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Facile Synthesis of Hierarchically Porous Metal-TiO_2/graphitic Carbon Microspheres by Colloidal Crystal Templating Method

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Hierarchically porous metal-TiO_2/graphitic carbon microspheres (M-TiO_2/GCM) (where M= W, Sn, Ni, Co, or Ce) were synthesized for the first time by a simple colloidal crystal templating method. X-ray diffraction, energy dispersive spectroscopy, nitrogen adsorption–desorption, scanning electron microscopy, and transmission electron microscope analysis techniques were used to characterize the samples. It was observed that the amount of acetone solvent had great influence on the morphology of composites, and the obtained M-TiO_2/GCM composite microspheres possessed hierarchical porosity with large specific surface area, high metallic compound content, and graphitic carbon frameworks, giving the materials wide potential applications as catalysts, adsorbents and electrode materials.

Keywords: Metal-TiO_2; colloidal crystal templating method; graphitic carbon; microsphere.

1. INTRODUCTION

Porous carbon composites [1-3] have attracted much attention because the characterizations of the porous carbon and other component endow them with important applications in catalyst supports, [4, 5] energy storage materials, [6, 7] adsorption and separation. [8-11] Metallic element or metal oxide/porous carbon composites have attracted significant attention in environment [12] and energy sources [13,14] owing to the specific features of metallic element and metal oxide. Upto now, some groups have synthesized metallic element or metal oxide/porous carbon composites [15-18] by various methods. Among the synthesized metallic element or metal oxide/porous carbon composites, TiO_2/porous carbon composites [19-22] are the most promising and challenging investigated materials due to TiO_2 characteristics of powerful photocatalytic properties, [23] superior charge transport

properties, [24] high chemical stability, corrosion resistance and low cost. [25] However, low quantum efficiency and low efficient photoreduction [16, 26, 27] within the TiO_2/porous carbon composites are still the main obstacles for their practical applications. In this regard, metal doping may be an efficient way to tackle the problems.

W doped TiO_2, [28, 29] Sn doped TiO_2, [30, 31] Ni doped TiO_2, [35, 36] Co doped TiO_2, [37, 38] Ce doped TiO_2, [39, 40] Ni doped TiO_2/carbon, [41, 42] and Ce doped TiO_2/carbon [43] have been exploited for diverse applications as heterogeneous catalysts and lithium-ion electrode materials. Metal doping is used to narrow the band gap and broaeden the conduction band of composites which can effectively facilitate photocatalysis capability [28, 29, 35-38, 40-43] and are beneficial for high-rate capability in lithium-ion batteries. [30,31-34] To the best of our knowledge, no studies have been reported on the hierarchically porous metal-TiO_2/graphitic carbon microspheres (where metal= W, Sn, Ni, Co, or Ce). And the disadvantage of tedious experimental procedures required by the current routes still exists.

Herein, we present a route for facile synthesis of the hierarchically porous metal-TiO_2/graphitic carbon microspheres with high metallic compound content in the graphitic carbon matrix via colloidal crystal templating method (where metal= W, Sn, Ni, Co, or Ce). The synthesis was achieved using SiO_2 colloidal crystal and titanium tetrachloride as the template and Ti precursor, respectively. In the microemulsion consisting of metal salt, titanium tetrachloride, soybean oil and acetone, the colloidal superparticles of SiO_2 microspheres were formed. Going through the heat treatment process of carbonaceous polymerization/graphitization and treated with NaOH aqueous solution, the metal-TiO_2/graphitic carbon microspheres were synthesized. The synthesized composites possess hierarchical porosity with high specific surface area and large pore volume, which make their ideal candidates for important applications, such as catalysts or electrode materials. The present synthetic method need not has tedious treatment and is sustainable for exploiting the hierarchically porous metal-TiO_2/graphitic carbon microspheres with high metallic compound content.

2. EXPERIMENTAL

2.1. Chemicals

Absolute alcohol, ammonia, tetraethoxysilane, acetone, WCl_6, $SnCl_2•2H_2O$, $Ni(NO_3)_2•6H_2O$, $Co(NO_3)_2•6H_2O$, $Ce(NO_3)_3•6H_2O$, and NaOH were obtained from Shanghai Chemical Corp. Soybean oil was obtained from Shanghai Wal-mart supermarket. All chemicals were used as received without further purification.

