂O), citric acid (C₆H₈O₇·H₂O), ethanol, deionized water, potassium hydroxide (KOH) and ITO coated glass were used as received from Uni-onward corporation.

2.2. Synthesis of UTSA-16

Cobalt–citrate metal–organic framework (UTSA-16) was prepared by a solvothermal method in the light of the previous papers. [7, 8] First, Co(OAc)₂·4H₂O (0.249 g, 1 mmol) were dissolved in 10 mL of a mixed ethanol/water (1/1 v/v) solution in the 45 mL Teflon-lined autoclave. Then we added C₆H₈O₇·H₂O (0.21 g, 1 mmol) and KOH (0.168 g, 3 mmol) slowly and sequentially. And the mixed solution should be magnetically stir for at least 10 min when adding another new material. After mixing for a period of time, the Teflon-lined autoclave was sealed in a hydrothermal kettle and was heated to 120 °C in a furnace for 24 h. After that, the autoclave was naturally cooled to room temperature. The violet precipitates were collected by centrifugation and washed with deionized water and ethanol for three consecutive times. Finally, the violet powder was dried at 60 °C for 2~3 h in a furnace. In the beginning of experiment, the color of cobalt acetate diluted in ethanol and DI water was magenta. However, UTSA-16 transformed to violet after heating for 24 hours. Herein, the UTSA-16 could also be synthesized by transforming the total volume of ethanol/deionized water (1/1 v/v) to 7.5/7.5, 10/10, 15/15 and 20/20 mL respectively.

2.3 Synthesis of UTSA-16/ITO or TiO₂ composites

As for the synthesis of UTSA-16/ITO nanocomposites, we employed the preceding approach of UTSA-16 to the development of UTSA-16 on the ITO coated glass. That is, the synthesis was established on the pure UTSA-16. After we finished the process of mixing Co(OAc)₂·4H₂O (0.249 g, 1 mmol) + C₆H₈O₇·H₂O (0.21 g, 1 mmol) + KOH (0.168 g, 3 mmol) + ethanol/deionized water, two pieces of 1cm x 2cm ITO coated glass were cautiously placed at the bottom of the Teflon-lined autoclave. It is important to mention here that the conductive slide must face upward. The latter procedures of heating and collecting sample were the same as synthesis of UTSA-16. The synthesis of UTSA-16/TiO₂ nanocomposites was definitely similar to the synthesis of UTSA-16/ITO composites. The difference was that the substrate was substituted for TiO₂ glass. All of the materials needed, and steps were equal. The mixed solution was heated at 120 °C for 24 h before placing two pieces of 1cm x 1cm TiO₂ glass. (Figure.1)

2.4 Device fabrication

ITO coated glasses were first cut into two pieces from the original size, and then cleaned using soap, ethanol and deionized water for the purpose of avoiding contamination. It’s more convenient and safe to conserve these ITO coated glasses in isopropanol. Usually, the multimeter was used to measure the conductive slide of ITO coated glasses.
3. Result and discussion

In our experimental section, because ITO glass is one of the most widely used and most popular transparent conducting oxides, we make an attempt to synthesize UTSA-16 on ITO glass and then confirm there is any interaction between them [11]. In our research, we have done one part of the analysis of XRD, UV-Vis absorption and SEM. For the purpose of verifying whether samples have the property of crystallinity, XRD was used to verify the formation of both the TiO\(_2\) and UTSA-16 components in the composites. According to Bragg’s law established by Lawrence Bragg and William Henry Bragg in 1913, only crystalline solids generated amazing patterns of reflected X-rays. And at some specific wavelengths and incident angles, there were several intense peaks of reflected radiation [12]. The relation of the wavelength $\lambda$ and angle $\theta$ is:

