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Preparation and Photoreduction CO_2 Activity of Phthalocyanine Modified Titania Catalysts

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Titania was modified by macrocyclic complexes using a new *in situ* chemical synthesis strategy. Metal phthalocyanine (MPc) was synthesized during TiO_2 gel synthesis and nanocatalyst MPc-TiO_2 with particle size of less than 15 nm was obtained as well. The catalysts were characterized by UV-VIS, DRS, FT-IR and XRD to verify the loading of metal phthalocyanine. The dopping of metal phthalocyanine narrowed the band-gap of TiO_2 and it was responsive to visible light irradiation, the as synthesized CoPc-TiO_2 heated at 300 ºC showed band gap energy of 1.84 eV. The as-prepared MPc-TiO_2 catalyst can be applied in the photocatalytic reduction of CO_2 under visible light, giving the yield of formic acid of 2863.3 μmol/g-catal. after 10 h of reaction. The photosensitivity of CoPc and ZnPc were better than that of NiPc. The electron density of cobalt was higher so it was beneficial to the election transformation from excited CoPc to the conduction band of TiO_2. The photo-efficiency is greatly increased.

Keywords: Visible light photocatalyst, Anatase TiO_2, Nanocomposite, Metal phthalocyanine, CO_2 reduction.

INTRODUCTION

Recently, the increased concentration of CO_2 in the atmosphere has gradually aroused global concern. It is generally known that carbon dioxide is the largest contributor to the greenhouse effect. So many researchers are working to reduce CO_2 emission. Photocatalytic reduction of carbon dioxide is an effective method which can reduce the amount of CO_2 without damaging environment. The nano-TiO_2 is used as the catalysts in the reaction of CO_2 reduction and many useful organic products such as formic acid, formaldehyde are produced. Photocatalytic reduction of CO_2 using semiconductor in aqueous solution and metal complex in organic solvent have already been studied[1,2]. Several authors[3-5] studied the effect of different noble metal ion dopants on nanocrystalline TiO_2. According to these reports, high effective solid photocatalysts have been developed. For Example, metal complex was fixed on Nafion film or solid, which was beneficial to the separating of catalysts from reaction system. Besides, in this system no organic solvent was employed and so decreased cost and pollution was achieved.

Metal phthalocyanine (MPc) complex has two absorbing bands named Q band and B band which are generated by electron transition of $\alpha_{1u}(\pi)$-$e_g(\pi^*)$ and $\alpha_{2u}(\pi)$-$e_g(\pi^*)$. Q band located in the visible region of 600-800 nm. Metal phthalocyanine has been studied as a bionic model in biological oxidation reduction process and used in the photodegradation of organic pollutants[6,7]. It can reduce the overpotential in the process of electrooxidation of cysteine and nitrite[8-10]. Metal phthalocyanine can also be made to film and dispersed on the surface of solid or bundled in the cavity of molecular sieve[11-13]. Based on the previous studies[14-16], the photocatalyst of MPc-TiO_2 is prepared by using the *in situ* chemical synthesis method. Metal phthalocyanine is thoroughly separated in matrix instead of being overlapped on its surface. With increased stability, the photocatalyst could also be reused.

In this paper, the composite material of MPc-TiO_2 is obtained using the *in situ* chemical synthesis method, with *o*-phthalodinitrile the fragment and Co(II), Zn(II), Ni(II) the template. In this experiment, the metal phthalocyanine and TiO_2 are successfully synthesized in sol, then the xerogel is heated under appropriate temperature.

EXPERIMENTAL

Titanium(IV) butoxide was purchased from Enterprise group chemical reagent Co., Ltd. (China). 1,2-Benzendicarbonitril, $CoCl_2$, $NiCl_2$, $ZnCl_2$ were all purchased from Tianjin Kermel chemical reagent Co., Ltd. (China). All of the reagents were analytical grade and without further purification.

General procedure: CoPc-TiO_2 was prepared by *in situ* chemical synthesis with titanium(IV) butoxide as the precursor. To avoid precipitation during polycondensation and formation of unstable colloidal sols, the hydrolyzing water was homogeneously released by the esterification of alcohol and acetic acid. Then *o*-phthalodinitrile and cobalt chloride were added into the sol precursors with the ratio of Co/Ti of 3 wt %. The pH of mixed solutions were adjusted to 1 by addition of HCl and stirred for 20 h at ambient temperature followed by ageing for 24 h, finally the resulted xerogels were calcined at appropriate temperature (180-500 °C) for 2 h. For comparison, the $ZnPc-TiO_2$ and $NiPc-TiO_2$ catalysts were prepared using the same method. All of the reagents used were analytically pure.

