Fabrication of Z-scheme Ag$_3$PO$_4$/TiO$_2$ Heterostructures for Enhancing Visible Photocatalytic Activity

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Abstract

In this paper, a synthetical study of the composite Ag$_3$PO$_4$/TiO$_2$ photocatalyst, synthesized by simple two-step method, is carried out. Supplementary characterization tools such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and UV-vis diffuse reflectance spectroscopy were adopted in this research. The outcomes showed that highly crystalline and good morphology can be observed. In the experiment of photocatalytic performance, TiO$_2$/Ag$_3$PO$_4$ shows the best photocatalytic activity, and the photocatalytic degradation rate reached almost 100% after illuminating for 25 min. The reaction rate constant of TiO$_2$/Ag$_3$PO$_4$ is the largest, which is 0.02286 min$^{-1}$, twice that of Ag$_3$PO$_4$ and 6.6 times that of the minimum value of TiO$_2$400. The degradation effect of TiO$_2$/Ag$_3$PO$_4$ shows good stability after recycling the photocatalyst four times. Trapping experiments for the active catalytic species reveals that the main factors are holes (h$^+$) and superoxide anions (O·$^-$ 2), while hydroxyl radical (·OH) plays partially degradation. On this basis, a Z-scheme reaction mechanism of Ag$_3$PO$_4$/TiO$_2$ heterogeneous structure is put forward, and its degradation mechanism is expounded.

Keywords: Composite, Heterostructures, Superoxide anion, Photocatalytic degradation

Background

Semiconductor photocatalysts have attracted increasing interest due to extensive use in organic pollutant degradation and solar cells [1–6]. As the representative of semiconductor-based photocatalysts, TiO$_2$ has been extensively investigated because of its excellent physical-chemical properties [7, 8]. However, the pure TiO$_2$ photocatalyst has certain disadvantages in practical applications such as its wide band gap (3.2 eV for anatase and 3.0 eV for rutile), which leads to poor visible response.

A silver-based compound such as Ag$_2$O, AgX (X = Cl, Br, I), Ag$_3$PO$_4$, Ag$_2$CrO$_4$, have been recently used for photocatalytic applications [9–12]. Among others, silver orthophosphate (Ag$_3$PO$_4$) has already attracted attention from many researchers because Ag$_3$PO$_4$ has a band gap of 2.45 eV and strong absorption at less than 520 nm. The quantum yield of Ag$_3$PO$_4$ is over 90%. It is a good visible-light photocatalyst. However, due to the formation of Ag$^0$ on the surface of the catalyst (4Ag$_3$PO$_4$ + 6H$_2$O + 12h$^+$ + 12e$^-$ → 12Ag$^0$ + 4H$_3$PO$_4$ + 3O$_2$) during the photocatalytic reaction, the reuse of Ag$_3$PO$_4$ is a major problem. Therefore, it is a common practice to reduce photocatalytic corrosion of Ag$_3$PO$_4$ and ensure good catalytic activity of Ag$_3$PO$_4$. Based on literature precedence, it is known that compounding can effectively improve the photocatalytic performance of both semiconductor materials. After compounding, the separation effect of photogenerated electrons and holes is strengthened, contributing to enhance the photocatalytic activity of composite materials. Numerous researchers have investigated heterojunctions such as Bi$_2$O$_3$/Bi$_2$WO$_6$, TiO$_2$/Bi$_2$WO$_6$, ZnO/CdSe, and Ag$_3$PO$_4$/TiO$_2$ [2, 13–15]. Compared with single-phase photocatalysts, heterojunction photocatalysts can expand the light response range by coupling matched electronic structure materials. And because of the synergistic effect between components, charge can be transferred through many ways to further improve heterojunction photocatalytic activity.
Based on the above analysis, Ag_3PO_4-based semiconductor composites with synergistic enhancement effect were designed to improve carrier recombination defects and Ag_3PO_4-based semiconductor composites catalytic performance. In this paper, nano-sized TiO_2 was prepared by solvothermal method, and then the nanoparticles of TiO_2 were deposited on the surface of Ag_3PO_4 at room temperature to obtain TiO_2/Ag_3PO_4 composites. The photocatalytic activity of TiO_2/Ag_3PO_4 composite was tested using RhB dye (rhodamine B).