$$2d \sin \theta = n\lambda, \quad (1)$$

where $n$ is a positive integer and $d$ is interplanar distance in a crystalline solid. [13] When the result of x-ray diffraction is in line with equation (1), the pattern indicates that sample has great property of crystallinity. Figure 2a and Figure 2b show a XRD pattern of the UTSA-16 crystal on TiO\(_2\) nanoparticles where the volume of ethanol/deionized water (1/1 v/v) were 10mL/10mL and 7.5mL/7.5mL respectively. As you can see in the two patterns, the main diffraction peaks of Figure 2a are observed at 7.3°, 25.1° and 32.6°. On the other hand, the manifest diffraction peaks of Figure 2b are located at 7.3°, 27.8° and 32.6°. Those peaks present the high crystallinity of the UTSA-16. Obviously, the strongest peak which is at 7.3° is identical to the previous paper [7]. Nevertheless, there are some other peaks appearing in the following figures except for 7.3°. These signals might come from the TiO\(_2\) nanocomposites.

![XRD pattern of the UTSA-16 crystal on TiO\(_2\) nanoparticles (the volume of ethanol/deionized water (1/1 v/v) were 10mL/10mL and 7.5mL/7.5mL)](image)

By imagining and conceiving the microstructures and morphologies of the composites, SEM brought further evidence of these composites. Figure 3 displays a SEM image of the UTSA-16. These patterns illustrate that the UTSA-16 crystal consists of a large number of irregular particles. These particles look like a variety of tiny pyramids with polyhedral morphology. Figure 4 also shows EDS spectrum of the UTSA-16, which demonstrates there are four elements (cobalt, carbon, oxygen, potassium) in this sample.
Another analysis is to estimate the UV-Vis absorption. UV/Vis absorption spectroscopy is conventionally used in analytical chemistry for the quantitative determination of different samples, such as transition metal ions, highly conjugated organic compounds and so on. This means that the absorption in the visible light range directly affects the perceived color of the chemical elements involved in the sample. The principal of UV-Vis absorption elaborates that molecules which contain π-electrons or non-bonding electrons can absorb ultraviolet or visible light to excite these electrons to the higher anti-bonding molecular orbitals[14]. In this analysis, we carried out in the presence of solid rather than in solutions. The transition metal ions in solutions can be colored by means of absorbing visible light because d electrons within the metal atoms can be excited from one electronic state to another state. As a consequence, the color of metal ion solutions is strongly affected by the presence of other ligands. As for UTSA-16, the transition metal ion is cobalt ion, and the ligands are water, fully dehydroxylated citrate anion (Cit) and citrate anion (Hcit).

![Figure 3. SEM image of UTSA-16](image)

![Figure 4. EDS spectrum of the UTSA-16](image)
The statement of Beer’s law is that the absorbance of a solution is proportional to the concentration of the absorbing element in the solution\cite{15}. Therefore, for a fixed path length, UV-Vis absorption spectroscopy can be employed to determine the concentration of the absorber in a solution.

In our analysis, the range of light is from 200 to 2500 nm. The UV-Vis absorption spectrum of UTSA-16 on TiO\textsubscript{2} nanoparticles where the volume of ethanol/deionized water (1/1 v/v) was 10mL/10mL is dominated by two doublets at about 600 and 1200 nm (Figure 5a). And there is another peak at 210 nm in Figure 5a. As for the part of Figure 5b, the UV-Vis absorption spectrum of UTSA-16 on TiO\textsubscript{2} nanoparticles where the volume of ethanol/deionized water (1/1 v/v) was 7.5mL/7.5mL also have the strongest signals at about 600 and 1200 nm. These two figures are similar to each other except the intensity of absorption. Compared with the UV-Vis absorption spectrum of UTSA-16 in previous study\cite{8}, the spectrum was dominated by two doublets at about 500 and 1250 nm. That could be the reason of the difference that TiO\textsubscript{2} nanoparticles was on our composites sample.

There is another discussion that the result of UV-Vis absorption spectroscopy is depended by crystallinity of UTSA-16. Focused on the concentration of UTSA-16 which total volume of ethanol/deionized water is 10mL/10mL, it has stronger intensity of XRD peak at 7.3°. But for the UV-Vis absorption spectrum, the absorption is a bit weaker compared to the other concentration.