The photocatalytic reduction was carried out in a Pyrex glass cell with an optical window (volume of the solution was 100 mL). Catalyst powder of 150 mg was suspended in 100 mL of NaOH aqueous solution. Illuminations were performed with a visible light source of 500 W tungsten-halogen lamp. The reactor was tightly closed during the reaction and stirred continuously by a magnetic stirring bar to prevent sedimentation of the catalyst, then bubbled CO_2 was introduced for at least 50 min to purge air and to saturate the solution. The yields for the formation of methanol, formaldehyde and formic acid were determined with UV-visible spectrophotometer or gas chromatograph equipped with FID detector and the HP5 column for methanol and ethanol analysis. Helium was used as a carrier gas. Gaseous products CO and CH_4 were analyzed in a GC equipped with thermal conductivity detection and a 2 m carbon molecular sieve column.

Blank tests were done to verify that hydrocarbon production was due to the photocatalysis reduction of CO_2. One of the tests was in the dark with the catalyst and CO_2 and the other one was VIS-illuminated with CO_2 and no catalyst was included. Both tests were under the same experimental conditions and no product was detected.

Detection method: The crystalline phase of the prepared catalysts were confirmed by X-ray diffraction spectra (XRD) recorded on a Rigaku 2304 diffractometer with Ni-filtered CuK_α radiation from 8-80° at a scanning speed of 2°/min. FT-IR and UV-visible spectra were recorded on a Perkin-Elmer FT-IR1760 spectrometer and a Lambda Bio40 spectrophotometer. A diffusive reflective UV-visible spectrophotometer (DRS) was employed to measure the UV-visible absorption and estimate the bandgap of the catalysts. The specific surface area and pore structure of the prepared catalysts were measured by adsorption/desorption of nitrogen using a Thermo Electron Corporation Sorptomatic 1990 and evaluated by the BET and BJH methods, respectively.

RESULTS AND DISCUSSION

Characterization of $MPc-TiO_2$ photocatalyst: The XRD patterns are shown in Fig. 1 and the crystallite size are summarized in Table-1. It is verified that the samples are mainly crystallized to be anatase phase with a small quantity of rutile. That is, a mixture of anatase and rutile is formed by the *in situ* chemical synthesis. Noticeably, no peaks attributed to $MPc-TiO_2$ are observed at 5-30° indicating the complete dispersion of metal phthalocyanine into TiO_2 sol with the form of molecular or with low loading quantity. From Fig. 1 it can be seen that diffraction peak attributed to the (101) plane is broadened indicating a small particle size. The average grain size of TiO_2 and $CoPc-TiO_2$ are 62 and 11 nm, respectively, indicating that the grain size of $CoPc-TiO_2$ decreases. And the crystal transfer temperature of $CoPc-TiO_2$ decreases. The rutile appears at 200 °C because of the existence of CoPc. The main crystal type is anatase after it is heated. The mixed crystal is advantageous to visible light absorbance.

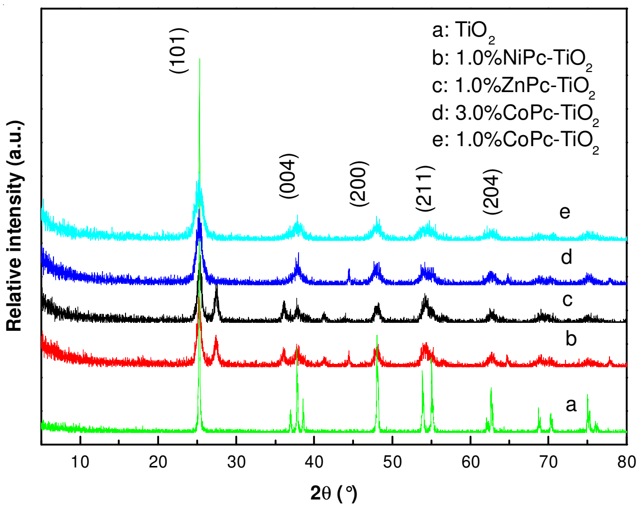

Fig. 1. XRD of TiO_2 and $MPc-TiO_2$

The properties of catalysts are listed in Table-1. It shows that the particle size of catalysts produced by *in situ* chemical synthesis is small, almost less than 15 nm. Koci *et al.*[17] reported that particle size, specific surface area and crystal microstructure have tremendous influence on photocatalytic activity of catalysts[17]. $MPc-TiO_2$ has smaller particle size and bigger specific surface area, so it has strong photocatalytic activity and a larger contact area than that of TiO_2. CO_2 can be reduced to formic acid, or further products formaldehyde and methanol.

