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ARTICLE

Preparation of Mesoporous TiO₂-C Composites as an Advanced Ni Catalyst Support for Reduction of 4-Nitrophenol

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To overcome the aggregation and recovery problems and regulate the electronic and chemical properties of Ni nanoparticles catalysts, ordered mesoporous TiO₂-C composites have been designed and synthesized as an advanced support, combined with the *in-situ* loading and reduction of Ni nanoparticles *via* a multi-component co-assembly method. The resultant mesoporous Ni/TiO₂-C composites show a high surface area (~ 340 m²/g), uniform pore size (~ 4 nm), moderate pore volume (~ 0.23 cm³/g), and magnetic value of ~ 5.1 emu/g. Corresponding Ni content was varied in a range from 2 to 13 wt%. More importantly, the mesoporous Ni/TiO₂-C composites show high catalytic activity towards the reduction of 4-nitrophenol to 4-aminophenol with NaBH₄. The maximum pseudo-first-order reaction rate constant obtained with mesoporous Ni/TiO₂-C composites (13 wt% Ni) was calculated to be ~ 0.40 min⁻¹, which is much higher than that of Ni/C, TiO₂-C and Ni/TiO₂ composites. In addition, these catalysts were examined to be stable for long time with its reusability for several times.

Introduction

Metal catalysts have attracted much attention from scientific and industrial perspectives because of their enormous impacts on the world economy.¹ Among them, nickel nanoparticles are of great interest due to their low-cost, magnetic property, environmentally benign, abundance in nature and their very important applications in catalysis, such as hydrogenation, hydrogenolysis, methane reforming, hydrolysis of ammonia-borane and other organic reactions.^{1c,2} It has been well established that their catalytic performances are highly dependent on the size of nickel nanoparticles.^{1c,2g,3} However, nickel nanoparticles often tend to aggregate during the synthesis and catalysis evolution processes, thus leading to a rapid decay in their catalytic activities.^{3b} In addition, the reuse of tiny Ni nanoparticles after catalytic reactions is another key obstacle for their broad applications. This is why many researchers have focused on their research to overcome those above mentioned difficulties by anchoring Ni nanoparticles on some support-materials such as graphene,^{2e,4} SiO₂,^{2g,5} TiO₂,⁶ ZrO₂,⁷ Al₂O₃,⁸ mesoporous carbon,⁹ etc. These supports can not only prevent Ni nanoparticles from migration and aggregation during the catalytic and recovery processes, but also influence the course of catalytic reactions through the interface interactions.

Mesoporous carbons have been regarded as a kind of excellent

catalytic supports due to their chemical inertness, high thermal stability, low cost, tunable mesostructure and porosity, high surface area.¹⁰ Moreover, it has been well demonstrated that carbon supports can *in-situ* reduce metal nanoparticles when annealing under an inert atmosphere, and additionally show good confinement effect to prevent the metal nanoparticles growth.^{1a,9,11} For example, ordered mesoporous carbon/nickel nanoparticles composites were synthesized by a multi-component co-assembly method.^{11a} Ghimbeu *et al.* fabricated cobalt nanoparticles highly dispersed in the porous carbon by a laser-assisted approach.^{11c} Wu *et al.* reported the synthesis of ordered mesoporous platinum@graphitic carbon composites through a CVD-assisted nanocasting method.¹² However, mesoporous carbon support generally shows weak interaction with metal nanoparticles, it is difficult to adjust the electronic and chemical properties of metal nanoparticles in respect of their optimized catalytic activity.^{12,13} As an alternative, metal oxides (*e.g.* TiO₂, Al₂O₃) have been widely investigated as electronic regulator supports for metal nanoparticles as a consequence of active metal-support interfaces.^{6b,14} Nevertheless, there are rare studies on synthesis of hybrid catalyst supports such as carbon-metal oxide composites, which can not only provide high surface area and *in-situ* reduce metal nanoparticles without external reducing agent, but also regulate the electronic and chemical properties of metal nanoparticles.