![Figure 5 (a and b). The UV-Vis absorption spectrum of UTSA-16 on TiO\textsubscript{2} nanoparticles (the volume of ethanol/deionized water (1/1 v/v) were 10mL/10mL and 7.5mL/7.5mL)](image-url)

**4. Conclusion**

The leaching efficiency of vanadium is 98.1% at the optimum condition of pH 12.5. In a nut shell, we synthesized the bioinspired cobalt–citrate metal–organic framework (UTSA-16) through a simple solvothermal route on the TiO\textsubscript{2} nanoparticles with different concentration of UTSA-16. However, there are still many unfinished experiments and analysis which now we’re trying to work. And we’ll check the characteristics of these samples in the future.

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References
[1] Pachauri, R. K. & Reisinger, A. IPCC Fourth Assessment Report (Intergovernmental Panel on Climate Change, 2007).
[2] Quadrelli, R. & Peterson, S. The energy-climate challenge: recent trends in CO2 emissions from fuel combustion, Energy Policy 35, 5938–5952 (2007).
[3] Yangcan Shen, Ziyin Li, Lihua Wang, Yingxiang Ye, Qing Liu, Xuiling Ma, Qianhuo Chen, Zhangjing Zhang and Shengchang Xiang, Cobalt–citrate framework armored with graphene oxide exhibiting improved thermal stability and selectivity for biogas decarburization, J. Mater. Chem. A, 2015, 3, 593-599
[4] N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C.S. Adjiman, C.K. Williams, N. Shah, P. Fennell, An overview of CO2 capture technologies, Energy Environ. Sci. 3 (2010) 1645–1669.
[5] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, Flexible metal–organic frameworks, Chem. Soc. Rev., 2014, 43, 6062-6096.
[6] Shengchang Xiang, Yabing He, Zhangjing Zhang, Hui Wu, Wei Zhou, Rajamani Krishna & Banglin Chen, Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions, Nature Communications volume 3, Article number: 954 (2012)
[7] Jing Jiang, Lan Huang, Xiaomin Liu, and Lunhong Ai, Bioinspired Cobalt–Citrate Metal–Organic Framework as an Efficient Electrocatalyst for Water Oxidation, ACS Appl. Mater. Interfaces, 2017, 9 (8), pp 7193–7201
[8] Masala A1, Vitillo JG, Bonino F, Manzoli M, Grande CA, Bordiga S, New insights into UTSA-16, Phys Chem Chem Phys. 2016 Jan 7;18(1):220-7.
[9] H. Xu, S. Ouyang, L. Liu, P. Reunchan, N. Umezawa, J. Ye, Recent advances in TiO2-based photocatalysis, J. Mater. Chem. A 2 (2014) 12642–12661.
[10] Li B, Wen HM, Cui Y, Zhou W, Qian G, Chen B, Emerging Multifunctional Metal-Organic Framework Materials, Adv Mater. 2016 Oct;28(40):8819-8860
[11] Angus Crake, Konstantinos C. Christoforidis, Andreas Kafizas, Spyridon Zafeiratos, Camille Petit, CO2 capture and photocatalytic reduction using bifunctional TiO2/MOF nanocomposites under UV–vis irradiation, Applied Catalysis B: Environmental Volume 210, 5 August 2017, Pages 131-140
[12] Bragg, W.H.; Bragg, W.L. (1913). "The Reflexion of X-rays by Crystals". Proc. R. Soc. Lond. A. 88 (605): 428–38. Bibcode:1913 RSPSA.88.428B. doi:10.1098/rspa.1913.0040.
[13] H. P. Myers (2002). Introductory Solid State Physics. Taylor & Francis. ISBN 0-7484-0660-3.
[14] Metha, Akul (13 Dec 2011). "Principle". PharmaXChange.info.
[15] Metha, Akul (22 Apr 2012). "Derivation of Beer-Lambert Law". PharmaXChange.info.