TiO$_2$ nanoparticles assembled on kaolinites with different morphologies for efficient photocatalytic performance

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Natural kaolinite clays with different dimensionalities (including kaolinite nanoflakes and nanorods) supported TiO$_2$ nanoparticles were successfully prepared via a facile sol-gel method. Moreover, comparisons between FK/TiO$_2$ and RK/TiO$_2$ nanocomposites are conducted in terms of matrix morphology, surface property, energy band structure and interfacial interaction. The effects of kaolinite microstructure, morphology and dimensionality on the interfacial characteristics and photocatalytic properties of the nanocomposites were investigated in detail. The results showed that TiO$_2$ nanoparticles are more easily attached on the kaolinite nanoflakes, and possess more uniform distribution and smaller particle size than that of kaolinite nanorods. In particular, the FK/TiO$_2$ nanocatalysts exhibit higher photocatalytic activity for the degradation of tetracycline hydrochloride than that of RK/TiO$_2$, and bare TiO$_2$, which is attributed to the stronger surface adsorptivity, higher loading efficiency and smaller grain size. Additionally, FK/TiO$_2$ composites show excellent stability, which is ascribed to the intimate interfacial contact between two-dimensional kaolinite nanoflakes and TiO$_2$ nanoparticles. Overall, the enhanced catalytic performance for FK/TiO$_2$ composites is the synergistic effect of two-dimensional morphology, better adsorption capability and more active photocatalysis TiO$_2$ species.

Heterogeneous nanocomposites has attracted increasing attention because of the synergetic properties and potential applications as green methods to solve the energy and environmental problems$^1$. In recent years, many technologies are proposed to tailor and promote the properties of nanocomposites, including element doping$^2$, surface loading$^3$–$^6$, morphology controlling$^7$–$^{11}$, heterostructure constructing$^{12}$–$^{16}$, energy-band engineering$^{17}$, and so on. Among them, loading functional nanoparticles on the surface of matrix materials is a promising alternative to control the nanoparticle size, and overcome inherent drawbacks of unsupported nanoparticles in terms of stability, agglomeration and reusability$^{18}$.

As is well known, the performance of nanocomposites depends not only on the chemical composition, but also on microstructure, dimension, size and morphology and so on. At present, much interest has been focused on nanoparticles anchoring on a single support or the morphology-controlled synthesis of functional particles via different strategies, and further studied the comparative catalytic efficiency of the synthesized samples. Yang et al.$^{19}$ synthesized a series of graphene-TiO$_2$ nanocomposites with different TiO$_2$ dimensionalities (including TiO$_2$ nanoparticles, nanotubes and nanosheets) via sol-gel method, alkaline hydrothermal process and one-step solvothermal method, respectively. Meshram et al.$^{20}$ reported synthesis of CuO nanostructures with different morphologies such as spherical, vesicular, nanosheet and platelet using chemical precipitation and hydrothermal methods. The photocatalytic activities of CuO nanostructures were evaluated by monitoring degradation of methylene blue, and the platelet-like CuO nanostructures were found to have the best catalytic activity. Thuy et al.$^{21}$ prepared TiO$_2$ particles with different morphologies via hydrothermal process, and investigated the morphological effect of TiO$_2$ on photocatalytic degradation of organic dyes. However, none of these reports investigate any particular insights into the morphology of the support which has been reported to be as important as its internal structure. Like synthetic MCM-41, as common matrix materials$^{22}$, have different morphologies, including mesoporous...
silica nanoparticles, nanofibers, nanotubes, ordered hollow spheres or core-shell structured spheres. It is significant to select an optimum morphology for a support to prepare a more efficient and reusable catalyst in a green process.

Kaolinite \([\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]\) is a 1:1-type clay mineral composed of stacked layers of \(\text{SiO}_4\) tetrahedral sheets and \(\text{AlO}_2(\text{OH})_4\) octahedral sheets and naturally possesses diverse morphologies, including one-dimensional (nanotubes and nanorods) and two-dimensional morphology (nanoflakes). The schematic drawing of the crystal structures of kaolinite nanoflakes and kaolinite nanorods as a combination of \(\text{AlO}_6\) octahedra with \(\text{SiO}_4\) tetrahedra is shown in Fig. 1d,h. Meanwhile, kaolinite clays possess plentiful hydroxyl groups on the surface, which is beneficial to surface modification and make kaolinite become a suitable matrix for anchoring of TiO\(_2\) nanoparticles to enhance the photocatalytic activity. Zhang et al. successfully synthesized TiO\(_2\)/kaolinite composites with mixed phase TiO\(_2\) (anatase and brookite) at low temperature. The crystal type of TiO\(_2\) nanoparticles could be controlled by the kaolinite matrix, and finally improve the catalytic performances. Hai et al. prepared acid-activated kaolinite via calcination and acid activation of coal-bearing kaolinite and then modified with TiO\(_2\) nanoparticles to improve its adsorbent and hence remove azo dyes. Kutlakova et al. prepared nanocomposite kaolinite/TiO\(_2\) using thermal hydrolysis of titanyl sulfate (TiOSO\(_4\)) in the presence of kaolin, and calcined kaolinite/TiO\(_2\) at 600°C. Thermal treatment was beneficial to the improvement of the photocatalytic activity of kaolinite/TiO\(_2\) composites. These studies are inclined to focus on the crystal structure changes of TiO\(_2\) on a substrate, but ignore the effect of matrix morphology on properties of TiO\(_2\). Therefore, preparing catalysts with kaolinites possessing the natural different morphologies is a very meaningful study to clarify the effect of clays dimensionality on the photocatalytic behavior and interfacial characteristics of kaolinite/TiO\(_2\) nanostructures.