**Methods**

**Hydrothermal Preparation of Nano-sized TiO_2**

0.4 g P123 was added to a mixed solution containing 7.6 mL absolute ethanol and 0.5 mL deionized water and stirred until P123 was completely dissolved. The clarified solution was labeled as A solution. Then a mixed solution containing 2.5 mL butyl titanate (TBOT) and 1.4 mL concentrated hydrochloric acid (12 mol/L) was prepared and labeled as B solution. The solution B was added to solution A by drop. After stirring for 30 min, 32 mL ethylene glycol (EG) was added to the solution and stirred for 30 min. Then, the solution was placed in oven, at 140 °C, high temperature, and high pressure for 24 h. Natural cooling, centrifugal washing, separation, collection of sediments, and drying at 80 °C oven for 8 h. The white precipitation was calcined in muffle furnace at different temperatures (300 °C, 400 °C, 500 °C) and marked as standby of TiO_2300, TiO_2400, and TiO_2500, respectively.

**Preparation of TiO_2/Ag_3PO_4 Photocatalyst**

The 0.1 g TiO_2 powder was added to the 30-mL silver nitrate solution containing 0.612 g AgNO_3 and then treated by ultrasound for 30 min to make TiO_2 dispersed uniformly. We added 30-mL solution containing 0.43 g Na_2HPO_4·12H_2O and stirred for 120 min at ambient temperature. By centrifugation, cleaning with deionized water and anhydrous ethanol, the precipitates were separated, collected, and dried at 60 °C. The products were named as TiO_2300/Ag_3PO_4, TiO_2400/Ag_3PO_4, and TiO_2500/Ag_3PO_4, respectively. Ag_3PO_4 was prepared without adding TiO_2 under the same conditions as the above process.

**Characterization**

The X-ray diffraction (XRD) patterns of the resulted samples were performed on a D/MaxRB X-ray diffractometer (Japan), which has a 35 kV Cu-Kα with a scanning rate of 0.02° s^−1, ranging from 10 to 80°. Scanning electron microscopy (SEM), JEOL, JSM-6510, and JSM-2100 transmission electron microscopy (TEM) assembly with energy dispersive X-ray spectroscopy (EDX) were used to study its morphology at 10-kV acceleration voltage. X-ray photoelectron spectroscopy (XPS) information were collected by using an ESCALAB 250 electron spectrometer under 300-W Cu Kα radiation. The basic pressure was about 3 × 10^−9 mbar. Combine to refer to the C1s line at amorphous carbon 284.6 eV.

**Photocatalytic Activity Measure**

The photocatalytic performance of TiO_2/Ag_3PO_4 catalysts was tested by using the photodegradation of RhB in aqueous solution as the research object. Fifty milligrams of the photocatalyst was mixed with 50 mL of RhB aqueous solution (10 mg L^−1) and stirred in darkness for a certain time before illumination to ensure adsorption balance. In the reaction process, cooling water is used to keep the system temperature constant at room temperature. A 1000-W Xenon lamp provides illumination to simulate visible light. LAMBDA35 UV/Vis spectrophotometer was used to characterize the concentration (C) change of RhB solution at λ = 553 nm. The decolorization rate is indicated as a function of time vs C_t/C_0. Where C_0 is the concentration before illumination, and C_t is the concentration after illumination. Used catalysts were recollected to detect the cycle stability of the catalysts. The experiment was repeated four times.

**Results and Discussion**

XRD analysis is used to determine the phase structure and crystalline type of catalyst. The XRD spectra of the prepared catalysts were shown in Fig. 1, including TiO_2400, Ag_3PO_4, TiO_2/Ag_3PO_4, TiO_2300/Ag_3PO_4, TiO_2400/Ag_3PO_4, and TiO_2500/Ag_3PO_4. It can be obtained from the figure that the crystal structure of TiO_2400 is anatase (JCPDS No. 71-1166). In the XRD spectra of Ag_3PO_4, the diffraction peaks located at 20.9°,
29.7°, 33.3°, 36.6°, 47.9°, 52.7°, 55.1°, 57.4°, 61.7°, and 72.0° belong to the characteristic peaks of (110), (200), (210), (211), (310), (222), (320), (321), (400), and (421) planes of Ag₃PO₄ (JCPDS No. 70-0702), respectively. The synthesized composite photocatalysts showed characteristic peaks consistent with TiO₂ and Ag₃PO₄, and the characteristic peaks of TiO₂ were 25.3° at the composite TiO₂, TiO₂300/Ag₃PO₄, TiO₂400/Ag₃PO₄, TiO₂500/Ag₃PO₄, which was consistent with the calcination temperature of TiO₂ rises, the crystallinity of TiO₂ becomes higher.

