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A sandwich structured graphene modified TiO$_2$ mesoporous single crystals (GR-MSCs) by using the graphene embedded silica spheres as the hard template, via a hydrothermal treatment. The selective photocatalysis of TiO$_2$ can be achieved by controlling the location of graphene in TiO$_2$, mesoporous single crystals. The sandwich structured graphene-TiO$_2$ composite has a photooxidation surface, and the core-shell structured TiO$_2$@graphene has a photoreduction surface. It provides a new pathway to realize the selectivity of photocatalysis by controlling the location of graphene in the TiO$_2$ MSCs for the first time.

Recently, mesoporous TiO$_2$ single crystals (MSCs) have attracted much attention for their large specific surface areas, perfect single-crystalline structures, catalytically active facets, and capacities for high electron mobility.$^{1-3}$ However, MSCs do not afford the low recombination rates of electrons and holes necessary for effective photo-catalysis. This is especially true for micrometer scale MSCs that produce extremely high recombination rates in the bulk or on the TiO$_2$ surface, resulting in low photo-catalytic activities.$^{4}$ The use of graphene may address this limitation, because graphene is an ideal electron attractor and site for electron accumulation. As a result, the holes prefer to transfer to the surface of the exposed (110) facet due to the high surface energy found there.$^{19-22}$ This directional electron transfer significantly reduces the recombination of electrons and holes in these composites. Through this mechanism, GR-MSCs exhibit highly active photocatalytic properties of high energy facets, this technique can be used to enhance the separation of electrons and holes, potentially resolving the low photo-oxidation efficiency inherent to conventional TiO$_2$ single crystals. Until now, to the best of our knowledge, graphene sheets have not been successfully inserted into the bulk of TiO$_2$ single crystals. This challenge likely stems from the difficulties associated with preparing graphene-modified TiO$_2$ sandwiched composites that results from the closely packed growth pattern of solid single crystals of TiO$_2$.

Here, we report the first successful preparation of sandwiched graphene-modified TiO$_2$ MSC composites (GR-MSCs). These materials were prepared by a hydrothermal method with graphene-embedded silica spheres as the hard template. The sandwiched graphene of the GR-MSCs serves as an electron attractor and site for electron accumulation. As a result, the holes prefer to transfer to the surface of the exposed (110) facet due to the high surface energy found there.$^{19-22}$ This directional electron transfer significantly reduces the recombination of electrons and holes in these composites. Through this mechanism, GR-MSCs exhibit highly active surfaces for photo-oxidation. To highlight the unique and useful properties of sandwiched GR-MSCs, control materials comprised of core-shell structured TiO$_2$/graphene composites (mesoporous composites of MSCs@GR and solid composite of TiO$_2$@graphene) were also prepared by an ultrasonic-bubbling method that affords selective photo-reduction surfaces. By controlling the location of graphene in the TiO$_2$ MSCs with exposed (110) facets, rapid and selective photo-catalysis can be achieved.

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**Graphene Modified Mesoporous Titania Single Crystals with Controlled and Selective Photoredox Surfaces**

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Fig. 1 illustrates the process of inserting graphene into the TiO$_2$ MSCs by hydrothermal treatment. During the preparation of the silica template, the graphene oxides (GO) are dispersed into the spaces separating the closely packed silica spheres. The addition of seeds of TiO$_2$ crystals into the graphene-embedded silica template is vital for obtaining sandwiched GR-MSCs. The in situ growth of crystal seeds on the graphene surface induces the involvement of the graphene in the microcrystal lattice growth during the subsequent hydrothermal treatment. From this process, the graphene is introduced into the bulk of TiO$_2$. The graphene can also be wrapped around the surface of TiO$_2$ MSCs or solid single crystals to obtain core-shell structured MSCs@GR or TiO$_2$@GR using a simple ultrasonic-bubbling method.

Raman and XRD spectra indicate that all the graphene-modified TiO$_2$ MSCs are of the same crystalline form as rutile and the successful reduction of GO in GR-MSCs and MSCs@GR (Fig. S1a,b). The concentration of graphene present in the composites can be quantified by thermogravimetric and differential thermal analyses (Fig. S2), which indicates the proportions of graphene in GR-MSCs and MSCs@GR are 8.94 % and 7.46 %, respectively. Interestingly, although the sandwiched GR-MSCs have a slightly higher concentration of graphene and absorb slightly more strongly compared to core-shell structured MSCs@GR (Fig. S3), the bandgap of GR-MSCs is almost identical to that of MSCs@GR (inset of Fig. S3). After modification with graphene, all the TiO$_2$ MSCs clearly feature enhanced absorptions in the visible light region. The absorption bands of GR-MSCs and MSCs@GR exhibit a significant redshift compared with the pure TiO$_2$ MSCs, owing to the generation of chemical bonds between TiO$_2$ and graphene.