In this work, based on the features of kaolin clays, unique layered structure, with similar chemical composition, but natural different morphologies (one-dimensional nanorods and two-dimensional nanoflakes), we have successfully assembled uniform TiO\(_2\) nanoparticles on the surface of kaolinite clays by a facile sol-gel method. The effects of kaolinite clays microstructure and dimensionality on the interfacial characteristics and catalytic properties of the composites were investigated in detail. TiO\(_2\) nanoparticles were efficiently deposited on the surface of kaolinites. The photocatalytic activity of this porous material was evaluated by tetracycline hydrochloride degradation. The clays/TiO\(_2\) simultaneously covered their excellent properties of TiO\(_2\) and kaolinites, exhibited high photocatalytic activity and adsorption property, and endowed this material with a bright perspective in degradation of antibiotics.

Results

Morphological and structural characteristics. The general morphologies of different samples were observed by electron microscope. Typical SEM and TEM analysis indicates that kaolinite clays used in the experiments naturally possess different morphologies, and the kaolinite particles all possess smooth surface without contamination (Fig. 1a,b,e,f). Kaolinite nanoflakes exhibit an irregular angular shape and the length of particles are in the range of microns (Fig. 1a,b). Nanorod-like kaolinites with smooth surface (Fig. 1e,f) are mostly 2–5 μm in length and 0.1–0.3 μm in diameter with a length to width ratio of about 20:1. It can be seen from Fig. 2d, bare TiO\(_2\) nanoparticles are obtained via the sol-gel method combined heat treatment. However, the dispersion of bare TiO\(_2\) nanoparticles is poor and exists obvious aggregation. In the presence of clays, the aggregation of TiO\(_2\) nanoparticles is markedly inhibited (Fig. 2a,e) and TiO\(_2\) nanoparticles are uniformly deposited on the surface.

Figure 1. Morphology and schematic drawing of the samples. SEM, TEM images and Zeta potential (the insets are the schematic view of surface charge distributions) of (a–c) FK, (e–g) RK. Schematic drawing of the crystal structures of (d) FK and (h) RK as a combination of AlO\(_6\) octahedra with SiO\(_4\) tetrahedra.
of clays. After loading TiO₂ nanoparticles, the clay supports show different loading results at the same experiment conditions. The TiO₂ nanoparticles exhibit much more uniform and smaller for FK/TiO₂ (Fig. 2a) and aggregation seriously for RK/TiO₂ (Fig. 2e), which indicates that the morphology of supports have a seriously effect on the particles size. The HRTEM (Fig. 2b,f) results indicate that TiO₂ nanoparticles have high crystallinity with well-defined lattice fringes of 0.189 nm corresponding to (200) plane, and 0.352 nm corresponding to (101) plane, in accordance with XRD results (Fig. 2h). Moreover, obvious interfaces are observed between the TiO₂ and clays. The intimate interaction enables the electron to more easily transfer from TiO₂ nanoparticles to kaolinite nanoflakes during the photoexcitation process. Meanwhile, the mean size of TiO₂ nanoparticles for FK/TiO₂ and RK/TiO₂ measured on TEM images (Fig. 2a,e) are 7.6 and 37.9 nm, respectively, as shown in Fig. 2c,g. It is clear that the grain size of TiO₂ nanoparticles is strongly depended on the morphology of the supports. Meanwhile, the TiO₂ nanoparticles on kaolinite clays are much smaller than that of bare TiO₂ (Fig. 2d), indicating the dispersion effect on TiO₂ clusters on the surface of kaolinite clays. The measured surface zeta potential curves and the surface charge distributions sketches of pristine kaolinites with different morphologies are showed in Fig. 1c,g. It is clear that kaolinites with different morphologies carry a net negative charge, which allows for its good dispersibility in water and provided a strong electrostatic adsorption force to the positively charged molecules on the surfaces. But they possess the different surface charge distributions, thus leading to the different surface natures, which allows the adjustable grain size of TiO₂ nanoparticles and further affects the photocatalytic performances.