In this work, we report the synthesis of mesoporous TiO₂-C composites as an advanced Ni catalyst support for the catalytic reduction of 4-nitrophenol. Briefly, a multi-constituent co-assembly approach was explored to synthesize magnetic mesoporous Ni/TiO₂-C composites by using soluble triblock copolymer Pluronic F127 as a template, phenolic resol as a carbon source, nickel nitrate

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and titanium tetrachloride as metallic precursors. In this approach, carbon not only plays the role of reducing agent during the thermal treatment, leading to simultaneous reduction of the Ni precursors to metallic Ni without using hydrogen or other reducing agents,^{11c,12} but also confines the domain growth of TiO₂ nanocrystals to form uniform mesoporous composites. The obtained nanocomposites have high surface areas (319 – 342 m²/g), uniform pore sizes (3.6 – 3.8 nm), moderate pore volume (~ 0.23 cm³/g), uniform and well-dispersed Ni nanoparticles (~ 20 nm), and magnetic separability. Ni content in the resultant composites can be tuned in a range from of 2 – 13 wt%. As a result, Ni/TiO₂-C-13 (13 wt%) composite shows high catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol in NaBH₄ solution, which is superior to Ni/C and Ni/TiO₂ composites. The improved catalytic performance can be attributed to the synergistic effect between TiO₂-C composite support and Ni nanoparticles.

Experimental section

Synthesis. Mesoporous Ni/TiO₂-C composites (denoted as Ni/TiO₂-C-x, in which x is the content of Ni in the resultant mesoporous composites, determined by ICP-AES analysis) were prepared by a one-pot multi-constituent co-assembly method (Fig. 1). In a typical synthesis, 1.5 g of Pluronic F127 was dissolved in a solution containing 1.0 g of deionized water and 8.0 g of ethanol with stirring for 2 h at 40 °C. In another breaker, ethanol (7.5 g), deionized water (0.5 g), and titanium tetrachloride (1.1 mL) solution were mixed together stirred at 0 °C and allowed to stir for 30 min. An orange color solution was formed after mixing the above two solutions at 40 °C. After stirring for 20 min, the phenolic resol (5.0 g) prepared according to the previous reports¹⁵ was dropped into it and stirred for 20 min. Then 0.5 g of Ni(NO₃)₂·6H₂O was added, the mixture was further stirred for 20 min and transferred to dishes. The dishes were placed in an oven for 5 – 8 h at 40 °C to evaporate ethanol, and then polymerize at 100 °C for 24 h. The powders were scraped from dishes and put into a tubular furnace and carbonized at 550 °C for 30 min in N₂ (Ni/TiO₂-C-5).¹⁶ The contents of Ni in the resultant samples could be adjusted by the addition of nickel nitrate.

For comparison, mesoporous carbon and TiO₂ were prepared according to the references.^{15,17} Mesoporous Ni/C and Ni/TiO₂ composites were synthesized by an impregnation method. Typically, the mesoporous carbon (0.1 g) was impregnated with Ni(NO₃)₂·6H₂O ethanol solution (8wt%, 2.1 g) at room temperature for 12 h. Then the mixtures were dried at 60 °C for 6 h and calcined at 550 °C for 2 h in N₂ to obtain the Ni/C composites. The mesoporous TiO₂ composite (0.2 g) was impregnated with Ni(NO₃)₂·6H₂O ethanol solution (8wt%, 2.4 g) at room temperature for 12 h. After drying at 60 °C for 6 h and calcination at 500 °C for 2 h in air, the composites were reduced at 400 °C in a 5 % H₂/Ar flow for 4 h, and the fresh Ni/TiO₂ composites were obtained.

Catalysis. The reduction of 4-nitrophenol (4-NP) was carried out in a quartz cuvette and monitored by using UV-vis spectroscopy at 25 °C. In a typical experiment, 400 μL of 4-NP aqueous solution (10⁻⁴ M) was mixed with 400 μL of aqueous NaBH₄ solution (0.2 M) and 2 mL of H₂O. Subsequently, 3.4 mg of catalysts was added to start the reaction, and the UV-vis spectrometry was employed to *in-*

situ monitor the reaction. For recycling study, the mixture was first separated by an applied magnetic field, and then washed with ethanol and water for four times. Finally the collected samples were re-dispersed in the previous mixture maintaining the same reaction conditions as described above.

