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A novel Ag-based photocatalyst Ag$_2$Nb$_4$O$_{11}$ is firstly obtained, which exhibits the universal high-efficiency photodegradation activity for RhB, MB and MO organic dyes. The persistent cycle reaction of 40 times and recovery characteristic indicate the Ag$_2$Nb$_4$O$_{11}$ photocatalyst has high stability, durability and regenerated ability.

Developing high-efficient semiconductor photocatalytic materials for eliminating organic contaminants in purification of environments has been considered to be an important field in the photocatalysis researches. In recent years, Ag-based compounds as photocatalysts have been widely researched and believed to be a kind of promising photocatalytic materials, which usually exhibit the high-efficiency photocatalytic oxidation ability for liberating $\text{O}_2$ from the water and degrading organic pollutants. One of the most important reasons is that the unique filled $d^{10}$ electronic configuration of $\text{Ag}^{+}$ ions can take part in composition and hybridization of energy band structure. A representative is a series of AgX (silver halide) and Ag/AgX SPR (Surface Plasma Resonance) photocatalysts prepared by in-situ growth of silver nanoparticles on the silver halide surfaces. Another one is Ag-based composite oxide photocatalysts. Especially, Ag$_3$PO$_4$ reported by J. H. Ye and co-workers displays the high-performance oxygen liberation ability from the water and photodegradation activity for organic dyes. Up to now, the majority of experimental and theoretical works have been carried out to improve the photocatalytic activity of AgX and Ag$_3$PO$_4$ photocatalysts by using various techniques, such as manipulating morphology, controlling lattice plane, building hierarchical structure, constructing heterojunction and so forth. Nevertheless, these materials are so sensitive to light that they can take place photocorrosion unavoidably, which result in the shortening of operating life and reduction of photocatalytic activity. In addition, some other p- and d-block composite oxides containing Ag have been developed, in which the most works usually concentrate on improving photocatalytic activity, controlling morphology and designing band gap engineering. However, it is regretful that the requisite durability, stability and regeneration ability are rarely considered, which are significant for photocatalyst to meet the requirement of recycling use in practical application. As far as the Ag-based compounds are concerned, possessing the high photocatalytic activity, long-term durability and regenerated ability are still a tremendous and difficult challenge.

At present work, a novel Ag-based photocatalyst Ag$_2$Nb$_4$O$_{11}$ is firstly achieved, which can degrade RhB, MB and MO organic dyes under UV-visible light. Interestingly, it has not obvious inactivation throughout the circle operations of 40 times enduring 1400 min reaction, which demonstrates that the merely slight photocorrosion has a little influence on the photocatalytic activity. The encouraging result is that the regeneration of Ag$_2$Nb$_4$O$_{11}$ is achieved by a simple re-calcination process and the degradation activity of paligenetic Ag$_2$Nb$_4$O$_{11}$ almost reaches to the primal level of the fresh sample.

![Image](image_url)

**Fig. 1** SEM images (a), EDS spectra (the insert of a), TEM image (b), SAED pattern (the insert of b), XPS spectra (c) and UV-vis spectrum (d) of Ag$_2$Nb$_4$O$_{11}$ sample.

The SEM image (Fig. 1a) exhibits that the sample has irregular bulk distribution morphology and the EDS spectrum (the insert of Fig. 1a) indicates that the sample is composed of Ag, Nb and O elements. The TEM image (Fig. 1b) further reveals that these bulks are aggregated by particles with size about 1-3 μm, which is attributed to the high-temperature calcination. The SAED pattern (the insert of Fig. 1b) performed on the whole bulk shows the bright diffraction rings, which indicates that the sample presents a polycrystalline characteristic.

The survey XPS spectrum (Fig. S1, ESI†) displays that the sample is composed of Ag, Nb and O elements in line with the EDS spectrum. From the XPS spectra of sample in Fig. 1c: two binding energy peaks at 529.9 and 533.1 eV indicate that oxygen has two