As a result, the kaolinite clays with different morphologies can serve as supporting materials for in situ growth of TiO₂ nanoparticles. The TiO₂ nanocrystals attached on kaolinite nanoflakes have better dispersion and much smaller grain size than that of bare TiO₂ and RK/TiO₂ samples, resulting from the intimate interaction and good interfacial contact. Therefore, the TiO₂ particles size can be controlled by clays and form interaction with clays surface, which would lead to exposing more catalytic reaction sites, improving photoelectrons transiting and enhancing the photocatalytic activity.

Figure 2h shows the XRD patterns of as-synthesized samples to study the crystal structure and crystalline phase of TiO₂ in the nanocomposites. It can be clearly seen that kaolinite clays possessed the natural different morphologies have the similar crystal structure and their XRD patterns are in good agreement with the standard PDF card of JCPDS 14-0164 for kaolinite-1A33. The XRD pattern of bare TiO₂ shows the highly crystalline anatase phase TiO₂ (JCPDS No. 21-1272)34. The diffraction peaks of FK/TiO₂ and RK/TiO₂ composites are in good agreement with the anatase phase TiO₂ and kaolinite, showing that the structure of kaolinite is maintained during the introduction of TiO₂ nanoparticles. Meanwhile, the diffraction intensities of kaolinites in FK/TiO₂ and RK/TiO₂ composites are decreased, indicating the successful loading of TiO₂ on the surface of kaolinites. The average grain size of TiO₂ nanoparticles for FK/TiO₂ and RK/TiO₂ estimated by the Scherrer’s formula are 9.1 and 32.4 nm, respectively, which is consistent with the results based on TEM images. Moreover, the grain size of bare TiO₂ is 16.8 nm. By comparison to the standard JCPDS diffraction patterns of anatase phase TiO₂, it can be seen that the diffraction peaks of TiO₂ on FK/TiO₂ are much more obvious than that of RK/TiO₂, which indicates that FK has relatively higher loading efficiency for TiO₂ nanoparticles at the same experiment conditions. In order to further confirm the results, elemental analysis (Table 1) was employed in the experiment. It is shown that the relative content of titanium in FK/TiO₂ is higher than that of RK/TiO₂, which is consistent with the XRD results.

The nitrogen adsorption-desorption isotherms of different samples and BJH pore size distribution are shown in Fig. 3, and the textural parameters calculated from the corresponding isotherms are summarized in Table 2. As shown in Fig. 3a, the adsorption-desorption isotherms of bare TiO₂ almost have no hysteresis loop, and the
BET specific surface area is only 13 m²/g due to the seriously aggregation, while the adsorption-desorption isotherms of clays/TiO₂ exhibit typical characteristic of type-IV with distinct type H3 hysteresis loop, indicating the formation of mesoporous structures 35. However, the adsorption-desorption isotherms of clays almost have no hysteresis loop, and the specific surface area are only about 27 m²/g, indicating clays nanoparticles can easily aggregate and result in the performance decline. After supporting TiO₂ nanoparticles on the surface of clays, the BET specific surface area (S_BET) and pore volume (V_pores) of composites are increased, as summarized in Table 2. It shows that the mesopore structure can be formed after loading TiO₂ nanoparticles by revealing increased surface area from 27 to 114 m²/g for FK/TiO₂, and from 26 to 109 m²/g for RK/TiO₂. The pore volume of FK/TiO₂ and RK/TiO₂ are 0.25 and 0.35 cm³/g, respectively. Obviously, FK/TiO₂ has relatively higher specific surface area and lower pore volume, compared with RK/TiO₂, which might be because the smaller size and uniform distribution of TiO₂ nanoparticles attached on kaolinite nanoflakes. These results are further confirmed by the observation from their pore size distribution calculated by BJH method (Fig. 3b). These characteristics seem to be responsible for enhanced catalytic activity and stability on the clays/TiO₂ in comparison with bare TiO₂. These properties are also attributed to the formation of small particles through oxide-support interaction to provide more active sites for photocatalysts.

### Interfacial characteristics

The surface properties of TiO₂ species play an important role in aqueous phase photocatalytic reaction, and a large surface area of FK/TiO₂ is responsible for the efficient catalytic activity. In addition, the interactions between TiO₂ and clays are also important to suppress the aggregation of TiO₂ nanoparticles during the reaction, and the oxide-support interactions are measured by FTIR and XPS, which can provide additional information on the structure of clays/TiO₂ nanocomposites.