Results and Discussion

Mesoporous Ni/TiO₂-C composites can be synthesized by using the multi-constituent co-assembly method (Fig. 1). SAXS patterns of the mesoporous Ni/TiO₂-C-x composites with different Ni contents show resolved scattering peaks (Fig. 2A), suggesting an ordered 2D hexagonal mesostructure. While compared with the mesoporous Ni/C sample prepared *via* an impregnation method, the mesoporous Ni/TiO₂-C composites exhibit similar SAXS patterns with a little left-shift and slight increase in the scattering intensity, indicating stable and ordered mesostructure. This result indicates that the multi-component co-assembly method is favorable to synthesize bimetallic (Ni, Ti) ordered mesoporous carbon composites.

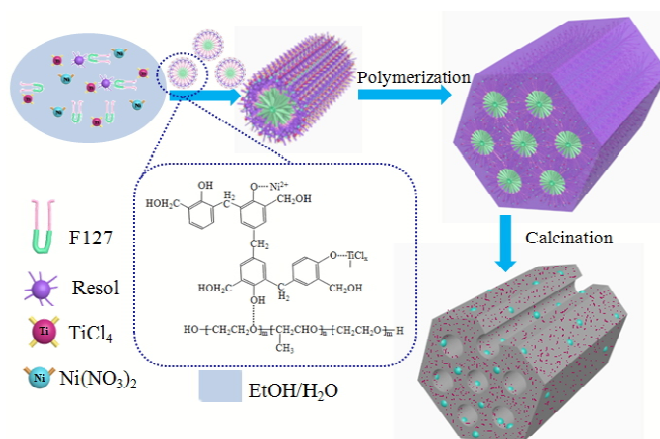


Fig. 1 Schematic formation processes of the mesoporous Ni/TiO₂-C composites *via* the multi-component co-assembly approach.

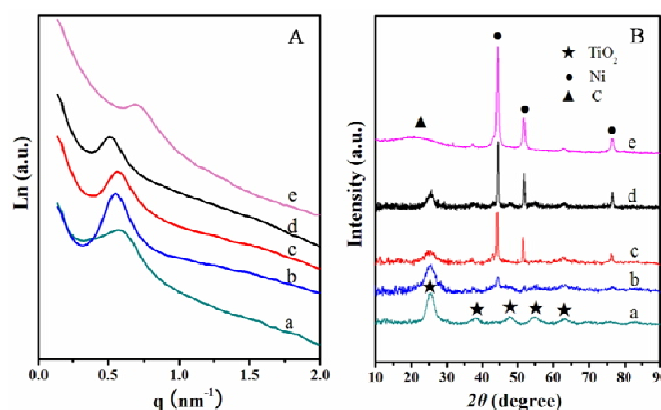


Fig. 2 SAXS (A) and Wide-angle XRD patterns (B) of the mesoporous Ni/TiO₂-C composites prepared *via* a multi-component co-assembly method with different Ni contents and Ni/C sample obtained by using an impregnation method: (a) Ni/TiO₂-C-0, (b) Ni/TiO₂-C-2, (c) Ni/TiO₂-C-5, (d) Ni/TiO₂-C-13, (e) Ni/C sample, respectively.

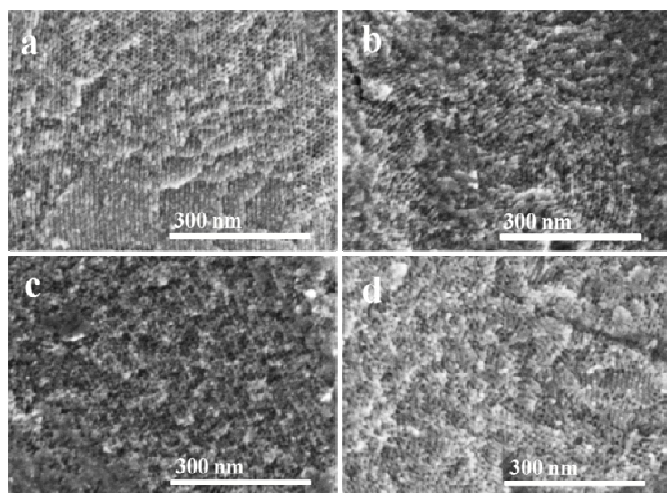


Fig. 3 FESEM images of the mesoporous Ni/TiO₂-C composites synthesized with different Ni contents *via* a multi-component co-assembly method: (a) Ni/TiO₂-C-0, (b) Ni/TiO₂-C-2, (c) Ni/TiO₂-C-5, (d) Ni/TiO₂-C-13.