Figure 2 shows the SEM, TEM, and EDX diagrams of the catalysts of TiO₂400, Ag₃PO₄, and TiO₂400/Ag₃PO₄. Figure 2a is the spherical nanostructure TiO₂400 prepared by solvothermal method with a diameter ranging from 100 to 300 nm. Figure 2b is the Ag₃PO₄ crystal with a regular hexahedral structure. Its particle size ranges from 0.1 to 1.5 μm and has a fairly smooth surface. Figure 2c is the SEM image of the composite TiO₂400/Ag₃PO₄. It can be seen that the nanoparticles of TiO₂400 are deposited on the surface of Ag₃PO₄. The morphology of TiO₂400/Ag₃PO₄ was further explored with TEM and the TEM diagram of TiO₂400/Ag₃PO₄ is displayed in Fig. 2d. It can be observed that 200-nm nano-sized TiO₂ particles adhere to the surface of Ag₃PO₄. Figure 2e is the HRTEM of TiO₂400/Ag₃PO₄. It can be found that TiO₂ particles are closely bound to Ag₃PO₄, and the lattice spacing of TiO₂400 and Ag₃PO₄ are 0.3516 and 0.245 nm, respectively, corresponding to (101) and (211) surfaces of TiO₂ and Ag₃PO₄. Figure 2f is the EDX diagram of TiO₂400/Ag₃PO₄. It can be seen that the sample consists of four elements: Ti, O, Ag, and P. The obvious diffraction peak of copper element is
produced by the EDX excitation source, Cu Ka. EDX confirmed the corresponding chemical elements of TiO$_2$/Ag$_3$PO$_4$. In conclusion, it can be clearly judged that TiO$_2$ is loaded on the surface of Ag$_3$PO$_4$ crystals in granular form and has a good hexahedron morphology.

The product X-ray photoelectron spectroscopy (XPS) is investigated in Fig. 3. Figure 3a is the survey XPS spectrum of the product. Ti, O, Ag, P, and C five elements can be observed in the graph, of which C is the base, implying that composite coexisted with TiO$_2$ and Ag$_3$PO$_4$. Figure 3b is the high-resolution spectrum of Ag 3d. The two main peaks centered at binding energy 366.26 eV and 372.29 eV, assigning to Ag 3d5/2 and Ag 3d3/2, respectively. It shows that Ag is mainly Ag$^+$ in the photocatalyst of TiO$_2$/Ag$_3$PO$_4$ [16]. Figure 3c shows the XPS peak of P 2p, which corresponds to P$^{5+}$ in the PO$_4^{3-}$ structure at 131.62 eV. Two peaks located at 457.43 eV and 464.58 eV can be attributed to Ti 2p3/2 and Ti 2p1/2 in the XPS spectrum of Ti 2p orbital (Fig. 3d). Figure 3e is the XPS of O 1s. The whole peak can be divided into three characteristic peaks, 528.9 eV, 530.2 eV, and 532.1 eV. The peaks at 528.9 eV and 530.2 eV are ascribed to oxygen in Ag$_3$PO$_4$ and TiO$_2$ lattices, respectively. The peaks at 532.1 eV indicate hydroxyls or the oxygen adsorbed on the surface of TiO$_2$/Ag$_3$PO$_4$. The results of XPS analysis further prove that Ag$_3$PO$_4$ and TiO$_2$ have been compounded.