The FTIR spectra of the samples are shown in Fig. 4a to analyze the vibrational bands and the interface interaction. For FK and RK, the peak at 1033 cm⁻¹ corresponds to the stretching vibration of the skeleton Si-O network (Si-O-Si and O-Si-O) 36. The broad band between 1631 cm⁻¹ is assigned to adsorbed water. The other bands at 3658 and 1116 cm⁻¹ are assigned to inner surface hydroxyl out-of-phase stretching vibration and apical

### Table 1. The chemical composition of different samples (mass %).

| Samples | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | TiO₂ | K₂O | Na₂O | Ig.loss |
|---------|------|-------|-------|-----|-----|------|-----|------|--------|
| FK      | 46.90| 38.14 | 0.15  | 0.01| 0.11| 0.14 | 0.30| 0.19 | 13.98  |
| RK      | 46.78| 38.51 | 0.96  | 0.04| 0.03| 0.05 | 0.19| 0.02 | 13.82  |
| FK/TiO₂ | 23.75| 19.14 | 48.21 | 0.11| 0.01| 0.06 | 0.21| 0.12 | 8.39   |
| RK/TiO₂ | 29.51| 20.32 | 42.16 | 0.53| 0.02| 0.01 | 0.11| 0.01 | 7.33   |

### Table 2. The textural characteristics of all samples. Notes: S_BET = BET specific surface area, V_pores = total pore volume, d_pores = average pore diameter.

| Material   | S_BET (m²/g) | V_pores (cm³/g) | d_pores (nm) | Band gap energy (eV) |
|------------|--------------|-----------------|--------------|----------------------|
| FK         | 27           | 0.09            | 11.8         | —                    |
| RK         | 26           | 0.06            | 9.2          | —                    |
| FK/TiO₂    | 114          | 0.25            | 8.7          | 3.21                 |
| RK/TiO₂    | 109          | 0.35            | 12.5         | 3.19                 |
| TiO₂       | 13           | 0.04            | 11.4         | 3.20                 |

### Figure 3. Textural characteristics of the samples. (a) Nitrogen adsorption-desorption isotherms, (b) corresponding BJH pore size distribution of different samples.
Si-O stretching vibration, respectively. The absorption bands at 3694, 3620, and 915 cm\(^{-1}\) are ascribed to an inner-surface hydroxyl (Al-OH) stretching vibration, which are rarely influenced by intercalation\(^{29}\). The peak at 3740 cm\(^{-1}\) is assigned to the outer-surface hydroxyl (Si-OH) stretching vibrations. The bands at 793, 753 and 690 cm\(^{-1}\) are due to the translational vibration of O-Al-OH. Meanwhile, the bands at 545 and 470 cm\(^{-1}\) are attributed to the vibration of Si-O-Al. There is little change in the band positions of RK compared with FK, only the overall intensity are slightly reduced. FK/TiO\(_2\) and RK/TiO\(_2\) show the characteristic bands of kaolinite at 3694, 1116 and 915 cm\(^{-1}\) and TiO\(_2\) at between 1600 and 1200 cm\(^{-1}\). The absorption band at 3740, 3658 and 3620 cm\(^{-1}\) ascribed to surface hydroxyl groups vibration are disappeared, indicating the structural dehydroxylation of the kaolinite, which might be caused by immobilization of TiO\(_2\) nanoparticles on the surface of kaolinite or the bonding on Ti atoms on these sites, leading to a reduction of hydroxyl groups. The Si-O stretching band at about 1033 cm\(^{-1}\), which shifts to 1019 and 1012 cm\(^{-1}\) for FK/TiO\(_2\) and RK/TiO\(_2\), respectively. The shifting of the skeleton Si-O network stretching band indicates the formation of hydrogen bonding between the outer surface of the kaolinites (tetrahedral sheet) and TiO\(_2\). Moreover, the new broad band around 3440 cm\(^{-1}\) is assigned to Ti-O and its intensity for FK/TiO\(_2\) is higher than that of RK/TiO\(_2\). Furthermore, the bands at 793, 753, 690, 545 and 470 cm\(^{-1}\) are disappeared for FK/TiO\(_2\), while still remained for RK/TiO\(_2\). These results provide evidences for the existence of interaction between kaolinite and TiO\(_2\) and confirm that the FK can be coated by TiO\(_2\) nanoparticles.

Figure 4. Interfacial characteristics of the samples. (a) FTIR spectra and (b) XPS survey spectra of different samples. (c) Ti 1 s, (d) O 1 s, (e) Si 2p and (f) Al 2p fitted XPS spectra of different samples.
Figure 5. Optical spectroscopic study of the samples. (a) UV-vis diffuse reflectance spectra of different samples, (b) the corresponding plots of ($\alpha$hv)$^2$ vs. photon energy ($hv$), (c) the photoluminescence spectra of different samples.

much more effectively and the binding force is much stronger than that of RK, which is consistent with the TEM (Fig. 2) and XRF results (Table 1).