TABLE-1
PROPERTIES OF CATALYSTS

Catalysts	Crystallize size[a] (nm)	Content of rutile (%)	Surface area (m^2/g)	Band gap[b] (eV)	Total organic carbon (TOC)
TiO_2	61.99	19.08	9.29	3.21	221.03
3.0 % $CoPc-TiO_2$ ([c]200 °C)	11.02	15.89	71.22	1.86	2698.21
3.0 % $CoPc-TiO_2$ (300 °C)	11.20	18.36	76.18	1.84	2863.30
3.0 % $CoPc-TiO_2$ (400 °C)	13.89	27.56	79.84	2.03	1672.02
3.0 % $CoPc-TiO_2$ (500 °C)	17.56	29.75	65.72	2.01	1233.54
1.0 % $CoPc-TiO_2$ (365 °C)	11.35	9.48	73.23	1.85	1522.26
3.0 % $ZnPc-TiO_2$ (300 °C)	16.08	23.81	66.37	2.25	1028.69
3.0 % $NiPc-TiO_2$ (300 °C)	14.11	24.75	69.48	2.48	828.49

[a]Estimated from XRD by Scherrer equation. [b]Estimated from UV-visible spectra. [c]Temperature of heating.

The UV-visible spectra of the extracts of MPc-TiO_2 and CoPc in DMF are shown in Fig. 2. The MPc-TiO_2 and CoPc were solved in DMF, extracted under ultrasonic and then filtrated. The band at 550-700 nm region is attributed to the characteristic Q-band absorption of CoPc. Two weak peaks at 589 and 633 nm in curve b (pure CoPc) might be assigned to the vibronic band due to the dimers and multimers. The dimers could affect the UV-visible absorption spectra of metal phthalocyanine and decrease the optical characteristics of it. Peaks of 605 and 670 nm were the absorption of monomers and should be assigned to π-π^* transition of monomer from the HOMO to the LUMO of the Pc^{2-} ring. It can be seen from Fig. 2 that metal phthalocyanine was synthsised and loaded successfully on surface of TiO_2 and existed mainly in the form of monomers. The intensity of characteristic absorbance of metal phthalocyanine is strengthened with the increase of metal phthalocyanine content. Fig. 3 presents the spectra of diffusion reflectance spectroscopy (DRS) of MPc-TiO_2. It showed that the visible-light absorbance of CoPc-TiO_2 excelled than that of ZnPc-TiO_2 and NiPc-TiO_2. The dz^2 HOMO of cobalt is similar to that of ligand and a intensive blend exists between metal d_{xy} orbit and N p orbit of benzpyrole. So the centre metal of cobalt showed redox activity. The d orbit of Ni and Zn has little influence on d orbit of complexes. So the photocatalytic activity of CoPc-TiO_2 was higher than that of ZnPc-TiO_2 and NiPc-TiO_2. In addition, with the increase of CoPc content, the visible absorbance of CoPc-TiO_2 increased. But the visible absorbance of CoPc-TiO_2 decreased when the heating temperature is increased. So the increased CoPc content and decreased of heating temperature are beneficial to photocatalyst which is consistent with the data of Table-1. The absorption edge is shifted to longer wavelengths with increasing CoPc content. But while the content of CoPc is too much, it can lead to dimer generation.

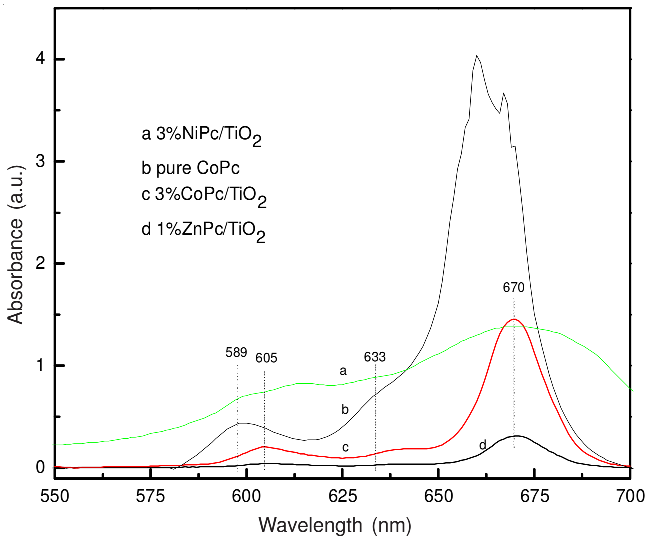

Fig. 2. UV-visible spectra of synthesis CoPc-TiO_2 photocatalyst dissolving in DMF