Wide-angle XRD patterns of the mesoporous Ni/TiO₂-C composites (Fig. 2B) show several well-resolved diffraction peaks, which can be indexed as the nickel (JCPDS: 04-0850) and anatase TiO₂ (JCPDS: 21-1272), respectively. This result clearly depicts the formation of well crystalline TiO₂ and Ni nanoparticles after calcination at 550 °C under N₂ atmosphere. Consequently, the reduction of Ni precursors to metallic Ni nanoparticles occurs during the thermal treatment process of carbon matrix. Moreover, the intensities of the diffraction peaks from metallic Ni gradually increase with the rise of Ni content, implying an increase in particle size. The average particle sizes of Ni nanoparticles are estimated by Scherrer formula to be 18, 20 and 25 nm for Ni/TiO₂-C-2, Ni/TiO₂-C-5, Ni/TiO₂-C-13 samples, respectively. Compared to the mesoporous Ni/TiO₂-C composites, the Ni-loading/mesoporous-carbon Ni/C sample shows stronger and sharper diffraction peaks for metallic nickel, which obviously suggests larger size of nickel particles in Ni/C sample. As shown in Fig. 1S, the large Ni nanoparticles are of ~ 32 nm in size, which indicates a possible particles aggregation outside the mesostructure or inside the pore channels. Thermogravimetric analysis (TGA) curve for the Ni/C sample shows a significant weight loss in the range of 300 – 600 °C, which fairly supports the Ni content to be ~ 25 wt% (Fig. 2S). This value is in consistent with the result obtained from ICP-AES analysis (~ 22%)

Field-emission scanning electron microscopy (FESEM) images of the mesoporous Ni/TiO₂-C-x composites show ordered and opened mesopores in a large domain (Fig. 3). All the samples with different Ni contents show similar 2D hexagonal mesostructure. No obvious aggregated metal nanoparticles are observed outside of the mesopores, implying that they are well confined throughout the carbon matrix. This clearly confirms that the metal nanoparticles are effectively incorporated in the carbon frameworks without any large particles outside to block the mesopores.