The interactions between TiO$_2$ and kaolinite clays in the composites are further investigated by using XPS spectra. Figure 4b shows the XPS survey spectra of FK, RK, FK/TiO$_2$ and RK/TiO$_2$ in the range 0–1200 eV. The XPS survey spectra of FK/TiO$_2$ and RK/TiO$_2$ clearly indentify the signals of the Al, Si, Ti and O elements. The weak signals of Si and Al elements for clays/TiO$_2$ indicate that the kaolinite surface are coated with a layer of dense nano-sized TiO$_2$ particles.

The high-resolution XPS spectra of Ti 2p, O 1s, Si 2p and Al 2p for samples are exhibited as Fig. 4c–f, respectively. As shown in the high-resolution spectra of Ti 2p electrons (Fig. 4c), two bands located at 458.77 and 464.47 eV for RK/TiO$_2$ and 458.57 and 464.27 eV for FK/TiO$_2$ can be assigned to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ spinorbital splitting photoelectrons in the Ti$^{4+}$ chemical state, respectively. Meanwhile, Ti$^{4+}$ combines with kaolinite and forms Si-O-Ti bond. This interaction of chemical bond can immobilize TiO$_2$ to prevent it from movement and agglomeration. The slight shifts for FK/TiO$_2$ and RK/TiO$_2$ can be due to a change in the chemical state or coordination environment of Ti 2p, that is, the interaction between kaolinite with different morphologies and TiO$_2$ nanoparticles. Moreover, the larger peak area of Ti 2p for FK/TiO$_2$ indicates that TiO$_2$ nanoparticles are more easily loaded onto the surface of kaolinite clays, the reduction of hydroxyl groups and slightly shifts for clays/TiO$_2$ indicate the interaction between the two components.

The high resolution O 1s spectra of kaolinites can be deconvoluted into two fitted peaks (Fig. 4d). The peak at around 532.6 eV can be assigned to lattice oxygen in the kaolinites, and the other peak at about 531.7 eV is derived from the hydroxyl group. For clays/TiO$_2$, the peaks at 532.6 eV and 530.6 eV are assigned to oxygen from Si-O-Si and Ti-O-Si, and the peak at 531.2 eV is assigned to oxygen from hydroxyl group. The result is in good consistent with that of Ti 2p (Fig. 4c) and confirms the existence of Ti-O-Si and surface hydroxyl. Moreover, the shifts of surface hydroxyl groups and the new formed Ti-O-Si demonstrate the integration between TiO$_2$ and kaolinite and intense interaction between the two components. Moreover, the larger peak area of Ti-O-Si for FK/TiO$_2$ further indicates FK/TiO$_2$ has relatively higher loading efficiency of TiO$_2$ nanoparticles than that of RK/TiO$_2$.

Figure 4e,f shows the Si 2p and Al 2p spectra of different samples, and the peak positions for kaolinite are observed at 103.3 eV (Si-OH), 102.7 eV (Si-O), 75.1 eV (Al-OH) and 74.3 eV (Al-O), respectively. After supporting TiO$_2$ nanoparticles on the surface of clays, the reduction of hydroxyl groups and slightly shifts for clays/TiO$_2$ nanocomposites indicate the interaction between the two components.

**Optical spectroscopic study.** The UV-vis diffuse reflectance spectra are used to determine the optical properties of the synthesized samples. As shown in Fig. 5a, the FK and RK show clear absorption in the UV region, and a visible light absorption around 500 nm for RK can be observed. It is obvious that bare TiO$_2$ nanoparticles have no or relatively weak visible light absorption, while clays/TiO$_2$ nanocomposites exhibit enhanced light absorption capacity in the UV-vis region, indicating that the weak absorption in the visible light region can be attributed to the kaolinites. In comparison to kaolinites, the absorptions attributed to crystalline TiO$_2$ around 400 nm are present, which further confirms that the crystalline TiO$_2$ nanoparticles are successfully attached on the surface of kaolinite clays/TiO$_2$ nanocomposites. Meanwhile, the positions of absorption onsets of clays/TiO$_2$ nanocomposites exhibit a significant shift compared to bare TiO$_2$ nanoparticles, which is due to the quantum size effect and dispersion effect of kaolinite clays. The shift of absorption edge for FK/TiO$_2$ is stronger than RK/TiO$_2$. It might be due to the smaller size of TiO$_2$ in FK/TiO$_2$, which is well consistent with the TEM results (Fig. 2).

