Application of pea-like yolk–shell structured Fe₃O₄@TiO₂ nanosheets for photocatalytic and photo-Fenton oxidation of bisphenol-A†

Xingxing Li, Mingcan Cui, Yonghyeon Lee, Jongbok Choi and Jeehyeong Khim‡*

Uniform pea-like yolk–shell (PLYS) structured magnetic TiO₂(PLYS-Fe₃O₄@TiO₂) nanosheets have been prepared via a combined kinetics-controlled mechanical force-driven and hydrothermal etching assisted crystallization method and characterized. The resulting PLYS-Fe₃O₄@TiO₂ nanosheets possess well defined yolk–shell structures with a large BET surface area (~187.26 m² g⁻¹) and a strong magnetic susceptibility (~17.4 emu g⁻¹). The reaction rate constant was 24.2 × 10⁻² min⁻¹ as a result of oxidative decomposition of BPA using UV/PLYS-Fe₃O₄@TiO₂/H₂O₂ system. This is 1.1 and 8.34 times faster than the BPA decomposition reaction rate constant in UV/TiO₂/H₂O₂ and UV/Fe₃O₄/H₂O₂ systems, respectively. The synthesized catalyst also exhibited excellent recycle capability and excellent acid decomposition performance.

1. Introduction

Emerging organic contaminants (EOCs) are a burgeoning and extremely diverse class of contaminants that are not routinely monitored but have the great potential to enter the environment and may cause known or suspected adverse ecological and human health effects. EOCs of major concern include endocrine disrupting chemicals, pharmaceuticals and personal care products, surfactants, and various industrial additives as well as hormones. BPA, classified as an endocrine disruptor, is a contaminant of importance because it is extensively used in the production of polycarbonates, epoxy resins, and other plastics. Due to the low concentration, high chemical stability and low biodegradability of BPA, the effectiveness of conventional treatment technologies such as adsorption, membrane filtration, and biological treatment are typically limited. As an alternative, advanced oxidation processes (AOPs) have been demonstrated as a highly efficient technology for the destruction and mineralization of organic pollutants through powerful reactive oxidation species such as hydroxyl radicals (HO·). Among various AOPs, homogeneous Fenton reaction based on ferrous ions and hydrogen peroxide is of great importance owing to the environmentally friendly characteristics. However, the narrow working pH range, difficulties to recover the dissolved metal ions and necessity for further treatment of ferric hydroxide sludge greatly hinder its wide application for practical water treatment. To this end, heterogeneous Fenton process is developed as a valid approach to overcome these kinds of drawbacks.

Recently, Nemanja et al. prepared an effective photo-Fenton catalyst of Fe/TiO₂ by deposition–precipitation method for degradation of thiacloprid. However, the catalyst separation issue seems to be a big challenge. Although Lejin et al. synthesized Fe₃O₄ magnetic particles via the co-precipitation of Fe³⁺ and Fe²⁺ method and observed the effect of different parameters, the degradation efficiency of 2,4-dichlorophenol is not high. Xiaoliang et al. demonstrated the heterogeneous Fenton-like process for the treatment of methylene blue (MB), whereas the core–shell structured Fe₃O₄@C nanoparticles only worked well in acidic environment. Sheng-Tao et al. showed the core–shell structured Fe₃O₄@SiO₂ nanoparticles as efficient Fenton-like catalyst in neutral environment for the degradation of MB but the mechanism still requires farther investigations. In addition, yolk–shell material with a distinctive core–void@shell configuration, has stimulated considerable interest because of the void space between the core and the shell which can provide as a reactor. Dan et al. reported that yolk–shell structured Fe₃O₄@TiO₂ nanoparticles as a high-performance catalyst for the combination of photo-Fenton degradation of tetracycline. However, due to Fe₃O₄ was fully covered by the TiO₂ shell, it can cause lots of disadvantages.