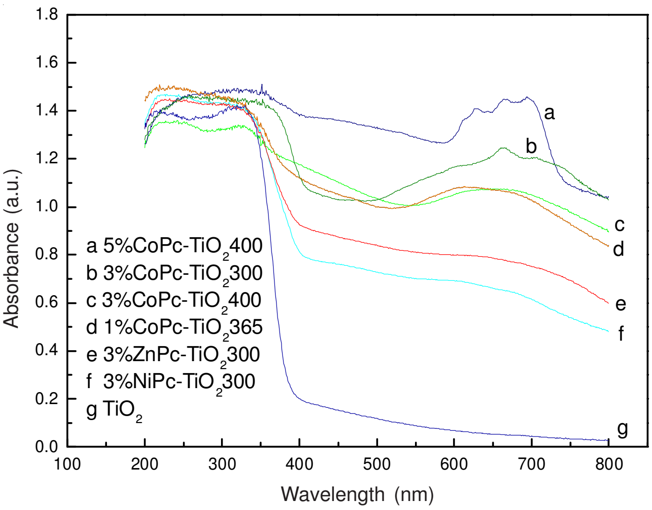

Fig. 3. Spectra of diffusion reflectance spectroscopy (DRS) of MPc-TiO_2 and TiO_2

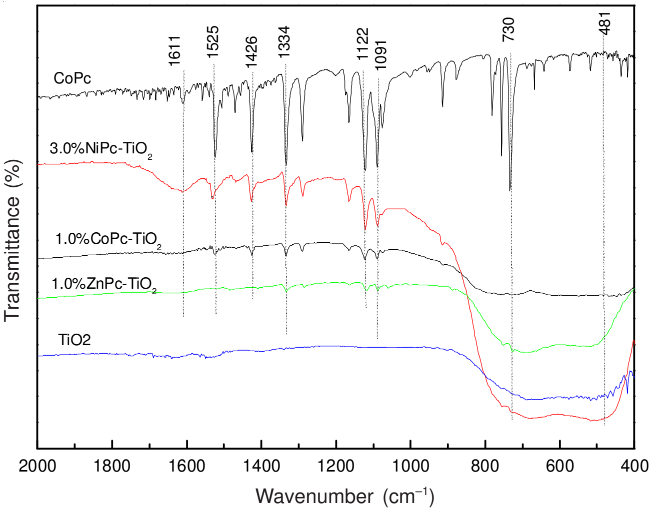

Fig. 4. FT-IR spectrum of CoPc-TiO_2, ZnPc-TiO_2, NiPc-TiO_2, CoPc and TiO_2

The FT-IR and UV-visible spectra of phthalocyanine are extremely sensitive to the changes of functional groups. So the spectral results are good proofs whether the metal phthalocyanine molecules are chemisorbed on the surface of TiO_2 or not[18]. The FT-IR spectrum displays (Fig. 4) four characteristic vibration of CuPc at 730, 1091, 1122 and 1333 cm^{-1}. The vibration at 730 cm^{-1} is assigned to the bending vibration of phthalocyanine ring's C-N, a C-H bending vibration at 1122 cm^{-1}. The vibration at 1334 cm^{-1} is assigned to the macrocyclic ring's C-C stretching, 1426 cm^{-1} to the pyrrole ring's C-C stretching. In addition, C-C and C-N stretching vibrations can be observed at 1503 and 1605 cm^{-1} in the FTIR spectrum. So it is proved that metal phthalocyanine is successfully loaded on surface of TiO_2. Comparing with that of CuPc, the vibration of aromatic ring framework of NiPc-TiO_2 at 1525 cm^{-1} has blueshifted 22 cm^{-1}. The vibration at 481 cm^{-1} is assigned to the Ti-O bond of P25, which is blue shifted 21 cm^{-1}in MPc-TiO_2. It is concluded that metal phthalocyanine molecules are chemisorbed on the surface of TiO_2, which is benefical for the electron transfer between metal phthalocyanine molecules and TiO_2.