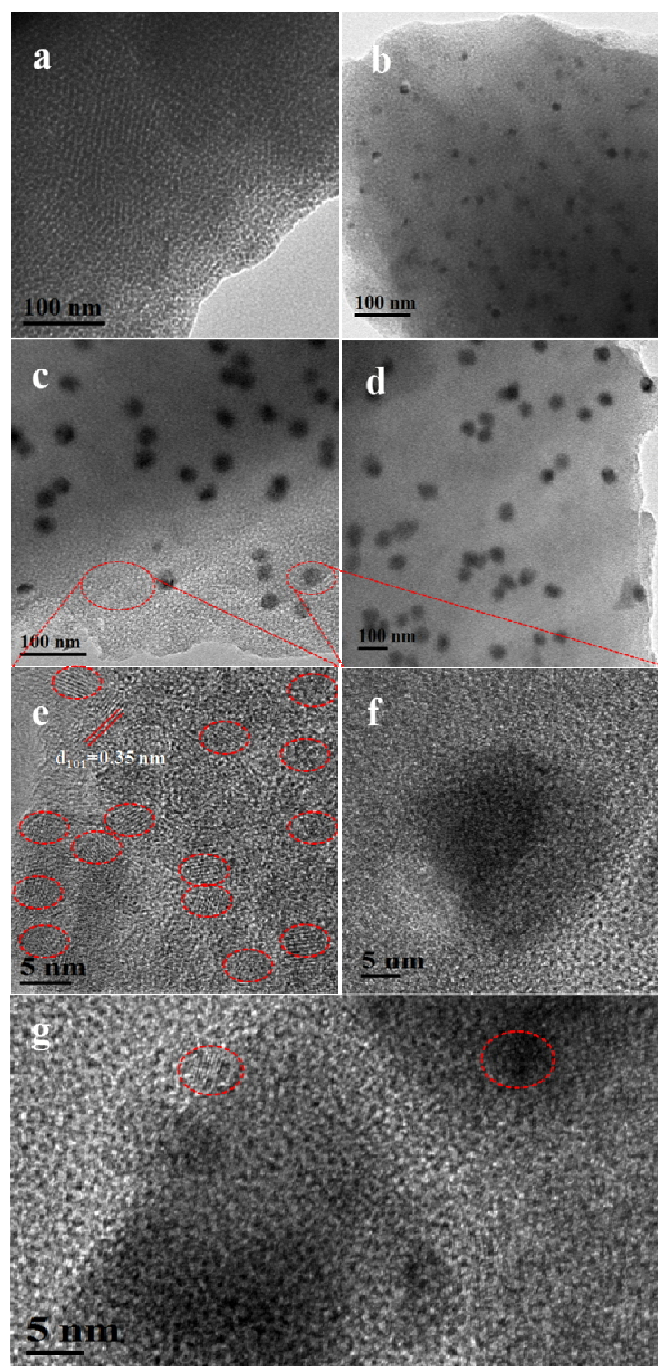


Fig. 4 TEM images of the mesoporous Ni/TiO₂-C composites with different Ni contents *via* a multi-component co-assembly method: (a) Ni/TiO₂-C-0, (b) Ni/TiO₂-C-2, (c) Ni/TiO₂-C-5, (d) Ni/TiO₂-C-13. (e, f, g) HRTEM images of Ni/TiO₂-C-5.

Transmission electron microscopy (TEM) images of the mesoporous Ni/TiO₂-C-x (x = 2 – 13) composites show that uniform Ni nanoparticles with a mean size of about 21 nm are highly dispersed in the mesoporous TiO₂-C matrix over the large domains (Fig. 4, Fig. S3a). As the Ni content increases, the size of uniformly dispersed Ni nanoparticles increases gradually. These observations are in good agreement with the XRD results. TEM images (Fig. 4a, b) of the mesoporous TiO₂-C (Ni/TiO₂-C-0) matrix and Ni/TiO₂-C-2 composite show cylindrical mesopores array in large domains, further confirming ordered hexagonal mesostructure. Meanwhile,

Ni nanoparticles with a size of ~ 18 nm in the Ni/TiO₂-C-2 sample are homogeneous dispersed in the pore walls and partially exposed in the mesopore channels. The mesostructure of the composite Ni/TiO₂-C-13 sample with a higher nickel content (13 wt%) is a slightly degenerated (Fig. 4d), which coincides with the SAXS results. High-resolution TEM (HRTEM) images (Fig. 4e – 4g) clearly show that a large number of well-crystallized TiO₂ nanoparticles with a size of about 4 nm are embedded in the carbon pore walls, revealing the characteristic lattice fringe of 0.35 nm for anatase (101) plane. This result further proves that the Ni and TiO₂ nanoparticles are mostly embedded in carbon walls instead of being dispersed inside the mesopores or aggregated outside the pore walls. Specifically, the HRTEM image (Fig. 4g) of the sample Ni/TiO₂-C-5 reveals that interfacial contact may be happened between the nickel nanoparticles and TiO₂ nanoparticles. Energy-dispersive X-ray (EDX) analysis of composites reveals C, Ti, Ni and O elements, suggesting the elemental composition of the mesoporous Ni/TiO₂-C-x composites (Fig. S3b).