In this study, we design and prepare an advanced PLYS-Fe₃O₄@TiO₂ nanosheets as a heterogeneous photocatalytic photo-Fenton catalyst. Instead of TiO₂ shell, TiO₂ nanosheets are coated whereas the core–shell structured Fe₃O₄@C nanoparticles only worked well in acidic environment. The PLYS-Fe₃O₄@TiO₂ nanosheets can provide as a reactor. Dan et al. showed the core–shell structured Fe₃O₄@SiO₂ nanoparticles as efficient Fenton-like catalyst in neutral environment for the degradation of MB but the mechanism still requires farther investigations. In addition, yolk–shell material with a distinctive core–void@shell configuration, has stimulated considerable interest because of the void space between the core and the shell which can provide as a reactor. Dan et al. reported that yolk–shell structured Fe₃O₄@TiO₂ nanoparticles as a high-performance catalyst for the combination of photo-Fenton degradation of tetracycline. However, due to Fe₃O₄ was fully covered by the TiO₂ shell, it can cause lots of disadvantages.
2. Materials and methods

2.1 Reagents

Iron chloride hexahydrate (FeCl₃·6H₂O), sodium citrate tribasic dehydrate, sodium acetate (NaAc), bisphenol-A, concentrated ammonia solution (28 wt%), n-butanol, titanium(v) isopropoxide (TiPO), TiO₂ (P25, 20% rutile and 80% anatase) and tetraethyl orthosilicate (TEOS) were analytical grade and purchased from Sigma-Aldrich (USA). Sodium hydroxide (NaOH), hydrochloric acid (HCl, 36%), perchloric acid (HClO₄), potassium bi-phthalate (C₆H₄O₂K₂), ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), potassium bi-phthalate (C₆H₄O₂K₂), ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), ethylene glycol and ethanol were purchased from Samchun Pure Chemicals. All chemicals were analytical grade and used as received without further purification. Corp. deionized water was used for all experiments.

2.2 Preparation of catalysts

2.2.1 Synthesis of Fe₃O₄ nanoparticles. The superparamagnetic Fe₃O₄ nanoparticles were prepared via a solvothermal method reported previously. Briefly, FeCl₃·6H₂O (3.25 g), sodium citrate tribasic dehydrate (1.3 g), and sodium acetate (NaAc, 6.0 g) were dissolved in ethylene glycol (80 mL) with agitation. The mixture was stirred vigorously for 1 h at room temperature and then transferred into a Teflon-lined stainless-steel autoclave (100 mL). The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with deionized water and ethanol for 3 times, respectively.

2.2.2 Synthesis of Fe₃O₄@SiO₂@TiO₂ nanoparticles. The core-shell Fe₃O₄@SiO₂ nanoparticles were prepared according to a Stöber sol–gel method. For a typical synthesis, an ethanolic dispersion of the Fe₃O₄ magnetite particles obtained above (6.0 mL, 0.05 g mL⁻¹) was added to a three-neck round-bottom flask with ethanol (70 mL), deionized water (30 mL) and concentrated ammonia solution (2.0 mL, 28 wt%). The mixture was sonicated for 20 min. Then, 1.0 mL of TEOS was added dropwise in 5 min, and the reaction was allowed to proceed for 1 h under continuous mechanical stirring at room temperature. The resultant products (denoted as Fe₃O₄@SiO₂) were separated and collected with a magnet, followed by washing with deionized water and ethanol for 3 times, respectively.

The as-prepared Fe₃O₄@SiO₂ nanoparticles were further coated with a TiO₂ shell through a kinetic-controlled Stöber method. Briefly, the core–shell Fe₃O₄@SiO₂ nanoparticles (0.1 g) were dispersed in ethanol (100 mL), and mixed with concentrated ammonia solution (0.80 mL, 28 wt%) under ultrasound for 15 min. Subsequently, 0.75 mL of TiPO was added dropwise in 5 min, and the reaction was allowed to proceed for 24 h at 45 °C under continuous mechanical stirring. The resultant products (denoted as pea-like core–shell Fe₃O₄@SiO₂@TiO₂) were separated with a magnet and washed with deionized water and ethanol for 3 times, respectively.

2.2.3 Synthesis of PLYS-Fe₃O₄@TiO₂. The PLYS-Fe₃O₄@TiO₂ nanoparticles were prepared through an alkaline hydrothermal etching assisted crystallization method. The above obtained Fe₃O₄@SiO₂@TiO₂ nanoparticles (1.0 g) were mixed with NaOH solution (30 mL, 1.0 M), then transferred into a Teflon-lined stainless-steel autoclave (100 mL in capacity). The autoclave was heated at 200 °C for 24 h and then cooled to room temperature. The products were collected by a magnet and added in HCl solution (50 mL, 0.1 M) for 15 min, washed with deionized water until pH value was around 7 and subsequently dried at 60 °C thoroughly in vacuum oven.

The resultant products (denoted as PLYS-Fe₃O₄@TiO₂) were calcined 400 °C in N₂ atmosphere for 2 h, then the PLYS-Fe₃O₄@TiO₂ nanosheets were obtained.