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different chemical states\textsuperscript{12} which derive from lattice O\textsuperscript{2−} is state of Ag\textsubscript{2}NbO\textsubscript{4} and adsorbed hydroxyl species.\textsuperscript{13} In addition, the binding energy peaks of Ag 3d\textsubscript{5/2} (367.7 eV) and Ag 3d\textsubscript{3/2} (373.6 eV) can be assign to the Ag\textsuperscript{0} chemical state.\textsuperscript{13} The non-broadening and symmetric shape indicates that silver may only possesses one Ag\textsuperscript{0} chemical state. Moreover, the XPS spectrum of Nb coincides with 3d\textsubscript{5/2} and 3d\textsubscript{3/2} states at 209.4 and 206.6 eV, in which the spin-orbit separation of 2.8 eV implies that Nb\textsuperscript{4+} ions exist in the sample.\textsuperscript{12} In addition, the peaks at 364.2 and 380.5 eV ascribe to the Nb\textsuperscript{3+} 3p\textsubscript{3/2} and 3p\textsubscript{1/2} states,\textsuperscript{13} respectively. The surface atomic ratio approximates to stoichiometric proportion (2:4:11) (Table S1, ES\textsuperscript{†}), which indicates that the pure Ag\textsubscript{2}NbO\textsubscript{4} sample is obtained.

The UV-visible DRS spectrum of sample (Fig. 1d) presents a strong absorption within 387 nm. The steep shape indicates that the absorption is due to the intrinsic band gap transition of sample rather than impurity levels. The band edge and semiconductor type of Ag\textsubscript{2}NbO\textsubscript{4} are estimated with empirical equations of the crystal semiconductor (Fig. S2, ES\textsuperscript{†}). The results indicate that Ag\textsubscript{2}NbO\textsubscript{4} exhibits the indirect band gap of 3.09 eV as well as direct transition of 3.30 eV, respectively.\textsuperscript{6} The narrower band gap of Ag\textsubscript{2}NbO\textsubscript{4} than that of Nb\textsubscript{2}O\textsubscript{5} (3.4 eV)\textsuperscript{13} implies the easy exciting electrons from the VB to CB to improve photocatalytic activity. It arises from that Ag\textsuperscript{+} ions introduced into Nb\textsubscript{2}O\textsubscript{5} participate in construction of the new crystal structure and energy band structure.

![Fig. 2 Dynamic curves of RhB solutions over different sample (a), photocurrent responses (b) and EIS spectra (the insert of b) of Ag\textsubscript{2}NbO\textsubscript{4} and Nb\textsubscript{2}O\textsubscript{5} as electrodes, circle operation of the RH solution degradation (c), XRD pattern and color of the fresh, used and regenerated Ag\textsubscript{2}NbO\textsubscript{4} samples (d).](image)

The dynamic curves of RhB solution degradation (Fig. 2a) show that RhB is completely degraded over Ag\textsubscript{2}NbO\textsubscript{4} within 35 min which is less than that of Nb\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2}. No-shifting and vanishing of the absorption peaks of RhB solutions from ultraviolet to visible region (Fig. S3, ES\textsuperscript{†}) prove that the benzene/heterocyclic rings of RhB molecule are decomposed into small organic/inorganic molecules or/and ions products.\textsuperscript{16} Even if MB and relatively stable MO azo dye are serve as target molecules, the removal rates can also exceed 96% and 80% after 25 and 90 min, respectively (Fig. S4-S5, ES\textsuperscript{†}). The above results indicate that the photocatalytic activity of Ag\textsubscript{2}NbO\textsubscript{4} photocatalyst is conspicuous superior to that of Nb\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2}, and exhibits universality for degradation of various organic dyes.

The photocatalytic reaction can be further regarded as a photoelectrochemical process.\textsuperscript{17} The positive slope of Mott-Schottky plots of Ag\textsubscript{2}NbO\textsubscript{4} and Nb\textsubscript{2}O\textsubscript{5} electrodes (Fig. S6, ES\textsuperscript{†}) indicates that they are n-type semiconductor. The flat-band potential of Ag\textsubscript{2}NbO\textsubscript{4} (−0.72 V) is higher than that of Nb\textsubscript{2}O\textsubscript{5} (−0.62 V). Therefore, the CB of Ag\textsubscript{2}NbO\textsubscript{4} is more negative because the CB is approach to flat-band potential in n-type semiconductors,\textsuperscript{18} which is consistent with the calculated results using empirical formulae (Table S2, ES\textsuperscript{†}). It means that Ag\textsubscript{2}NbO\textsubscript{4} has the more intense reducing capacity in favour of capturing H\textsubscript{2}O\textsubscript{2} molecules to yield hydroxyl radical (•OH) decomposing dyes. Moreover, the Ag\textsubscript{2}NbO\textsubscript{4} electrode presents a more intense photocurrent response than Nb\textsubscript{2}O\textsubscript{5} electrode (Fig. 2b), which evidences the more effective separation of carriers and faster charge transfer through Ag\textsubscript{2}NbO\textsubscript{4} electrode interface.\textsuperscript{19} The result is further proved by EIS (Electrochemical Impedance Spectra) of them (the insert of Fig. 2b). The arc radius on the Nyquist plot of Ag\textsubscript{2}NbO\textsubscript{4} electrode is smaller than that of Nb\textsubscript{2}O\textsubscript{5} electrode, which implies that the former has better high-efficiency charge transfer ability. Therefore, the improved separation and transfer efficiency of carriers may be main reason for the high degradation activity of Ag\textsubscript{2}NbO\textsubscript{4}.\textsuperscript{17} In addition, the large BET specific surface area of Ag\textsubscript{2}NbO\textsubscript{4} (4.582 m\textsuperscript{2} g\textsuperscript{−1}) relative to Nb\textsubscript{2}O\textsubscript{5} (1.997 m\textsuperscript{2} g\textsuperscript{−1}) is also play a role for improving degradation activity.