Fig. 5 presents the N_2 adsorption-desorption isotherms of CoPc-TiO_2 which shows the type IV with hysteresis loops according to the Brunauer-Deming -Deming-Teller (BDDT) classification and attributed to "ink-bottle" pores. The adsorption curve increases slowly while the curve of desorption decreases abruptly when the relative pressure P/P_0 is 0.78. The

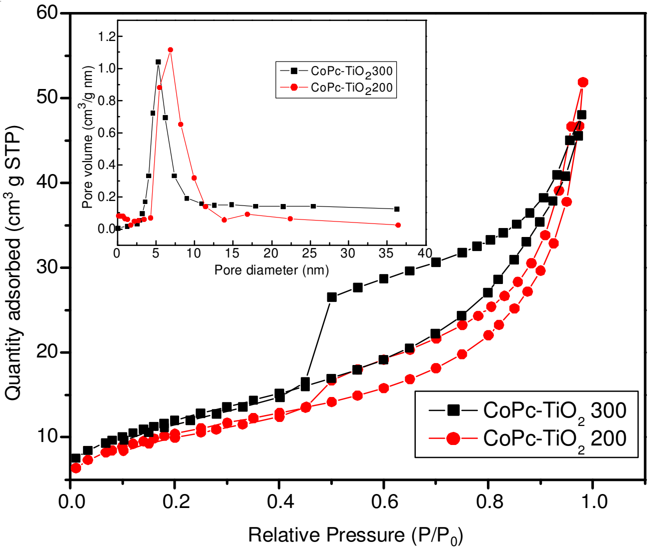

Fig. 5. N_2 low temperature adsorption-desorption isotherms and pore size distribution of CoPc-TiO_2

metal phthalocyanine is dispersed uniformly in these bores. This "cage" effect prevents metal phthalocyanine from aggregation with each other, leading to the increased availability. The pore size distribution of CoPc-TiO_2 heated at 300 and 200 ºC was showed in the insets of Fig. 5. The results show a uniform pore distribution. The mode pore radiuses were 5.17 and 6.83 nm respectivly, which is larger than that of CoPc molecule (1.6 nm). Therefore, the encapsulation of CoPc molecules in varied nanometer "cage" prevented them from colliding with each other, suppressing dimerization and improving the productivity of reduction CO_2.

Photocatalytic reduction of CO_2: The effect of metal ion on reduction products of CO_2 illumination after 10 h is shown in Fig. 6. It can be seen clearly that the reduce yield of CoPc-TiO_2 is better than that of ZnPc-TiO_2 and NiPc-TiO_2. The metal ion is the important factor having effect on the feature of phthalocyanine complex and photoactivity. CoPc and NiPc have higher selectivity at gas-diffusion electrodes for reduction of CO_2, the current efficiency of them is almost 100 %[19]. The metals of groups VIII-X have higher activity in catalytic hydrogenation of CO_2.

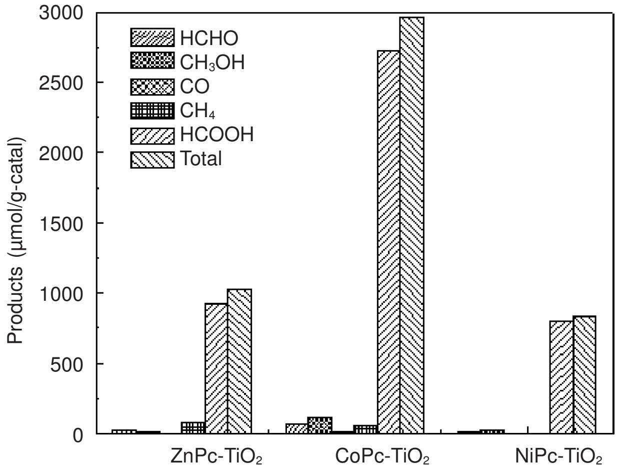

Fig. 6. Different metal phthalocyanine dependence of products yield over MPc-TiO_2 catalysts

The time dependence of formic acid yield over MPc-TiO_2 catalysts is shown in Fig. 7. It can be seen that CoPc-TiO_2 gives higher yield. The effect of irradiation time on the reduction of CO_2 is investigated with visible light of radiation for periods of 0-50 h. Three products are produced with formic acid as the main product and other products such as methanol, formaldehyde could also be formed. The formic acid could achieve 2863.3 μmol/g-catal. being illuminated for 20 h. The yield of formic acid slightly decreased when the illuminating time exceeds 20 h, because as an intermediate product, the formic acid is consumed to produce further products such as formaldehyde and methanol as has been proved in our previous work[15].