2.3 Materials characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Prior to measurements, the samples were degassed in a vacuum at 180 °C for 6 h. The Brunauer–Emmett–Teller (BET) model was utilized to calculate the specific surface areas (S_{BET}) using adsorption data in the relative pressure range P/P₀ = 0.04–0.2. Using the Barrett–Joyner–Halenda (BJH) model, the pore size distributions were derived from the adsorption branches of the isotherms, and the total pore volumes (V) were estimated from the adsorbed amount at the relative pressure P/P₀ = 0.995. Transmission electron microscopy (TEM) was carried out on a JEOL 2011 microscope (Japan) operated at 200 kV. For TEM measurements, the sample was suspended in ethanol and supported on a holey carbon film on a Cu grid. High-resolution transmission electron microscopy (HRTEM) observations were performed on JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV equipped with a post-column Gatan imaging filter (GIF-Trium). Scanning electron microscopy (SEM) images were taken using a Zeiss ultra 55 ultrahigh resolutions thermal FEG with an in-lens electron optic operating at 3 kV. The magnetization was measured using a Vibrating Sample Magnetometer (EV9 including automatic sample rotation, Microsense, Japan) under a magnetic field of 10 kOe and a temperature of 24 °C.

2.4 Experimental procedure

All experiments were conducted in cylindrical batch reactors (Φ2.0 × 10.0 cm, total volume: 50 mL) with a shaking water bath to mix and maintain the temperature (Fig. S1†). A thermometer (Tecpel DTM-318) was used to measure the temperature. The light source (Fig. S2†) was HANSUNG G12T5 UV lamp (λ = 254 nm, 5 × 10 W) and the light intensity in the centre of the BPA solution was 800 μW cm⁻². The reaction suspension was prepared by adding appropriate amounts of catalyst and H₂O₂ into 30 mL BPA solution. The desired pH value was adjusted by HClO₄ or NaOH and measured by a pH meter (Orion 3 Star). Prior to addition of H₂O₂, the mixture was mixed in dark for 30 min to reach the adsorption/desorption equilibrium between the catalyst and pollutants. Afterwards, 1.0 mL of the suspension was removed using a 2 mL syringe at given time intervals and filtered via a membrane with a pore size of ~0.45 mm. Furthermore, 10 μL 0.5 M n-butanol was added to the sample above to terminate the reaction and the BPA concentration in each sample was analysed on a high-performance liquid chromatography.
like Fe₃O₄@SiO₂@TiO₂ particles with an average thickness of a magnetic core, resulting in a coating with silica and titania. The PLYS-Fe₃O₄@TiO₂ nanospheres possess a uniform spherical shape with an average diameter of 130 nm (Fig. 2(a)). The particles exhibit excellent dispersibility in polar solvents such as water and ethanol because of numerous peaks can be clearly distinguished compared with XRD pattern of pure Fe₃O₄ nanoparticles.

N₂ sorption isothermal (Fig. 3(b)) shows that the PLYS-Fe₃O₄@TiO₂ nanoparticles have a nanoporous structure and the BET surface area is calculated to be 187.26 m² g⁻¹ which is a little decrease compared with PLYS-Fe₃O₄@TiO₂ (208.38 m² g⁻¹). The integrated energy dispersive X-ray spectroscopy (EDS) analysis of PLYS-Fe₃O₄@TiO₂ (Fig. S8†) further confirms the presence of elements Ti, Fe and O. In addition, the Fe content is ∼13.17 wt%.

Meanwhile, the saturation magnetization value of pure Fe₃O₄ and PLYS-Fe₃O₄@TiO₂ nanoparticle (Fig. 3(c)) were measured to be 51.7 and 17.4 emu g⁻¹ respectively, which could be ascribed to the existence of TiO₂ nanosheets.

Furthermore, to observe the mechanism of the formation of PLYS-Fe₃O₄@TiO₂ double-shelled yolk–shell microspheres, a series of experiments were carried out. With the change of ammonia content (0.4, 0.5, 0.6 and 0.7 mL), the typical sandwich sphere structure was converted to a pea-like yolk–shell structure (Fig. S3†). And using different diameter of mixing paddle (4, 5 and 6 cm), the length of pea-like particles was changed (Fig. S4†) with different concentration of sodium hydroxide solution, the structure of PLYS-Fe₃O₄@TiO₂ spheres had a big change (Fig. S6†), but there was no big difference for PLYS-Fe₃O₄@TiO₂ particles. However, the PLYS-Fe₃O₄@TiO₂ double-shelled structure will be collapsed under the high concentration of sodium hydroxide (Fig. S7A†). In addition, with higher concentration of hydrochloric acid, the pea-like yolk–shell structure would be changed (Fig. S7B†).