Furthermore, the circle operation of degrading RhB is performed (Fig. 2c). The photocatalytic ability of Ag\textsubscript{2}NbO\textsubscript{4} sample has not obviously loss after 40 recycles enduring 1400 min reaction. The removal rate still achieves 75% within 35 min in the last 40th circle. Meanwhile, the XRD pattern (Fig. 2d) shows that the fresh sample is well-indexed as hexagonal Ag\textsubscript{2}NbO\textsubscript{4} (PDF#21-1086). The sharp diffraction peaks imply the pure sample with high-crystallinity is achieved. After circle operation of 40 times, the color of sample changing white into dark grey suggests that Ag nanoparticles generates on the Ag\textsubscript{2}NbO\textsubscript{4} surface under light irradiation, which is similar to most Ag-based photocatalysts. It is worth noting that the XRD pattern of the used sample (Fig. 2d) is nearly unchanged, and in which no Ag phase is detected. It indicates that Ag\textsubscript{2}NbO\textsubscript{4} is a relatively stable Ag-based photocatalyst with slight photocorrosion. Moreover, when the used sample is performed by a re-calcination process, the dark grey changes into white again and the XRD pattern (Fig. 2d) still displays the pure Ag\textsubscript{2}NbO\textsubscript{4} phase as well as XPS spectra peaks of elements are almost same as that of the fresh sample (Fig. S7 ES\textsuperscript{†}). It demonstrates that the Ag\textsubscript{2}NbO\textsubscript{4} photocatalyst realizes regeneration. More importantly, the degradation ability of regenerated sample almost reaches to the primal level of the fresh sample (Fig. 2a). It indicates that Ag\textsubscript{2}NbO\textsubscript{4} as a novel Ag-based photocatalyst possesses the splendid stability, durability and regeneration ability.

![Fig. 3 Energy band diagram and DOS (a), crystal structure of Ag\textsubscript{2}NbO\textsubscript{4} (b).](image)

The activity and stability of photocatalyst are determined by its electronic structure and crystal structure in essence. The theoretical calculation are performed based on \textit{ab initio} density functional theory (ES\textsuperscript{†}). The calculated electronic band structure diagram of Ag\textsubscript{2}NbO\textsubscript{4} (Fig. 3a) confirms its indirect transition characteristic. The relative flatness of CB bottom and VB top implies that it also yields a direct transition under a little high energy, which agrees well with the result revealed by UV-vis DRS. Density of States (DOS) of Ag\textsubscript{2}NbO\textsubscript{4} indicates that VB top of Ag\textsubscript{2}NbO\textsubscript{4} is mainly composed of the hybridized Ag 4d and O 2p orbital, which leads to the VB top of Ag\textsubscript{2}NbO\textsubscript{4} shifting up relative to that of Nb\textsubscript{2}O\textsubscript{5} composed by only O 2p orbital. It brings about narrowing band gap and enhancing light harvest ability to improve photocatalytic activity. This hybridized
effect has also been reported in the most Ag-based photocatalysts.\(^3\)
In addition, the high degree of overlap indicates that the intense bonding effect exists in Ag 4d and O 2p orbital, which contribute
significantly to improving stability of Ag\(_7\)Ta\(_4\)O\(_{11}\). The CB bottom of
Ag\(_7\)Nb\(_6\)O\(_{11}\) is mainly composed of Nb 4d orbital and accompanied a
little O 2p and Ag 5s states. Because the mobility of charge carriers
is proportional to the reciprocal their effective mass, the little Ag 5s
state in the CB can reduce electron effective mass and increase
delocalization, thus also improving photocatalytic ability.\(^2\)