The UV-Vis diffuse reflectance absorption spectra of the catalysts of TiO$_2$/Ag$_3$PO$_4$ are...
exhibited in Fig. 4a. It can be seen from the figure that the optical absorption cutoff wavelengths of TiO$_2$400 and Ag$_3$PO$_4$ are 400 and 500 nm, respectively. When Ag$_3$PO$_4$ is loaded on TiO$_2$400, the light absorption range of the composite obviously broadens to 500–700 nm, indicating that there is interaction between Ag$_3$PO$_4$ and TiO$_2$400 in the composite system of TiO$_2$400/Ag$_3$PO$_4$, and the mechanism needs further study. Bandwidth of Ag$_3$PO$_4$, TiO$_2$400, and TiO$_2$400/Ag$_3$PO$_4$ catalysts is computed with the Kubelka-Munk formula [17]:

$$A_hv = c(hv - E_g)^n$$

where $A$, $h_v$, $c$, and $E_g$ are the absorption coefficient, incident photon energy, absorption constant, and band gap energy, respectively. The value of $n$ for direct semiconductor is 1/2, and that for indirect semiconductor is 2. Anatase TiO$_2$ and Ag$_3$PO$_4$ are indirect semiconductors, so $n$ takes 2.

The plots depicting $(\alpha h_v)^{1/2}$ versus incident photon energy ($h_v$) from Fig. 4b indicates the band gap energy diagrams for TiO$_2$400, Ag$_3$PO$_4$, TiO$_2$400/Ag$_3$PO$_4$, catalysts are 2.45 eV, 3.1 eV, and 2.75 eV, respectively. This further proves that TiO$_2$400/Ag$_3$PO$_4$ is a good visible-light photocatalyst with suitable band gap width and visible light capture ability.

Photocatalytic degradation of RhB by TiO$_2$400, Ag$_3$PO$_4$, TiO$_2$300/Ag$_3$PO$_4$, TiO$_2$400/Ag$_3$PO$_4$, and TiO$_2$500/Ag$_3$PO$_4$ was investigated in Fig. 5a. The results showed that pure TiO$_2$400 had the worst photocatalytic effect, and the photocatalytic degradation rate was only 30% within 25 min. The photocatalytic degradation efficiency of pure Ag$_3$PO$_4$ was 69% after 25 min of irradiation. The photocatalytic degradation rate of TiO$_2$300/Ag$_3$PO$_4$ reached 40% after 25 min. The photocatalytic degradation rate of TiO$_2$500/Ag$_3$PO$_4$ was 80% after 25 min of irradiation. The best photocatalytic activity was TiO$_2$400/Ag$_3$PO$_4$, and 100% of RhB was decomposed after 25 min of illumination.

Figure 5b studied the kinetics model of photocatalytic degradation of RhB. The reaction rate constant ($k$) values of each sample were shown in Table 1. The reaction rate constants of TiO$_2$400, Ag$_3$PO$_4$, TiO$_2$300/Ag$_3$PO$_4$, TiO$_2$400/Ag$_3$PO$_4$, and TiO$_2$500/Ag$_3$PO$_4$ were 0.00345 min$^{-1}$, 0.01148 min$^{-1}$, 0.00525 min$^{-1}$, 0.02286 min$^{-1}$, and 0.01513 min$^{-1}$, respectively. The sample TiO$_2$400/Ag$_3$PO$_4$ has the largest reaction rate constant, which is 0.02286 min$^{-1}$, twice that of Ag$_3$PO$_4$ and 6.6 times that of the minimum value of TiO$_2$400. This indicates that the combination of Ag$_3$PO$_4$ and TiO$_2$ can greatly contribute to the improvement of Ag$_3$PO$_4$ photocatalytic activity.

Figure 5c is the stability test result of four times of degradation of RhB solution by recycling of TiO$_2$400/Ag$_3$PO$_4$. The degradation activity of TiO$_2$400/Ag$_3$PO$_4$ shows good stability in four times of recycling, and in the fourth cycle experiment, the degradation effect of TiO$_2$400/Ag$_3$PO$_4$ was slightly higher than that of the third cycle. This may be due to the formation of composite material between Ag$_3$PO$_4$ and TiO$_2$ to accelerate photogenerated electron-hole pair transfer and in situ formation of a small amount of Ag in Ag$_3$PO$_4$ during photocatalysis to inhibit further photo-corrosion.