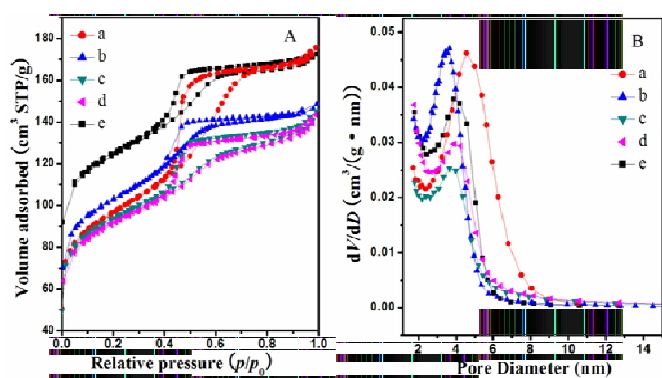


Fig. 5 (A) N₂ sorption isotherms and (B) pore size distribution curves of the mesoporous Ni/TiO₂-C composites with different Ni contents *via* a multi-component co-assembly approach and Ni/C sample obtained by using impregnation method: (a) Ni/TiO₂-C-0, (b) Ni/TiO₂-C-2, (c) Ni/TiO₂-C-5, (d) Ni/TiO₂-C-13, (e) Ni/C.

Table 1 Structural, textural, and magnetic properties of the mesoporous Ni/TiO₂-C composites obtained *via* a multi-component co-assembly approach and Ni/C obtained by using an impregnation method.

Sample	S _{BET} (m ² /g)	D _p (nm)	V (cm ³ /g)	K (min ⁻¹)	M ^{b)} (emu/g)	M _{Ni} ^{c)} (Wt%)
Ni/TiO ₂ -C-0	335	4.6	0.27	~ 0	0	0
Ni/TiO ₂ -C-2	342	3.6	0.23	0.09	0.4	2
Ni/TiO ₂ -C-5	323	3.6	0.22	0.18	1.7	5
Ni/TiO ₂ -C-13	319	3.8	0.22	0.40	5.1	13
Ni/C	430	3.8	0.27	0.05	nd ^{a)}	22

^{a)}(n.d.: not detected), ^{b)}(Magnetic saturation value), ^{c)}(Metal weight percentage)

N₂ adsorption-desorption isotherms (Fig. 5) of all the mesoporous Ni/TiO₂-C-x and Ni/C samples exhibit typical type IV curves with H2 hysteresis loops, suggesting a well-defined mesostructure. The pore size distributions derived from the

adsorption branches based on the BJH model show that all the samples have uniform mesopores. Moreover the mesoporous Ni/TiO₂-C-x composites with different Ni contents show similar type of sorption isotherms and pore-size distribution curves. Corresponding mean mesopore sizes and the surface areas are in a range of 3.6 – 3.8 nm and 319 – 342 m²/g, respectively. Compared with mesoporous TiO₂-C matrix without nickel, a slightly decrease in pore sizes from 4.6 to 3.8 and pore volumes from 0.27 m³/g to 0.22 m³/g is observed in the Ni/TiO₂-C-x composites (Table 1). Nevertheless, they still possess high surface areas, indicating that mesopores are uniform and opened. The above results further confirm that the Ni nanoparticles are confined with the carbon pore walls, preventing them from their aggregation during the heating process.

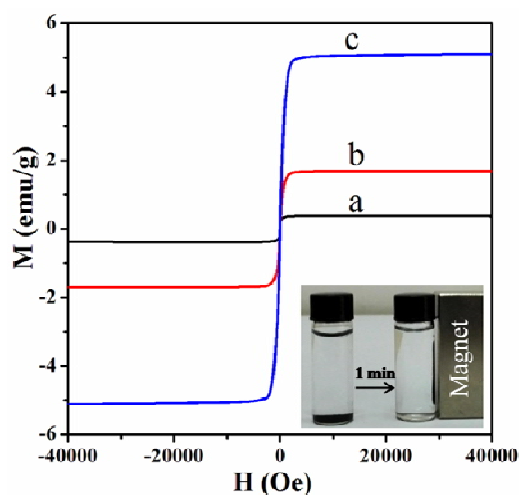


Fig. 6 The magnetic hysteresis loops at 300 K of the mesoporous Ni/TiO₂-C composites with different amount of Ni *via* a multi-component co-assembly method: (a) Ni/TiO₂-C-2, (b) Ni/TiO₂-C-5, (c) Ni/TiO₂-C-13. The inset is the photograph of magnetic separation of the Ni/TiO₂-C-13 sample in water.