On the basis of the above observations, we propose a combination of kinetics-controlled mechanical force-driven growth (Fig. S5†) and hydrothermal etching assisted crystallization method for the formation of the PLYS-Fe₃O₄@TiO₂ double-shelled yolk–shell nanoparticles. Because of the high initial ammonia content, the heterogeneous and homogenous nucleation processes simultaneously occur and the pea-like core–shell Fe₃O₄@SiO₂@TiO₂ nanoparticles can be formed under the mechanical force. Subsequently, the amorphous silica layer is etched by NaOH solution first, then the alkali solution can permeate and etch porous TiO₂ shell to form two layers titinate nanosheets.

### 3.2 Catalytic activity of PLYS-Fe₃O₄@TiO₂

#### 3.2.1 Degradation of BPA under different systems.

As shown in Fig. 4, BPA was used as a model pollutant to investigate the catalytic activity under different conditions within 2 h. According to the results, 0%, 17.3% and 6.5% BPA can be removed by only UV, H₂O₂ and catalyst in the dark.
independently. After being irradiated, the concentration of BPA decreases to 65.9%, 54.5% and 5.7% in UV/PLYS-Fe3O4@TiO2/H2O2, UV/TiO2(P25)/H2O2, UV/H2O2/Fe3O4, system, respectively.

Furthermore, the reaction kinetic constants were evaluated through fitting the experimental data with Langmuir–Hinshelwood model to better compare the catalytic performance. And the degradation kinetic curves can be assumed as pseudo first-order kinetic eqn (1).

\[-\ln(C/C_0) = kt + b\]  

where \(C_0\) is the initial concentration, \(C\) is the concentration at time \(t\), \(k\) is the apparent rate constant, respectively.

Fig. 4 shows the BPA decomposition reaction rate constants in different systems related to this study. Table S1† Comparing reaction rate constants in different systems and conditions.

The kinetic constant value of UV/H2O2/PLYS-Fe3O4@TiO2 is 24.2 × 10⁻³ min⁻¹ higher than the summation of UV/PLYS-Fe3O4@TiO2 (3.4 × 10⁻³ min⁻¹), UV/TiO2/H2O2 (11.5 × 10⁻³ min⁻¹), UV/Fe3O4/H2O2 (2.9 × 10⁻³ min⁻¹), UV/H2O2 (3.0 × 10⁻³ min⁻¹) and H2O2/PLYS-Fe3O4@TiO2 (2.7 × 10⁻³ min⁻¹).

The results indicate that the relatively poor adsorption efficiency of BPA on the PLYS-Fe3O4@TiO2 catalysts and the BPA oxidation capacity of H2O2 directly is weaker than hydroxyl radical. It also suggests that the synergetic effect between photocatalytic process and photo-Fenton process, which not only inhibits the recombination between electrons and holes, but also accelerates the reaction speed of Fe³⁺ to Fe²⁺ to increase the kinetic constant. This is similar to the value given in the ref. 22 and 23.
3.2.2 Effect of H$_2$O$_2$ dose. Hydrogen peroxide plays the important role of BPA degradation in heterogeneous photo-Fenton reaction. The effect of different initial H$_2$O$_2$ dose on the degradation of BPA in the heterogeneous photocatalytic photo-Fenton process was investigated (Fig. 5). When the H$_2$O$_2$ dose was increased from 6.3 to 18.9 mM, the kinetic constant of BPA degradation increased from $1.7 \times 10^{-3}$ to $19.0 \times 10^{-3}$ min$^{-1}$ correspondingly. However, the further increase of H$_2$O$_2$ dose to 31.5 mM led to a decrease of kinetic constant to $9.6 \times 10^{-3}$ min$^{-1}$. Theoretically, 72 mol of H$_2$O$_2$ are needed to completely degrade 1 mol of the BPA (eqn (2)-4)). From the results, it can be seen that the maximum degradation occurred with H$_2$O$_2$ to BPA molar ratio which is 3 times as large as stoichiometric ratio.