The results of TiO$_2$/Ag$_3$PO$_4$ capture factors are shown in Fig. 5d. After the addition of trapping agent IPA, the degradation activity decreased partially. When BQ and TEOA were added, the degradation degree of RhB decreased significantly, even close to 0. Therefore, we can infer that the main factors are holes ($h^+$) and superoxide anions ($O^-2$), while hydroxyl radical ($\cdot$OH) plays partially degradation.
A possible Z-scheme photocatalytic degradation mechanism was proposed in Scheme 1 to expatiate the photocatalytic degradation of RhB by TiO$_2$/Ag$_3$PO$_4$ based on free radical capture and photodegradation experiments. The band gap of Ag$_3$PO$_4$ is 2.45 eV, and its $E_{CB}$ and $E_{VB}$ potential are ca.0.45 eV and 2.9 eV (vs. NHE) [18], respectively. As shown in Scheme 1, under visible light irradiation, Ag$_3$PO$_4$ is stimulated by photons with energy greater than its band gap to produce photogenerated electron-hole pairs. The holes left in the valence band of Ag$_3$PO$_4$ migrated to the valence band of TiO$_2$ and then directly participated in the RhB oxidation and decomposition process, which adsorbed on the surface of TiO$_2$. At the same time, during the migration of photogenerated holes, the H$_2$O and OH$^-$ adsorbed on the composite surface can also be oxidized to form -OH, and the highly oxidizing -OH can further oxidize and degrade pollutants. This is mainly due to the energy of holes in the valence band of Ag$_3$PO$_4$ which is 2.9 eV, higher than the reaction potential energy of OH$^-$/OH (E(OH$^-$/OH) = 1.99 eV (vs. NHE)). However, the conduction potential of Ag$_3$PO$_4$ is 0.45 eV, the energy of photogenerated electrons is 0.45 eV, and the activation energy of single electron oxygen is $E$(O$_2$/O$^\cdot_2$) = 0.13 eV (vs. NHE). The photogenerated electrons on Ag$_3$PO$_4$ conduction band cannot be captured by dissolved oxygen. With the accumulation of photogenerated electrons on Ag$_3$PO$_4$ conduction band, a small amount of Ag nanoparticles has been formed due to the photocatalytic corrosion of Ag$_3$PO$_4$ photocatalyst. The formed Ag nanoparticles can also be stimulated by light energy to form photogenerated electron-hole pairs.

**Table 1** Photo degradation rate constants and linear regression coefficients of different catalysts from equation $-\ln(C/C_0) = kt.$

| Catalyst         | $K$ (min$^{-1}$) | Regression equation         | $R^2$  |
|------------------|------------------|-----------------------------|--------|
| TiO$_2$/Ag$_3$PO$_4$ | 0.02286         | $-\ln(C/C_0) = 0.02286x + 0.21496$ | 0.68755 |
| TiO$_2$/Ag$_3$PO$_4$ | 0.01513         | $-\ln(C/C_0) = 0.01513x + 0.15984$ | 0.753  |
| Ag$_3$PO$_4$     | 0.01148          | $-\ln(C/C_0) = 0.01148x + 0.1079$ | 0.71128 |
| TiO$_2$/Ag$_3$PO$_4$ | 0.00525         | $-\ln(C/C_0) = 0.00525x + 0.06354$ | 0.82635 |
| TiO$_2$          | 0.00345          | $-\ln(C/C_0) = 0.00345x + 0.0383$ | 0.78461 |

Fig. 5 a Effects of different catalysts on photocatalytic degradation of RhB under visible light. b First order kinetic fitting plots of photocatalytic degradation of RhB with different catalysts. c Cycling runs of TiO$_2$/Ag$_3$PO$_4$. d Trapping experiments of active species.