The bandgap energy of clays/TiO$_2$ samples can be confirmed roughly according to the plot of ($\alpha$hv)$^2$ versus energy ($hv$) of absorbed light (Fig. 5b), which is obtained on the basis of the Kubelka-Munk function ($F(R\alpha) = (1 - R)^2/(2R)$), where $\alpha$, $h$, $v$ and $R$ are absorption coefficient, Planck constant, light frequency and reflectance with the reflectance at 1000 nm set at 100%, respectively. As shown in Fig. 5b, the band gap energies of the TiO$_2$ species in FK/TiO$_2$ and RK/TiO$_2$ are 3.21 and 3.18 eV, respectively. For comparison, the bandgap energy of bare TiO$_2$ nanoparticles, calculated from the corresponding plot of ($\alpha$hv)$^2$ vs. photon energy ($hv$), is 3.2 eV. The results indicate that FK/TiO$_2$ possesses larger band gap energy, which can be attributed to the smaller grain size and the more intense interaction between TiO$_2$ and FK. It is conducive to the enhancement of photocatalytic performances.

The photoluminescence (PL) spectra of the samples at the excitation wavelength of 254 nm are shown in Fig. 5c. The PL peaks of clays/TiO$_2$ are much lower than that of bare TiO$_2$, thus suggesting the less recombinination of photogenerated electrons and holes, which would lead to improved photocatalytic activity. FK/TiO$_2$ nanocomposites have the intimate and uniform interfacial contact, in which photogenerated electrons from TiO$_2$
The smaller particles size and more efficient charge separation is achieved and consequently leads to higher photocatalytic activity, compared with RK/TiO₂ and bare TiO₂ nanoparticles.

**Photocatalytic properties.** The photocatalytic performances of as-prepared photocatalysts were measured to degrade antibiotics under UV light irradiation (Fig. 6). Figure 6a shows the degradation curves of tetracycline hydrochloride using FK, RK, FK/TiO₂, RK/TiO₂, and bare TiO₂ photocatalysts. For the blank experiment analysis, the result shows that tetracycline hydrochloride can be hardly degraded after 60 min under UV light irradiation without catalysts, excluding the possibility of self-photolysis in this system. The bare TiO₂, FK and RK exhibit 9, 22 and 19% of tetracycline hydrochloride adsorption after 30 min dark adsorption equilibrium, respectively. Upon UV light irradiation, the tetracycline hydrochloride can be slightly degraded with bare TiO₂, while there is no degradation by FK and RK. The photodegradation activity is enhanced by supporting TiO₂ nanoparticles on the kaolinites, and FK/TiO₂ composites show the highest photodegradation activity. After irradiation for 60 min, the photodegradation rate of FK/TiO₂ composite is 98%, but only 84% for the RK/TiO₂. It is reported that photocatalytic decomposition of tetracycline hydrochloride follows the pseudo-first-order reaction kinetics. As shown in Fig. 6b, the rate constant for bare TiO₂ is very small compared to that for clays/TiO₂ composites, and the rate constant of FK/TiO₂ is higher than that of RK/TiO₂. The enhanced photocatalytic activity for FK/TiO₂ composite can be attributed to the large surface area, decreased particle size and increasing density of active sites.

The stability and recyclability of FK/TiO₂ nanocomposite were evaluated by monitoring the reactivity of FK/TiO₂ during five reaction cycles. As shown in Fig. 6c, the photocatalytic activity of FK/TiO₂ can be easily recovered, and the photodegradation activity has no obvious decrease after five successive cycles. Moreover, the postmortem study shows that there is no significant changes for the supported structure of FK/TiO₂ after five reaction cycles, which indicates FK/TiO₂ has good stability. The good stability of FK/TiO₂ catalyst could be ascribed to the intense interaction between TiO₂ and FK, which can immobilize the active sites in photocatalysis. The well stability would greatly promote their practical application to eliminate the antibiotics.

**Discussions**

Based on the above results, a possible mechanism to explain the enhancement of the photocatalytic properties of the clays/TiO₂ nanocomposites is depicted in Fig. 6d. The proposed mechanism is the synergetic effects between the kaolinite clays and supported TiO₂ nanoparticles. The TiO₂ clusters act as a light absorber, while the kaolinite clays with different morphology are the physical adsorbents of tetracycline hydrochloride molecules. In the dark,
tetracycline hydrochloride molecules could be effectively adsorbed around the clays/TiO$_2$ nanocomposites and reach adsorption-desorption equilibrium on their surface, which could facilitate the photocatalytic reactions. TiO$_2$ nanoparticles supported on the clays could be excited to yield electrons (e$^-$) and holes (h$^+$) (Eq. (1)). These photo-induced electrons-holes reacted with oxygen molecules (O$_2$), H$_2$O or hydroxyl groups on the surface of kaolinites to yield hydroxyl radicals (*OH) and superoxide radical anions (O$_2$•$^-$) (Eq. (2–11))$^{41}$. These active species with strong oxidizability directly or indirectly interacted with tetracycline hydrochloride molecules already adsorbed on FK/TiO$_2$ and RK/TiO$_2$ in aqueous solutions (Eq. (12–13))$^{37}$. The complete equations of mechanism reactions are as follows:

$$\text{TiO}_2 + h^+ \rightarrow \text{TiO}_2(h^+ + e^-) \quad (1)$$

Reaction involving valence band h$^+$

$$\text{TiO}_2(h^+) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \cdot\text{OH} + \text{H}^+ \quad (2)$$

$$\text{TiO}_2(h^+) + \text{OH}^- \rightarrow \text{TiO}_2 + \cdot\text{OH} \quad (3)$$

$$\text{TiO}_2(h^+) + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{H}_2\text{O}_2 + 2\text{H}^+ \quad (4)$$

Reaction involving conduction band e$^-$

$$\text{TiO}_2(e^-) + \text{O}_2 \rightarrow \text{TiO}_2 + \text{O}_2^{••} \quad (5)$$

$$\text{O}_2^{••} + \text{H}^+ \rightarrow \text{HO}_2^{•} \quad (6)$$

$$\text{TiO}_2(e^-) + \text{HO}_2^{•} \rightarrow \text{TiO}_2 + \text{HO}_2^- \quad (7)$$

$$\text{TiO}_2(e^-) + \text{O}_2^{••} + 2\text{H}^+ \rightarrow \text{TiO}_2 + \text{H}_2\text{O}_2 \quad (8)$$

$$\text{TiO}_2(e^-) + \text{H}_2\text{O}_2 \rightarrow \text{TiO}_2 + \cdot\text{OH} + \text{OH}^- \quad (9)$$

$$\text{O}_2^{••} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \quad (10)$$

$$2\text{HO}_2^{•} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (11)$$

$$\text{R-H(TC molecules)} + \cdot\text{OH} \rightarrow \text{R}^+ + \text{H}_2\text{O} \quad (12)$$

$$\text{R-H(TC molecules)} + h^+ \rightarrow \text{R}^{••} \rightarrow \text{Degradation products} \quad (13)$$

Above-mentioned photocatalytic mechanism for tetracycline hydrochloride photodegradation, the surface adsorption and light-induced charge transfer are two primary factors affecting the photocatalytic activity. Strong adsorptivity contributes to the concentration of antibiotics from the solvent and consequently improves the photocatalytic activity. By comparison with FK/TiO$_2$ and RK/TiO$_2$ nanocomposites, FK/TiO$_2$ exhibits much stronger surface adsorption, compared to that of RK/TiO$_2$, which can originate from the large specific surface area. Moreover, the TiO$_2$ nanoparticles exhibit much more uniform and smaller for FK/TiO$_2$, while aggregation seriously for RK/TiO$_2$; has relatively higher loading efficiency of TiO$_2$ nanoparticles than that of RK/TiO$_2$, which can result in higher light-induced charge transfer, and finally enhance the photocatalytic activity. It is clear that the efficient photodegradation performance of FK/TiO$_2$ can be attributed to the synergistic effect of better adsorption capability and more active photocatalysis TiO$_2$ species. The specific surface area and the grain size of TiO$_2$ nanoparticles are strongly depended on the morphology of the kaolinite supports. Therefore, it is important to develop advanced technologies to control the particles morphology so that to enhance the catalytic performances.

In summary, this paper proposed a facile sol-gel method to synthesize clays/TiO$_2$ nanocomposites with high catalytic activity and stability. Based on the natural different morphologies and unique layered structure, the efficient assembly and high-density dispersion of uniform TiO$_2$ nanoparticles were successfully achieved on the surface of kaolinite clays. Degradation of antibiotics using clays/TiO$_2$ catalysts was investigated to elucidate the effects of kaolinite microstructure, morphology and dimensionality for a significant suppression of the TiO$_2$ nanoparticle aggregation during the reaction. FK/TiO$_2$ exhibited remarkably enhanced photoactivities toward degradation of tetracycline hydrochloride, and the overall degradation rate was up to 98% after light irradiation for 60 min. It could be attributed to the two-dimensional morphology, stronger surface adsorptivity, higher loading efficiency, smaller grain size and intimate interfacial contact. Therefore, our insight into the comparison of different dimensionality of kaolinite clays to photocatalytic performance could be a reference function to the similar investigation, and clays/TiO$_2$ composites have great potential applications to eliminate effectively antibiotics.
Methods

Materials. The kaolinite used was raw kaolin obtained from Fujian and Guangdong, China. The chemical compositions of flake-like kaolinite (FK) and rod-like kaolinite (RK) were listed in Table 1 and showed that kaolinites with different morphologies possessed the similar chemical composition. Other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were analytical grade and used without further purification.