The SEM and TEM images for different graphene-modified TiO$_2$ MSCs are shown in Fig. 2. The pure TiO$_2$ MSCs have the appearance of a perfect cuboid single crystal with exposed (110) facets and an ordered mesoporous structure (Fig. 2a). The pore size of this material is ~40 nm (inset of Fig. 2a). Also visible are channels of ~10-20 nm in diameter forming a 3D-network throughout the framework (Fig. 2b). The magnified images of the TiO$_2$ MSCs indicate that the edges of the MSCs are relatively smooth (Fig. 2c). The specific surface area of the MSCs is calculated to be 27.79 m$^2$/g. The type IV N$_2$ sorption isotherm curves and the Barrett-Joyner-Halenda pore size distribution centered at 40-50 nm also confirm the mesoporous nature of the structures (Fig. S4a,b). After the introduction of graphene into the TiO$_2$ MSCs, the MSCs decrease in size from 500-700 to 400-600 nm. This observation likely results from the inhibition of TiO$_2$ single crystal growth due to the introduction of graphene into the lattice (Fig. 2d). The absence of large, layered graphene suggests that most of the graphene has been incorporated into the MSCs. Compared with the smooth appearance of the surface of pure TiO$_2$ MSCs, the edges of GR-MSCs appear slightly rough because some fringes of sandwiched graphene are exposed to the surface (Fig. 2e,f). Interestingly, after the graphene is introduced into the bulk of the MSC, micropores of ~2 nm appear in the pore size distribution spectra shown in Fig. S4d. These features are indicative of aggregated pores resulting from the chemical linking between graphene and TiO$_2$. The presence of these micropores indicates that tight junctions between TiO$_2$ and graphene are present in the bulk of the MSCs instead of on the surface. Despite the strong chemical interaction between graphene and TiO$_2$, resulting from graphene’s flexible nature, micropores were not produced by surface wrapping after graphene was chemically bonded to the surface of MSC (MSCs@GR) (Fig. S4e,f). In contrast to the GR-MSCs, the core-shell structured MSCs@GR feature a thin layer of graphene coated onto the surface of the MSCs (Fig. 2g-i). A uniform distribution of TiO$_2$ micro-single-crystal aggregates in the graphene sheets, which have an appearance resembling beetles caught in a cobweb, is visible. MSCs@GR composites exhibit both crinkled and smooth textures that result from the presence of flexible and ultrathin graphene sheets (inset of Fig. 2i). TEM images confirm that the TiO$_2$ MSCs are firmly encapsulated by graphene sheets even after the composites were ultrasonically dispersed in order to enable TEM characterization. These features are indicative of strong interactions between MSC and graphene. TEM images of GR-MSC and MSCs@GR with different amount of graphene furtherly confirms the sandwich and core-shell structure, respectively (Fig. S5). We choose a GR-MSC particle at random from the TEM image to record the SAED and characterize the lattice fringe (Fig. S6). The SAED pattern further confirms the single-crystal-like nature of the material (inset of Fig. S6a), and indicates that the exposed (110) facets are dominant in the TiO$_2$ MSCs (Fig. S6b). The clear lattice fringes visible in Fig. S6c, d can be assigned with confidence to the (200) and (110) spacings of rutile and are in good agreement with the SAED pattern. In order to further demonstrate the synthesized MSCs, we indeed the mesoporous single crystal, the TEM image with proper magnification was given in Fig. S6e, f to reveal the interface information on MSCs.

The element mapping images of TiO$_2$ MSCs and GR-MSCs presented in Fig. S7 and Fig. S8 confirm the presence of sandwich structured GR-MSCs. When graphene has been introduced into the bulk of the TiO$_2$ MSCs, many clearly...
distinguishable red dots appear in the region corresponding to the bulk of the MSCs. And the absence of carbon at the edges of the GR-MSCs indicates that the graphene is indeed embedded inside the MSC, affording a sandwich-like structure (detailed discussion in the ESI).

The XPS spectra in Fig. S9 shed light on the catalytic effect of graphene in the systems investigated here. Compared to the reaction using blank TiO$_2$ MSCs, the use of sandwiched GR-MSCs affords a new peak at 288.3 eV resulting from the generation of Ti-O-C bonds between graphene and MSCs. $^{26, 27}$ When the graphene is wrapped around the surface of TiO$_2$ using an ultrasonic-bubbling treatment, the expected Ti-C bonds between TiO$_2$ and graphene are observed as indicated by the peaks appearing at 280.5 eV. $^{28-30}$ The FTIR results further confirm the interaction of TiO$_2$ with graphene (Fig. S10). The small peaks at 796 cm$^{-1}$ and 1099 cm$^{-1}$ are assigned to Ti-O-C bonds and Ti-C bonds, respectively. $^{3}$

GR-MSCs is also very close to that of MSCs@GR and much lower compared to that of blank TiO$_2$ MSCs and P25 (Fig. 3b). EIS changes of different samples under irradiation are similar to that in dark (Fig. S13). The impedance of blank TiO$_2$ MSCs is lower than that of commercial P25 owing to the presence of exposed (110) facets. $^{19}$