2.2. Synthesis Of Composites

Colloidal SiO_2 microspheres were prepared by Stöber method [44] according to literature with the ammonia molar concentration of 0.31 mol L^{-1} except enlarging the amount by ten times.

The colloidal crystal templating method was used to synthesize the hierarchically porous metal-

TiO_2/graphitic carbon microspheres. In a typical synthesis, 0.2 mmol of metal salt (WCl_6, $SnCl_2$•$2H_2O$, $Ni(NO_3)_2$•$6H_2O$, $Co(NO_3)_2$•$6H_2O$, or $Ce(NO_3)_3$•$6H_2O$), 10 mmol of titanium tetrachloride, and 5.0 g of soybean oil were dissolved into 45 mL of acetone. 2.5 g of grinding SiO_2 microspheres were added to above solution and the mixture was stirred about for half hour to obtain the suspension. Then, the mixture was aged for 3 days under room temperature and transferred into a tube furnace to carbonize the precursors at the temperature of 900 ℃ under Ar flow for 4 h with a heating rate of 2 K min^{-1}. The resultant composite was treated with 2 mol L^{-1} NaOH aqueous solution for several times to remove the silica template .

2.3. Characterization

X-ray diffraction (XRD) patterns were collected in θ-2θ mode using Rigaku D/Max2rB－Ⅱ diffractometer (CuK1 radiation, λ=1.5406Å), operated at 40 kV and 100 mA (scanning step: 5º per second). Energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) images analysis were performed on a Philips XL-30 scanning electron microscope operating at an acceleration voltage of 25 kV. The Brumauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The total pore volume was estimated at a relative pressure of 0.99. Transmission electron microscope (TEM) images were done using a JEOL JEM-2010 electron microscope with an acceleration voltage of 200 kV.

3. RESULTS AND DISCUSSION

3.1. Syntheisi Of M-Tio$_2$/Gcm Composites

The synthesis process of hierarchically porous metal-TiO_2/graphitic carbon microspheres by colloidal crystal templating method [45, 46] (illustrated in Figure. 1) is actually much simpler than traditional route which involved multi-step procedures. Under stirring, metal salt, titanium tetrachloride, soybean oil and acetone are mixed to form stable microemulsion. The microemulsion and monodisperse SiO_2 microspheres were mixed and stirred to obtain the suspension (shown in Figure. 1a). After 3 days, with the evaporation of the acetone in microemulsion droplets, the interactions between monodisperse SiO_2 microspheres increase and colloidal superparticles of SiO_2 microspheres (Figure. 1b) were formed. More specifically, the interspace between each colloidal SiO_2 microspheres is filled with microemulsion including soybean oil. The microemulsion with colloidal superparticles of SiO_2 microspheres is transferred into the tube furnace to go through the heat treatment process of carbonaceous polymerization/graphitization. Heat treatment is carried out at 900 ℃ under Ar atmosphere with a gradual increase of temperature and metallic crystal growth proceeded in situ and embedded into the graphitic carbon matrix accompanying the process of carbonaceous polymerization/graphitization (shown in Figure. 1c). The hierarchically porous metal-TiO_2/graphitic carbon microspheres (Figure. 1d) which can be classed as colloidal superparticles [47,

48] are obtained after the silica colloidal crystal sphere templates are removed by incubating in NaOH aqueous solution under room temperature. Figure. 1e is the synthesized Sn-TiO_2/graphitic carbon microsphere which is consistent with our design.