$$C_{15}H_{16}O_2 + 72HO^{-} \rightarrow 15CO_2 + 44H_2O \quad (2)$$

The enhancement of degradation rate is because of the increase in HO$^\cdot$. Moreover, further addition of H$_2$O$_2$ dose did not improve the degradation efficiency, which may be explained by the scavenging effect of HO$^\cdot$ at a higher H$_2$O$_2$ dose eqn (5).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\cdot + OH^- \quad (3)$$

$$C_{15}H_{16}O_2 + 72H_2O_2 \rightarrow 15CO_2 + 44H_2O \quad (4)$$

$$H_2O_2 + HO^\cdot \rightarrow H_2O + HO_2^- \quad (5)$$

3.2.3 Effect of catalyst dose. The BPA concentration change with catalyst dose from 0.5 to 5.0 g L$^{-1}$ and the pseudo first order reaction rate constants are shown in Fig. 6. The maximum kinetic constant ($24.2 \times 10^{-3}$ min$^{-1}$) was obtained with 1.5 g
The increase of the degradation rate might be attributed to a number of active sites on the surface of both Fe₃O₄ and TiO₂, which cannot only be occupied by H₂O₂, but also enhance the light utilization to generate more hydroxyl radicals. The decrease of kinetic constant after 1.5 g L⁻¹ might be due to three reasons, higher turbidity which can inhibit the further penetration of light into the reactor, the consuming of HO⁻ by excess Fe²⁺ and other radicals, such as HO₂⁻ eqn (6) and (7) and catalyst agglomeration.

\[
\text{Fe}^{2+} + \text{HO}^- \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (6)
\]
\[
\text{HO}^- + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (7)
\]

3.2.4 Effect of pH. It is well known that the pH value is an important parameter in the photocatalytic process. The effect of initial pH on BPA degradation in a range of 3 to 11 is shown in Fig. 7, which shows that the maximum kinetic constant at pH 3 is \(3.34 \times 10^{-3}\) min⁻¹. As the pH was increased from pH 5 to pH 11, the reaction rate constants were decreased to \(2.54 \times 10^{-3}\), \(1.45 \times 10^{-3}\) and \(9.9 \times 10^{-3}\) min⁻¹, respectively. This may be attributed to that pH affects TiO₂ through the charge (eqn (8) and (9)) on the particle surface and aggregation size which can cause the change of specific surface area and light absorption. On the other side, the increased oxidation efficiency at lower pH values can be due to the higher oxidation potential of hydroxyl radicals. Based on eqn (10) and (11) (Nernst equation), the redox potential of HO⁻/H₂O at pH 3, 5, 7, 9 and pH 11 are 2.623 V, 2.505 V, 2.387 V, 2.269 and 2.151 V, respectively. Meanwhile, H₂O₂ is more stable in acidic condition than alkaline condition (eqn (12)).

\[
\text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}^{2+} \quad (8)
\]
\[
\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (9)
\]
\[
E^\circ_{\text{OH}^-/\text{H}_2\text{O}} = 2.8 \text{ V} \quad (10)
\]
\[
E_{\text{OH}^-} = E^\circ_{\text{OH}^-/\text{H}_2\text{O}} - 0.059 \text{ pH} \quad (11)
\]

Fig. 9 Effect of different radical scavengers in photocatalytic photo-Fenton degradation of BPA at fixed [PLYS-Fe₃O₄@TiO₂] = 1.5 g L⁻¹, [H₂O₂] = 18.9 mM, [BPA] = 0.088 mM, pH = 7, light intensity = 800 μW cm⁻², T = 25 °C.

Fig. 10 Schematic illustration of the possible mechanism proposed for BPA degradation by PLYS-Fe₃O₄@TiO₂.

Fig. 11 (A) shows the curve of response time in photocatalytic photo-Fenton decomposition, (B) shows the XRD results of the catalyst before and after the reaction. Conditions: [PLYS-Fe₃O₄@TiO₂] = 1.5 g L⁻¹, [H₂O₂] = 18.9 mM, [BPA] = 0.088 mM, light intensity = 800 μW cm⁻², T = 25 °C, pH = 7.
In addition, it should be noticed that catalytic activity of PLYS-Fe₃O₄@TiO₂ was slightly affected by pH values from 5 to 7. This phenomenon is important because one of the major drawbacks of Fenton reaction is the narrow range of pH.

3.2.5 Effect of initial concentration of BPA. The effect of the initial concentration of BPA on the photocatalytic photo-Fenton degradation was evaluated from 0.044 to 0.132 mM as shown in Fig. 8. The kinetic constant was increased from $4.5 \times 10^{-3}$ to $24.2 \times 10^{-3} \text{ min}^{-1}$ with the increase of the initial concentration from 0.044 to 0.088 mM. When the initial concentration increased to 0.132 mM, the kinetic constant decreased to $2.5 \times 10^{-3} \text{ min}^{-1}$.