Although the GR-MSCs and MSCs@GR have a similar electron-transfer efficiency and electron-hole separation, they have totally different photo-catalytic activities. For instance, the sandwiched GR-MSCs catalyze the rapid photo-oxidation of phenol but only mildly catalyze the photo-reduction of water to H$_2$ (Fig. 3c,d). The rate of light-dependent phenol oxidation for the sandwiched GR-MSCs is ~2.1 times greater than that of the core-shell structured MSCs@GR and ~15.0 times greater than that of the solid TiO$_2$@graphene composite (It shares a similar core-shell structure with the MSCs@GR, as shown in Fig. S14). Each catalyst tested here exhibits similarly low amounts of phenol adsorption in the dark (Fig. S15), but the GR-MSCs exhibit the greatest overall solar light-dependent photodegradation activity. With increasing amount of graphene, the photocatalytic activity of sandwich or core-shell structured graphene modified mesoporous TiO$_2$ single crystals was increased then decreased. The original GR-MSCs and MSC@GR present the highest photocatalytic activities, respectively (Fig. S16). Moreover, GR-MSCs also shows the best photo-oxidation activity in the presence of Pt. (Fig. S17a)

The unique sandwiched GR-MSCs maintain high photooxidation activities for the degradation of phenol even after 4 catalytic cycles, indicating high catalytic stability (Fig. S18). Conversely, the MSCs@GR catalyze the rapid photo-reduction of water for H$_2$ generation but only mildly catalyzes the photo-oxidation of phenol (Fig. 3c, d). Moreover, the MSCs@GR with 0.377 wt% Pt loading shows the highest formation rate in the photocatalytic hydrogen generation and the photocatalyst without Pt loading shows no photocatalytic activity. (Fig. S17b) The rate of water photo-reduction for the MSCs@GR is ~3.6 times greater than that of the GR-MSCs and ~7.0 times greater than that of the solid TiO$_2$@graphene composite. These results indicate that selective photocatalysis can be achieved by controlling the location of graphene in TiO$_2$.

Terephthalic acid was used as the probe to measure the -OH concentration during the photocatalytic reaction. This was achieved by measuring the PL signal of ortho-hydroxyterephthalic acid (Fig. S19a). $^{32, 33}$ The concentration of -OH indirectly reflects the concentration of photo-generated holes. Among the catalysts, GR-MSCs exhibited the strongest PL signal, indicating the greatest production of -OH during the photocatalytic process. Upon the addition of hole trapping agents such as Na$_2$S$_2$O$_7$ to the solution containing the GR-MSCs, the resulting PL signal was greatly diminished. These results indicate that the GR-MSCs can produce many more holes on the MSC surface and are capable of photo-oxidative catalysis mainly under the solar light irradiation. Due to the lower potential of graphene, the photo-generated electrons prefer to transfer to the sandwiched graphene in the bulk of TiO$_2$ (Fig. S19c). $^{37, 34, 35}$ Simultaneously, the photo-generated holes tend to move to the exposed (110) facet due to the high
surface energy found there. Because phenol molecules are preferentially adsorbed to the surface of photocatalysts, the nature of this catalytic surface with regards to holes is vital to the catalytic photodegradation of this compound.

We employed Fe²⁺ as a probe to indirectly detect the electron concentration of different samples under solar light irradiation. Fe³⁺ is easily reduced to Fe²⁺ by photo-generated electrons. Fe²⁺ ions subsequently react with 1,10-phenanthroline monohydrate (Phen) to generate an orange product that absorbs strongly in the visual spectrum. Measuring the concentration of this colored product indirectly as a probe to indirectly detect the electron concentration of different samples under solar light irradiation. Fe²⁺ generated electrons. Fe³⁺ irradiation. Fe²⁺ electrons. Fe²⁺ ions subsequently react with 1,10-phenanthroline monohydrate (Phen) to generate an orange product that absorbs strongly in the visual spectrum. Measuring the concentration of this colored product indirectly as a probe to indirectly detect the electron concentration of different samples under solar light irradiation.

In summary, we have prepared the first sandwiched graphene-modified TiO₂ MSC composites using SiO₂ as a hard template. These materials exhibit excellent photo-oxidation properties compared with the conventional core-shell structured TiO₂/graphene composites. Unexpectedly, the location of the graphene in these materials appears to reliably dictate the selectivity of the catalysis. While conventional MSCs@GR are limited to featuring only a photoreduction surface, the sandwiched GR-MSCs described here also exhibited a unique photo-oxidation surface with catalytic activities greatly in excess of other core-shell TiO₂/graphene composites. This work provides a new method to achieve selective photocatalysis using TiO₂ and has potential applications in photocatalytic organics synthesis and other selective redox reactions.

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Notes and references