Ag\(_7\)Nb\(_6\)O\(_{11}\) is a typical layered structure niobiate, which belongs to
a member of family compounds with general formula \(A\)\(_{n}\)\(_{1}\)\(_{m}\)\(_{1}\)\(_{n}\)\(_{1}\)\(_{m}\)\(_{1}\)\(_{n}\) \((n = 1)\).\(^2\) As shown in Fig. 3b, the linked alternately NbO\(_6\) and AgO\(_6\)
octahedrons as well as NbO\(_6\) pentagonal bipyramids construct a
polyhedron layer in X-Y plane, respectively. Two polyhedron layers
alternately stack along Z-axis by corner-connecting to build the
three-dimensional framework. Most layer-structured compounds have
been previously developed as efficient photocatalysts because the
layered structure can improve the separation and transportation
of charge carriers.\(^2\) In the Ag\(_7\)Nb\(_6\)O\(_{11}\) crystal, the interlaced network of
AgO\(_6\) and NbO\(_6\) octahedrons in one layer of X-Y plane is
beneficial to separation and migration of charge carriers from the
hybridized Ag 4d and O 2p orbitals to the unoccupied Nb 4d orbitals.
Especially, it is similar to tantalate\(^2\) that the bond angle of Nb-O-Nb is
equal to 180° in NbO\(_6\), so the photogenerated charge carriers can
migrate easily in the framework of NbO\(_6\) units. In addition, the bond
angle of O-Nb-O reaches to 135.6° between NbO\(_6\) and NbO\(_6\), which
facilitates electron transfer in two layers. The NbO\(_6\) layers can serve
as electron transportation channel to improve the transfer and
separation efficiency of electron-hole pairs.\(^3\) Moreover, the
formation of Ag\(_7\)Nb\(_6\)O\(_{11}\) octahedrons is crucial to the stability of
Ag\(_7\)Nb\(_6\)O\(_{11}\), where the central Ag\(^+\) ion is encircled by surrounding
six O\(^-\) ions that plays a protection role via forming intense
coordinate bond. It restrains efficiently Ag\(^+\) ions dissociate from
Ag\(_7\)Nb\(_6\)O\(_{11}\) crystal and avoid being reduced by photogenerated
electrons. Meanwhile, the same layered NbO\(_6\) and the near layered
NbO\(_6\) connecting with AgO\(_6\) can rapidly export photogenerated
electrons generated in AgO\(_6\), which separates charge carriers and
inhibits the reduction of Ag\(^+\) ions in the crystal structure.

Scheme 1 Transferred and separated behavior of charge carriers in the
crystal along to (001) and (110) crystal lattice plane view and photocatalytic
reaction mechanism of dye over the Ag\(_7\)Nb\(_6\)O\(_{11}\) sample.

Scheme 1 illustrates the transfer and separation behavior of the
charge carriers in the Ag\(_7\)Nb\(_6\)O\(_{11}\) crystal along to (001) and (110)
crystal lattice plane view and photocatalytic reaction mechanism.
When Ag\(_7\)Nb\(_6\)O\(_{11}\) sample is exposed to the UV-visible light,
the electron-hole pairs are produced on AgO\(_6\) octahedrons. At the same
time, the electrons transfer to the dominant Nb 4d orbital at the CB
bottom, and the holes transfer to the hybridized Ag 4d and O 2p
orbital at the VB top. In consequence, the electron transport channels
are formed in NbO\(_6\) and NbO\(_6\) as well as the hole transport channels
are formed in AgO\(_6\), respectively. Finally, the electrons and holes
migrate to the sample surface through electron and hole transport
channels, respectively. Electrons further are captured by H\(_2\)O in the
solution to generate -OH activated species to decompose dyes. Holes
can also directly decompose dyes.

In summary, a novel Ag-based photocatalyst Ag\(_7\)Nb\(_6\)O\(_{11}\) is firstly
obtained, which exhibits universal degradation ability for Rh\(_b\), MB
and MO organic dyes under UV-visible light, as well as excellent
stability, durability and regeneration ability. Photoelectrochemical
characteristics reveal that the enhanced reducing capacity as a
result of shifting up of CB and improved separation efficiency of
charge carriers are mainly reason of the high degradation activity.
The unique electronic structure and crystal structure determine
its high photocatalytic activity and stability in essence. This work
exploits a stable and renewable Ag-based photocatalyst, which
makes an important step for the development of Ag-based
photocatalyst.

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