Magnetic properties of the mesoporous Ni/TiO₂-C-x composites were also investigated (Fig. 6). The near-zero coercivity and remanence on the magnetization curves indicate that the mesoporous composites are superparamagnetic in nature, owing to the Ni nanoparticles with a small size of about 21 nm. The saturation magnetization values of the samples Ni/TiO₂-C-2, Ni/TiO₂-C-5, Ni/TiO₂-C-13 are measured to be 0.4, 1.7, and 5.1 emu/g, respectively, which are consistent with the nickel content in the composites. It has been examined that the final mesoporous Ni/TiO₂-C composites can be conveniently separated out from the heterogeneous catalyst system by using an external magnetic field, promising for catalytic applications (Fig. 6 inset).

To evaluate the catalytic activities of the resultant mesoporous Ni/TiO₂-C composites, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with NaBH₄ was used as a model reaction (Fig. 7). This reaction was *in-situ* monitored by UV-vis absorption spectrophotometer. Initially, 4-NP solution shows a strong absorption peak at around 318 nm, which is consistent with the previous literatures.⁹ Upon addition of NaBH₄ solution, the absorption peak shifts from 318 to 400 nm (Fig. S4a), due to the formation of 4-nitrophenolate ions in the solution.^{9,18} The peak at

400 nm has no obvious change, even after 24 h, indicating that the reduction does not take place in the absence of catalyst (Fig. S4b). When the mesoporous Ni/C without TiO₂ was added into the mixed solution as the catalyst (Fig. 7b), the intensity of the peak at ~ 400 nm gradually decreases with reaction time. A new peak at ~ 300 nm appears and its intensity gradually increases with the reaction time, corresponding to the formation of 4-AP. It is clearly seen that ~ 50 % of 4-NP can be converted into 4-AP after 24 min. However, when the mesoporous Ni/TiO₂-C-13 sample is used as a catalyst, 4-NP can be completely reduced into 4-AP within 14 min. The catalytic activity of the Ni/TiO₂-C-13 is better than that of the Ni/C catalyst with a higher Ni content of ~ 22 %. In contrast, the mesoporous TiO₂-C composite without Ni loading (Ni/TiO₂-C-0) (Fig. 7a) show no catalytic activities towards this reduction reaction, clearly indicating that Ni nanoparticles are the effective catalysts and the presence of TiO₂ in composites can greatly enhance the catalytic activities. The significantly improved catalytic activity may be ascribed to the synergistic effect between TiO₂ and Ni nanoparticles. In addition, the catalytic activities of the Ni/TiO₂-C-2, Ni/TiO₂-C-5 and Ni/TiO₂-C-13 samples were also investigated under the same reaction condition (Fig. S5). It takes about 19 min for the mesoporous Ni/TiO₂-C-5 composites to achieve the complete conversion. Rate constant *k* of the reduction reaction was evaluated (Table 1 and Fig. S6). Considering excess NaBH₄ was used, the reduction could be pseudo-first-order kinetics, the equation may be abbreviated as: $\ln(C_t/C_0) = kt$. The value C_t/C_0 was obtained from the relative intensity of the absorbance A_t/A_0 at 400 nm. The reduction rate constants (*k*) for the mesoporous Ni/TiO₂-C-2, Ni/TiO₂-C-5 and Ni/TiO₂-C-13 composites are calculated to be 0.09, 0.18 and 0.40 min⁻¹, respectively (Fig. 7d), indicating that catalytic activity gradually increases with the enhancement of Ni content. Similarly, the rate constants (*k*) showed an increasing trend with temperature (Fig. S7, Table S1). It is clear that the mesoporous Ni/TiO₂-C-13 composite shows a high activity. Compared with some previous reports (Table S2), the activity is superior to the NiCo₂ alloys,^{19a} Ni NPs^{19b} and core-shell Ni@mSiO₂ catalysts and^{19c} The rate constant value is lower than that of Ni/grapheme^{2e} and Ni_xP_y, this might be due to the low Ni contents in the Ni/TiO₂-C-*x* composites.²⁰ The recycle tests of the mesoporous Ni/TiO₂-C-13 composite as an example show no obvious changes in catalytic performance even after five runs at the same catalytic reaction (Fig. S5d). The reduction time for 4-NP converted into 4-AP rises slowly with the recycle number. It takes about 18 min for the complete reduction after five cycles, which still exhibit high activity. The TEM images of the mesoporous Ni/TiO₂-C-13 composite after the above cyclic test still remain uniformly dispersed nanoparticles without obvious aggregation (Fig. S8). These results clearly indicate that the mesoporous Ni/TiO₂-C-*x* composite catalysts are stable and reusable with an excellent cyclability.