Liu et al. Nanoscale Research Letters (2019) 14:203
Then the electrons migrated to the conduction band of TiO$_2$, while the holes left on the Ag nanoparticles can be compounded with the photogenerated electrons generated on the conduction band of Ag$_3$PO$_4$, thus preventing the further corrosion of Ag$_3$PO$_4$ photocatalyst. Due to the forbidden band of TiO$_2$ is 3.1 eV, it cannot be excited under visible light and the $E_{CB}$ and $E_{VB}$ are ca. −0.24 eV and 2.86 eV (vs. NHE), respectively. Electrons injected into TiO$_2$ conduction band can degrade pollutants through trapping the oxygen adsorbed onto the TiO$_2$ surface. This is mainly due to the $E_{CB} = −0.24$ eV (vs. NHE) which is more negative than $E(O_2/O^- 2) = 0.13$ eV (vs. NHE). The results are in accordance with the trapping experiments. The main factors are holes (h$^+$) and superoxide anions (O$^-$ 2), while hydroxyl radical (·OH) plays partially degradation.

Basing on the above discussion, the degradation reaction of TiO$_2$/Ag$_3$PO$_4$ is expressed by the chemical equation as follows:

**Generation of photoelectron hole pairs:**
- Ag$_3$PO$_4$ + hv $\rightarrow$ Ag$_3$PO$_4$(e$^-$) + Ag$_3$PO$_4$(h$^+$)
- Ag$^+$ + Ag$_3$PO$_4$(e$^-$) $\rightarrow$ Ag + Ag$_3$PO$_4$
- Ag + hv $\rightarrow$ Ag(e$^-$) + Ag(h$^+$)

**Migration and transformation of photogenerated hole electron pairs:**
- Ag$_3$PO$_4$(h$^+$) + TiO$_2$ $\rightarrow$ TiO$_2$(h$^+$) + Ag$_3$PO$_4$
- Ag$_3$PO$_4$(e$^-$) + Ag(h$^+$) $\rightarrow$ Ag + Ag$_3$PO$_4$
- Ag(e$^-$) + TiO$_2$ $\rightarrow$ TiO$_2$(e$^-$) + Ag
- TiO$_2$(e$^-$) + O$_2$ $\rightarrow$ O$_2$ + TiO$_2$
- Ag$_3$PO$_4$(h$^+$) + 0H$^-$ $\rightarrow$ OH$^-$ + Ag$_3$PO$_4$

**Degradation of pollutants:**
- TiO$_2$(h$^+$) + RhB $\rightarrow$ Degradation product + CO$_2$ + H$_2$O
- O$_2^-$ + RhB $\rightarrow$ Degradation product + CO$_2$ + H$_2$O + Cl$^-$

**Conclusions**
In summary, a comprehensive investigation of the composite Ag$_3$PO$_4$/TiO$_2$ photocatalyst, prepared by a simple two-step method is presented. Complementary characterization tools such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and UV-vis diffuse reflectance spectroscopy (DRS) were utilized in this study. The results showed that the composite Ag$_3$PO$_4$/TiO$_2$ photocatalyst is highly crystalline and has good morphology. For Ag$_3$PO$_4$/TiO$_2$ degradation of RhB, TiO$_2$400/Ag$_3$PO$_4$ shows the highest photocatalytic activity. After 25 min of reaction, the photocatalytic degradation rate reached
almost 100%. The reaction rate constant of TiO$_2$/Ag$_3$PO$_4$ is 0.02286 min$^{-1}$, which is twice that of Ag$_3$PO$_4$ and 6.6 times that of the minimum value of TiO$_2$. The TiO$_2$/Ag$_3$PO$_4$ also exhibits good stability after cycling four times. The main active catalytic species are holes (h$^+$) and superoxide anions (O$_2^-$·), while hydroxyl radical (-OH) plays partially degradation from trapping experiments. In addition, a Z-scheme reaction mechanism of Ag$_3$PO$_4$/TiO$_2$ heterogeneous structure is proposed to explain the RhB degradation mechanism. The accumulation of photogenerated electrons on Ag$_3$PO$_4$ conductive band causes photobleaching of Ag$_3$PO$_4$ photocatalyst to form a small amount of Ag nanoparticles, consequently, accelerating photogenerated electron transfer in the Ag$_3$PO$_4$ conduction band, thus preventing further Ag$_3$PO$_4$ photocatalyst corrosion.

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This work presented here was performed in collaboration of all the authors. All authors read and approved the final manuscript.

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Availability of Data and Materials
The authors declare that materials and date are promptly available to readers without undue qualifications in material transfer agreements. All data generated in this study are published maps and institutional affiliations.

Competing Interests
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