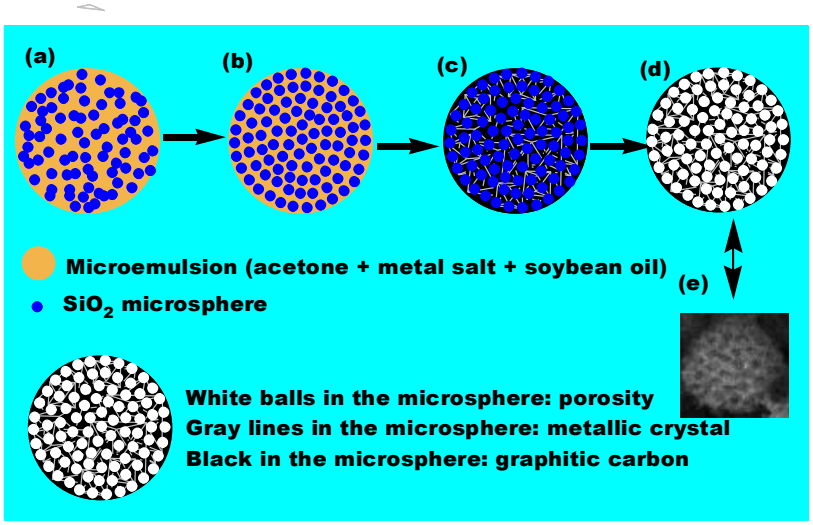

Figure 1. Illustration of the synthesis of the hierarchically porous metal-TiO_2/graphitic carbon microspheres by colloidal crystal templating method.

3.2. Xrd Analysis Of M-Tio₂/Gcm Composites

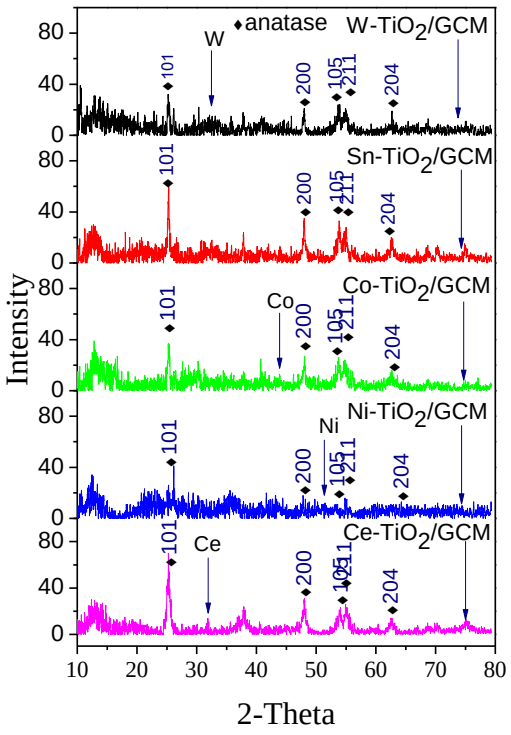

Figure 2. The XRD patterns of M-TiO_2/GCM composites.

Figure. 2 shows the XRD patterns of the prepared composites. XRD peaks assigned to the anatase form TiO_2 at 25º (101), 48º (200), 53º (105), 55º (211) and 63º (204) are seen in all of the as-synthesized composites. And the peak at around 25° (002) of graphite carbon is overlapped by that of anatase at 25° (101) in each sample. However, the metal characteristic peaks assigned to W, Sn, Co, Ni, and Ce are very weak because of the low metallic element content. But the spectrum datas (listed in Table 1) can verify the presence of metallic element (W, Sn, Ni, Co, or Ce) in the composites. In addition, XRD peaks assigned to the metal oxides (WO_x, SnO_x, NiO_x, CoO_x, or CeO_x) do not appear, affirming that metal oxides are not produced during sample preparation.

3.3. Eds Analysis Of M-Tio2/Gcm Composites

To confirm the composition of the particles, EDS spectras (Figure. S1) are collected. The spectrums confirm the presence of Ti, O, C, and M (where M= W, Sn, Ni, Co, or Ce) in the composites. The relative intensities of the Ti, O, C, and M peaks indicate that the hierarchical porous M-TiO_2/GCM composites possess the characteristics of high metallic compound and low carbon content. The contents of each element in samples are listed in Table 1.