Conclusions

In summary, ordered mesoporous Ni/TiO₂-C composites with highly dispersed nickel and TiO₂ nanoparticles have been synthesized *via* a multi-component co-assembly method. The resultant mesoporous Ni/TiO₂-C composites show a high surface area (~ 340 m²/g),

uniform pore size (~ 4 nm) and moderate pore volume (~ 0.23 cm³/g). Uniform Ni nanoparticles with tunable size are homogeneous dispersed and embedded within the carbon pore walls. Well-crystallized TiO₂ nanoparticles with the size of about 4 nm can also be co-assembled with carbon matrix and embedded in mesoporous composites, showing a strong interaction with Ni particles and a synergistic effect. The mesoporous Ni/TiO₂-C composites exhibit excellent catalytic activity towards the reduction of 4-nitrophenol to 4-aminophenol by NaBH₄. This high catalytic performance can be attributed to high surface area, well-dispersed Ni nanoparticles, uniform nanoparticle size as well as the synergistic effect between Ni and TiO₂ nanoparticles. The catalytic results show that with the increase of Ni content, the Ni/TiO₂-C-*x* composites exhibit improved catalytic performances. Most importantly, the mesoporous Ni/TiO₂-C composites catalysts can be easily recycled by magnetic separation under an applied magnetic field. We believe that the present results provide an efficient way to design and synthesize magnetic mesoporous catalysts with high performances.

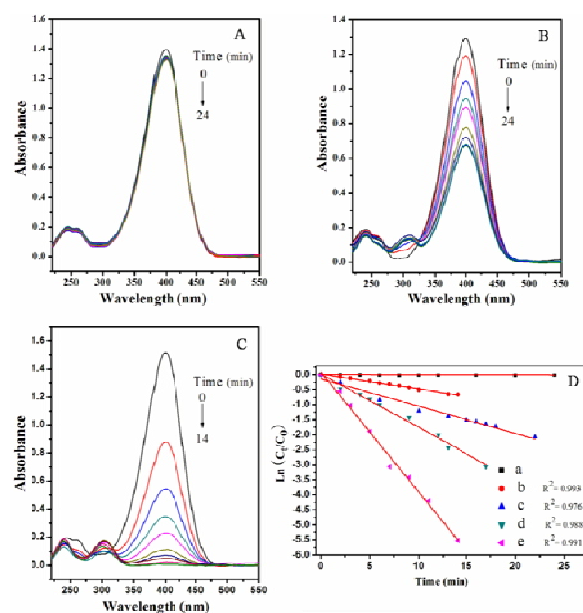


Fig. 7 UV-vis absorption spectra of the reaction solutions with different catalysts at 25 °C: (A) Ni/TiO₂-C-0 composite with 0 wt% of Ni, (B) Ni/C obtained by using impregnation method, (C) Ni/TiO₂-C-13 composite with 13 wt% of Ni. (D) The relationship between $\ln(C_t/C_0)$ and reaction time for the catalytic reduction of 4-NP at room temperature: (a) Ni/TiO₂-C-0, (b) Ni/C, (c) Ni/TiO₂-C-2, (d) Ni/TiO₂-C-5, (e) Ni/TiO₂-C-13.

Acknowledgements

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Ordered mesoporous Ni/TiO₂-C composites with highly dispersed nickel and TiO₂ nanoparticles have been synthesized *via* a multi-component co-assembly method.