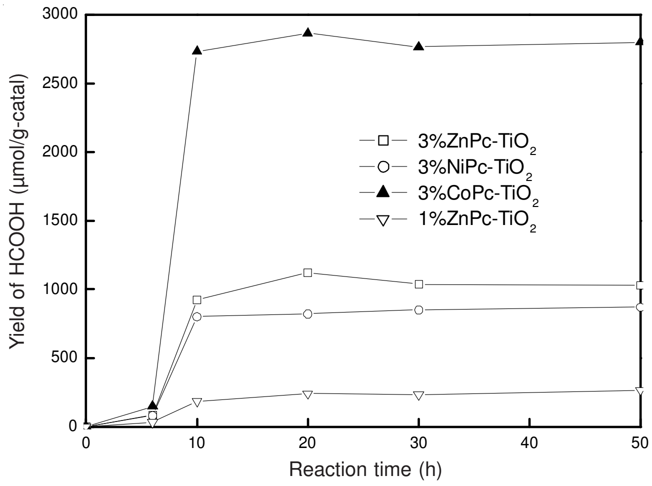

Fig. 7. Relationship Time dependence of HCOOH yield over MPc-TiO_2 catalysts

It can be seen from Table-2 that ZnPc has the higher binding energy than that of CoPc and NiPc, leading to a higher stability. In addition, ZnPc and NiPc are closed-shell system while CoPc is opened-shell. Zinc has strong axial coordination ability[2,20]. The photosensitivity of CoPc and ZnPc is better than that of NiPc. ZnPc and CoPc have strong electron donating ability. The electric charge of Co, Zn and Ni is 1.45, 1.53 and 0.79, respectively. While zinc's outer electronic is $3d^{10}4s^2$, having little influence on phthalocyanine macrocyclic. So the supply electron ability of ZnPc-TiO_2 is weak than that of CoPc-TiO_2, with NiPc-TiO_2 the weakest. CoPc-TiO_2 is the best catalyst for reduction of CO_2 compared with ZnPc-TiO_2 and NiPc-TiO_2.

TABLE-2
CHARACTERISTICS OF METAL PHTHALOCYANINES

MPc character	ZnPc	NiPc	CoPc
Electron array	$3d^{10}$	$3d^8$	$3d^7$
Ground state level	-1704.43423	-4550.77487	-3895.5006
Binding energy	30.31226	19.08431	22.85699
Electric charge	1.53	0.79	1.45
(τ) Exciton life	350 ns	–	0.035 ns

Conclusion

Titania is modified by macrocyclic complexes using a new method of *in situ* chemical synthesis. Metal phthalocyanine (MPc) is synthesized during TiO_2 gel synthesis and nanocatalyst

MPc-TiO_2 with particle size of less than 15 nm was obtained as well. Metal phthalocyanine was isolated homogeneously in the pores of the titania matrix and dimerization and aggregation of metal phthalocyanine molecules was decreased. Metal phthalocyanine was dispersed uniformly in "cage" of TiO_2 gel. It also alter the band-gap of the MPc-TiO_2 to the visible light region.The dopping of metal phthalocyanine narrows the band-gap of TiO_2 and so it is responsive to visible light irradiation, The as synthesized CoPc-TiO_2 catalyst heated at 300 ºC showed a band gap energy of 1.84 eV.

Visible-light induced photocatalytic reduction of CO_2 is studied with as synthesized MPc/TiO_2. Macrocyclic metal phthalocyanine is proved to be an important factor in extending the photocatalytic activity in the visible light range. The as-prepared MPc-TiO_2 catalyst can be applied in the photocatalytic reduction of CO_2 under visible light, CO_2 can be reduced to HCHO, CH_3OH, HCOOH, *etc.*, giving the yield of formic acid of 2863.3 µmol/g-catal. after 20 h of reaction. The photosensitivity of CoPc and ZnPc are better than that of NiPc. The electron density of cobalt is higher so it is beneficial to the election transformatioon from excited CoPc to the conduction band of TiO_2. The photo-efficiency is greatly increased.

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