Table 1. Element percentage of the hierarchically porous metal-TiO_2/graphitic carbon microspheres

Sample	Titanium (wt %)	Oxygen (wt %)	Carbon (wt %)	M (wt %)
W-TiO_2/GCM	37.60	48.08	10.29	W: 4.02
Sn-TiO_2/GCM	35.62	52.45	11.61	Sn: 0.31
Ni-TiO_2/GCM	31.99	50.02	16.728	Ni: 1.26
Co-TiO_2/GCM	37.47	49.95	12.31	Co: 0.27
Ce-TiO_2/GCM	40.12	42.35	15.15	Ce: 2.38

3.4. N_2 Adsorption-Desorption Of M-Tio$_2$/Gcm Composites

Figure. 3 shows the nitrogen adsorption/desorption isotherms and corresponding pore size distribution curves of the porous carbons to further present their specific textural properties. As shown in Fig. 3a, all the isotherm curves show a strong uptake of N_2 as a result of capillary condensation in a wide relative pressure (P/P0) range of 0.45–0.9, which indicates the existence of multiform pore distributions. [49] The small uptake at high pressure (P/P0 ~ 0.9–0.99) is associated with the void spaces between the particles. [50] Additionally, Fig. 3b reports the pore size distribution of materials. The majority of pores were located in the region of 3.0–4.6 nm and 14.1–178.6 nm, which provides the evidence of hierarchical porosity of composites. The textural properties of all hierarchically porous materials are summarized in Table 2. The hierarchically porous composites generally have BET surface areas in the range of 244–355 $m^2\ g^{-1}$, total pore volumes of 0.24–0.45 $cm^3\ g^{-1}$ and the average diameter of ~3.7 and ~66.6 nm. It should be noted that the hierarchical porosity of composites based

on the BJH method is accord with that obtained from SEM and TEM technique, indicating that the hierarchically porous M-TiO_2/GCM composites have been facilely prepared via the present colloidal crystal templating method.

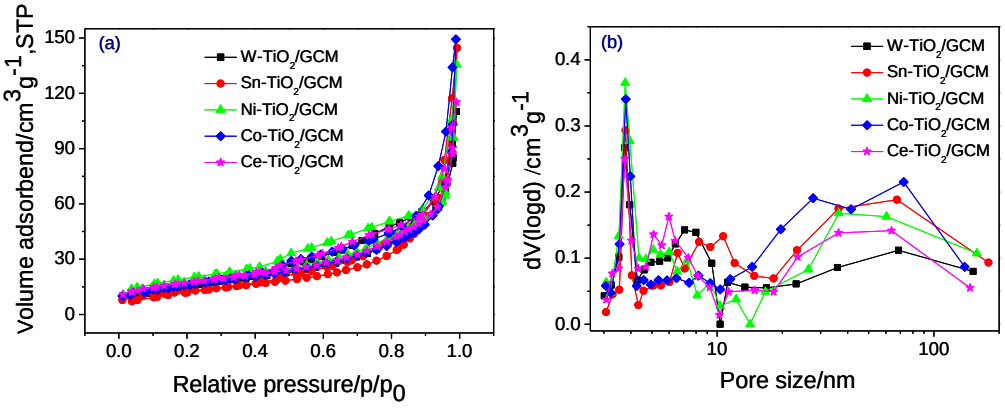

Figure 3. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution of the hierarchically porous M-TiO_2/GCM composites.

Table 2. Surface area, pore volume and pore size of M-TiO_2/GCM.

Samples	S_{BET} [a] ($m^2 g^{-1}$)	V_t [b] ($cm^3 g^{-1}$)	D_p [c] (nm)
W-TiO_2/CM	274.99	0.36	3.75, 68.66
Sn-TiO_2/CM	257.44	0.35	3.54, 67.62
Ni-TiO_2/CM	331.42	0.24	3.76, 60.46
Co-TiO_2/CM	244.24	0.45	3.79, 72.57
Ce-TiO_2/CM	354.84	0.41	3.75, 63.73

[a] S_{BET}: the specific surface area calculated using the BET method;

[b] V_t: the total pore volume at relative pressures 0.99;

[c] D_p: the pore diameter calculated from the desorption branch of the isotherm using the BJH method.

3.5. Sem Analysis Of M-Tio2/Gcm Composites

The morphology of the samples is examined by means of SEM technique. Making use of 45 mL of acetone as solvent, the representative SEM images of samples are show in Figure. 4. As can be seen from the figures, the microspherical morphology of monodisperse SiO_2 template is replicated into porous materials. The original colloidal SiO_2 particles are subsequently removed, leaving behind the composites with pores that preserve the most valuable property of the colloidal crystals — the long-ranged periodic structure. The long-ranged ordering of the hierarchical porosity opens a wide variety of potential applications in areas such as optical information processing, and storage, advanced coatings and emerging nanotechnologies. [51] This valuable property are further verified by studies of N_2 adsorption test (shown in Figure. 3) and TEM images (shown in Figure. 5). The diameter of each

M-TiO_2/GCM material is all about 1–2 μm, which corresponds to TEM images analysis.