This phenomenon may be related to the fact that the excessive dose of H₂O₂ and catalyst for lower initial concentration of BPA which leading to the scavenging effect of HO•. Furthermore, with the increasing of BPA concentration, more BPA molecules could be adsorbed on the surface of catalyst which can form the blocked active sites to decrease the generation of HO•.

3.3 Mechanism investigation
According to the results of other researchers, n-butanol can react with HO• which generated from both surface and bulk solution. The actual reactive species in the process was discriminated by determining the influence of n-butanol as radical scavenger on the degradation of BPA. As shown in Fig. 9, 1 M n-butanol in solution can scavenge most of the HO• produced in the system and the kinetic constant decreased to $3.7 \times 10^{-3} \text{ min}^{-1}$.

Based on all the information obtained above and previous studies by other researchers, an assumed mechanism of BPA degradation by PLYS-Fe₃O₄@TiO₂/H₂O₂ system is illustrated in Fig. 10. The BPA is mainly removed by HO• which was generated from photo-Fenton and photocatalysis process as shown in eqn (3), (14), (40–43) and (16). Benefiting from the yolk–shell and nanosheet structure, BPA molecules can easily permeate into the surface of Fe₃O₄ and degrade by hydroxyl radicals. Most importantly, the photo-induced electrons which generated from TiO₂ can not only promote the recovery of Fe³⁺ from Fe²⁺, but also inhibit the recombination of electrons and holes.

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HO}^2- \quad (12)
\]

\[
\text{Fe(OH)}^2+ + h\nu \rightarrow \text{HO}^- + \text{Fe}^{2+} \quad (13)
\]

\[
\text{H}_2\text{O} + h\nu \rightarrow 2\text{HO}^- \quad (14)
\]

\[
\text{TiO}_2 + h\nu \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+ \quad (15)
\]

\[
\text{H}_2\text{O} + h_{\text{VB}}^+ \rightarrow \text{HO}^- + \text{H}^+ \quad (16)
\]

3.4 Catalytic stability test
Recyclability is a crucial factor which can affect the catalyst application in economic perspective. In order to observe the stability, the catalyst was collected by magnetic separation after treatment, washed by deionized water and ethanol respectively, dried at 353 K and was evaluated by BPA degradation under the standard reaction conditions. As shown in Fig. 11(A), the degradation kinetic constant of reused catalyst is $24.2 \times 10^{-3}$, $21.1 \times 10^{-3}$ and $20.3 \times 10^{-3} \text{ min}^{-1}$ for the first, second and third run, respectively. In addition, the Fe leaching (Fig. S9†) was less than 0.21 mg L⁻¹ in the whole process. In addition, XRD analysis before and after the reaction of PLYS-Fe₃O₄@TiO₂ catalyst in Fig. 11(B) showed that the characteristics of the catalyst did not change. The results demonstrated that PLYS-Fe₃O₄@TiO₂ may be used as a promising catalyst for BPA degradation because of good recyclability and stability.

4. Conclusion
In summary, pea-like yolk–shell structured PLYS-Fe₃O₄@TiO₂ has been successfully synthesized via a combination of kinetics-controlled mechanical force-driven growth and hydrothermal etching assisted crystallization method. And the catalyst was first tested as a heterogeneous photocatalytic photo-Fenton catalyst for BPA degradation, catalyst and H₂O₂ dose, initial pH and concentration of BPA are important variables on the degradation process.

The rate constant of BPA degradation in PLYS-Fe₃O₄@TiO₂/H₂O₂/UV system was $24.2 \times 10^{-3} \text{ min}^{-1}$ (pH = 7). The BPA decomposition rate constant decreased with increasing pH. As a result of studying the rate of decomposition reaction according to the initial concentration of BPA, we found that there is an optimal BPA decomposition rate constant value at a certain concentration. Through the XRD analysis after the cycling experiment and before and after the reaction of the catalyst, the activity of the catalyst was still very stable, indicating that the catalyst had excellent stability and reusability. This study may provide useful information to further develop some effective heterogeneous photocatalytic photo-Fenton catalysts for degradation of organic pollutants.

Conflicts of interest
There are no conflicts to declare.

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Reference
1 W. T. Tsai, J. Environ. Sci. Health, Part C: Environ. Carcinog. Ecotoxicol. Rev., 2006, 24, 225–255.