Preparation. TiO₂/kaolinite nanocomposite materials were prepared through a facile precipitation method. In a typical synthesis, 0.2 g kaolinite was added to a mixture constituted by 30.0 mL of ethanol and 0.6 mL of deionized water under dispersing in the ultrasonic bath for 30 min. Subsequently, 3 mL of tetrabutyl titanate (TBOT) dissolved in 5 mL of ethanol were put drop-wise into the kaolinite suspensions. After continuous stirring for 2 h at 80 °C, the precipitates were collected by centrifugation and subsequently washed with deionized water repeatedly. The resultant products were dried overnight at 80 °C. Finally, the samples were calcined under 450 °C for 3 h in air with a heating rate of 5 °C/min. For comparison, the bare TiO₂ nanoparticles were also obtained via a similar process as TiO₂/kaolinite composite without adding kaolinite.

Photocatalytic degradation experiments. The photocatalytic activity of the catalysts for tetracycline hydrochloride was investigated at ambient temperature. In a typical process, 50 mg of catalyst was dispersed in 50 mL of 30 mg/L tetracycline hydrochloride solution. The suspension was vigorously stirred in the dark for 30 min to reach the adsorption-desorption equilibrium, and then irradiated with ultraviolet light. Afterwards, 2.5 mL aliquots of the reaction mixtures were collected and the catalyst was removed from the solution using a 0.45 μm cellulose acetate membrane filter. The tetracycline hydrochloride concentrations in the filtrates were measured at 380 nm using the UV-vis spectrophotometer. The stability of catalyst was evaluated by the catalytic cycle test. At the end of each cycle, the suspension was filtered and the catalyst was tested in the next cycle.

Characterization. The chemical composition of kaolinite minerals and nanocomposites were determined using X-ray fluorescence (XRF) spectrometer. The structural characteristics of the samples were examined by X-ray diffraction (XRD, Rigaku D/MAX2550VB+) using Cu Kα radiation (λ = 0.15406 nm) at a scanning rate of 0.02 °/s with a voltage of 40 kV and 40 mA. The microstructures of the samples were observed using a scanning electron microscopy (SEM, FEI Quanta-200) with an accelerating voltage of 5 kV, a transmission electron microscopy (TEM, JEOL JEM-2100F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010) operating at 200 kV. The TiO₂ clusters were identified by X-ray photoelectron spectroscopy and their size distributions were determined by counting the sizes of TiO₂ clusters on TEM images taken from different places. The textural properties of the samples were determined by N₂ porosimetry. The N₂ adsorption-desorption isotherms were recorded at 77 K and analyzed using an ASAP 2020 Surface Area analyzer (Micromeritics Co. Ltd.). The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation, and estimates of the pore size distributions were deduced by means of Barrett-Joyner-Halenda (BJH) methods. The zeta potential of the samples at different pH levels was measured on a zeta potential analyzer (Zetasizer Nano ZS90, Malvern) at solids content of about 0.1% in distilled water. The interface characteristics and their chemical nature were studied by Fourier transform infrared (FTIR, Nicolet Nexus 670) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). Diffuse reflectance ultraviolet-visible (UV-vis) spectra were obtained on a Hitachi (Shimadzu) Model UV-2450 spectrophotometer. The Photoluminescence (PL) spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer at room temperature using a Xe lamp with a wavelength of 254 nm as the excitation source. For the photocatalytic activity evaluation, a 150 W Xe lamp equipped with an optical cutoff filter (λ < 400 nm) was used as the light source, and the concentration of photodegraded tetracycline hydrochloride solution were recorded by a UV-vis spectrophotometer (UV2450).

Data availability statement. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Acknowledgements
This work was supported by the National Natural Science Foundation of China (51704030), the China Postdoctoral Science Foundation (2017M610617, 2018T111054, 2017M623182), Shaanxi Postdoctoral Science Foundation (2017BSHED2Z10), the Special Fund for Basic Science Research of Central Colleges of Chang’an University (310831171002, 300102318402), and Young Talent fund of University Association for Science and Technology in Shaanxi, China (20180411).

Author Contributions
X.Y.L. conceived the project and wrote the final paper. X.Y.L. wrote initial drafts of the work. X.Y.L. and K.P. designed the experiments, synthesized and characterized the materials, K.P., H.X.C. and Z.J.W. analyzed the data. All authors discussed the results and commented on the manuscript.

Additional Information
Competing Interests: The authors declare no competing interests.

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