The acetone amount has great influence on the morphology of composites. While the acetone amount is changed from 45 mL to 15 mL, the solvent amount is not enough and the microemulsion system is not stable. With the evaporation of the acetone in microemulsion droplets, the mixture clings to bulks step by step and the obtained composites poss the conventional macroporous structure (Figure. S2) via the same experimental conditions with M-TiO_2/GCM composites.

3.6. Tem Analysis Of M-Tio2/Gcm Composites

Further evidence for the structures of these hierarchically porous metal-TiO_2/graphitic carbon materials is provided by the TEM analysis. Low-magnification TEM images of M-TiO_2/GCM composites in Fig. 5 reveal that the hierarchically porous metal-TiO_2/graphitic carbon microspheres possessing the supercrystalline structure look like the blooming lotuses, where crystals of metallic element and TiO_2 are framework and carbon fills the interspace in the frame which makes microspheres more closely. The further high-magnification TEM images (Figure. 5) confirme that the composites have a certain degree of graphitic ordering in the framework and metal compounds are well deposited in the hierarchically porous graphitic carbon. In additon, the analysis result of EDS, SEM and TEM technologies shows that the high metallic compound content do not destory the graphitic carbon matrix, which can widen its applicable range.

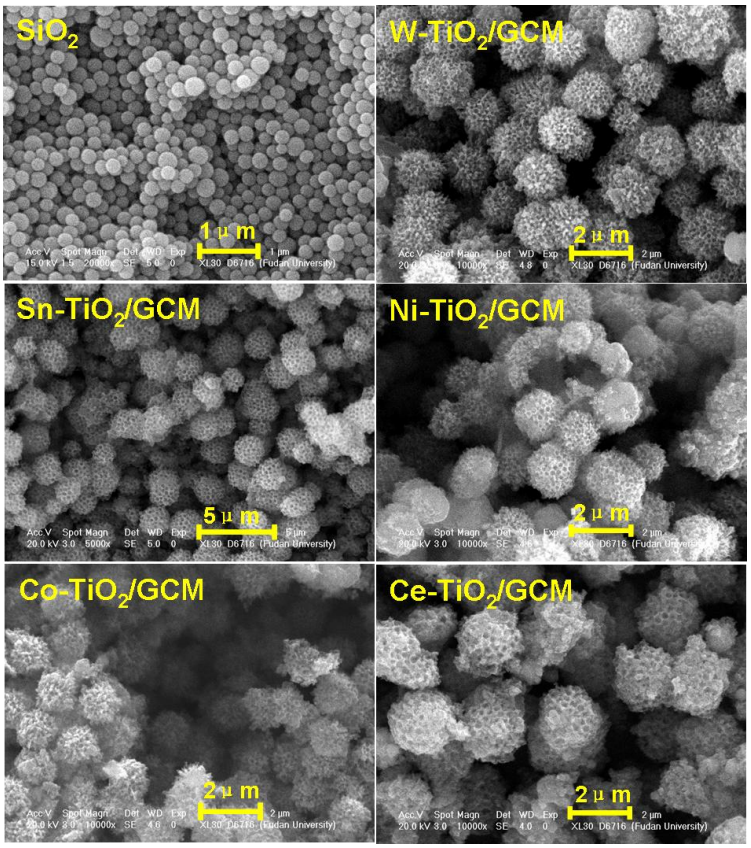

Figure 4. SEM micrographs morphologies of the hierarchically porous M-TiO_2/graphitic carbon microspheres with the acetone amount of 45 mL.

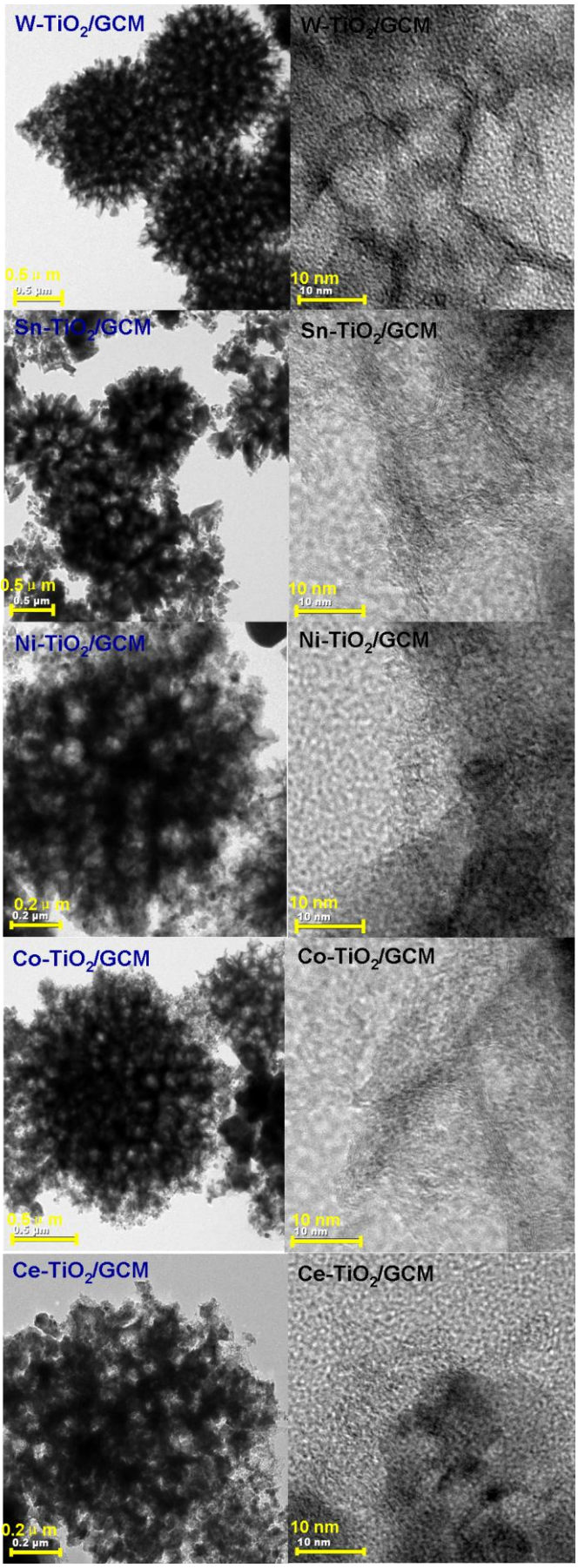

Figure 5. TEM micrographs of hierarchically porous metal-TiO_2/graphitic carbon microspheres.

4. CONCLUSIONS

In summary, the hierarchically porous metal-TiO_2/graphitic carbon microspheres (where metal= W, Sn, Ni, Co, or Ce) were synthesized by a simple colloidal crystal templating method using SiO_2 colloidal crystal and titanium tetrachloride as the template and Ti precursor, respectively. XRD, EDS, N_2 adsorption–desorption, SEM, and TEM results all consistently reveal that the obtained M-TiO_2/GCM materials possess the hierarchical porosity with large specific surface area, high pore volume, and graphitic framework. More specifically, the hierarchical porous metal-TiO_2/graphitic carbon microspheres have the characteristics of high metallic compound that do not destory the graphitic carbon matrix. Employing these characteristics and advantages, the hierarchical porous metal-TiO_2/graphitic carbon microspheres may be used as catalysts or electrode materials. In conclusion, the present method does not need tedious treatment and is a sucessful technology for the synthesis of the hierarchically porous metal-TiO_2/graphitic carbon microspheres with the characteristic of high metallic compound content. However, the microspheres dimension, M/TiO_2/C ration, and application still need further research and more endeavors. These works are in process.

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Notes :

† Electronic Supplementary Information (ESI) available: SEM micrographs morphologies of the macroporous M-TiO_2/graphitic carbon composites with the acetone amount of 15 mL, EDX spectrums of the hierarchically porous M-TiO_2/graphitic carbon microspheres.