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## Researching Advances of Chemically Modified Metal Surfaces by Organophosphonates

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# Researching Advances of Chemically Modified Metal Surfaces by Organophosphonates

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**Abstract.** Organophosphonates are key candidates as ligands for the construction of novel functional materials receiving considerable attention in the fields of both fundamental research and industrial application. We comprehensively introduce researching advances of chemically modified metal surfaces by organophosphonates based on Cu, Fe, Al, Mg and their alloys, which will extend the engineering application of organophosphonate-modified metallic materials in industrial fields and civilian sectors.

## 1. Introduction

In 1893, Werner published a paper entitled "Contribution to the structure of inorganic compounds", which proposed all the major concepts of coordination theory at that time and laid the foundation of coordination chemistry. In a sense, coordination compounds are the best medium for inorganic and organic matter and the unity of finite and infinite. The generation and development of coordination compounds have gradually blurred the boundaries of the traditional "four great chemistry". Organic phosphorylation, as an important part of coordination chemistry, has expanded the development of supramolecular chemistry, crystal engineering, material chemistry and other fields. It is widely used in chemical water treatment, magnetic materials, catalysis, bone targeting, oil field drilling, mineral processing, dental materials, enzyme inhibition, tumor treatment, corrosion control and other technical industries [1-9].

Metal corrosion has always been an important bottleneck affecting the application of metal materials, and has brought huge direct economic losses to human society accounting for 1-5% of a country's GNP. It's also caused the waste of resources and energy and some disastrous consequences [10-13]. Chemical surface modification can provide metal surface protective passive film, carbon atoms of organic phosphoric acid structural variability of chemical environment, a variety of proton process, with almost all of the metal ion complexing ability make the organic phosphoric acid an important unit of constructing new functional materials. Unique properties of organic phosphoric acid can provide long-term protection to metal materials. This paper summarizes and evaluates the research progress and the latest results of organic phosphoric acid on the surface chemical modification of copper, iron, aluminium, magnesium and other common metal materials in recent years, providing a way to expand the engineering background of phosphoric acid metal surface in industrial field and civil sector.

## 2. Surface modification of copper and copper alloys

Copper has a long history of application and is widely used in the chemical and microelectronics industries due to its excellent thermal, electrical conductivity and mechanical processing properties. It

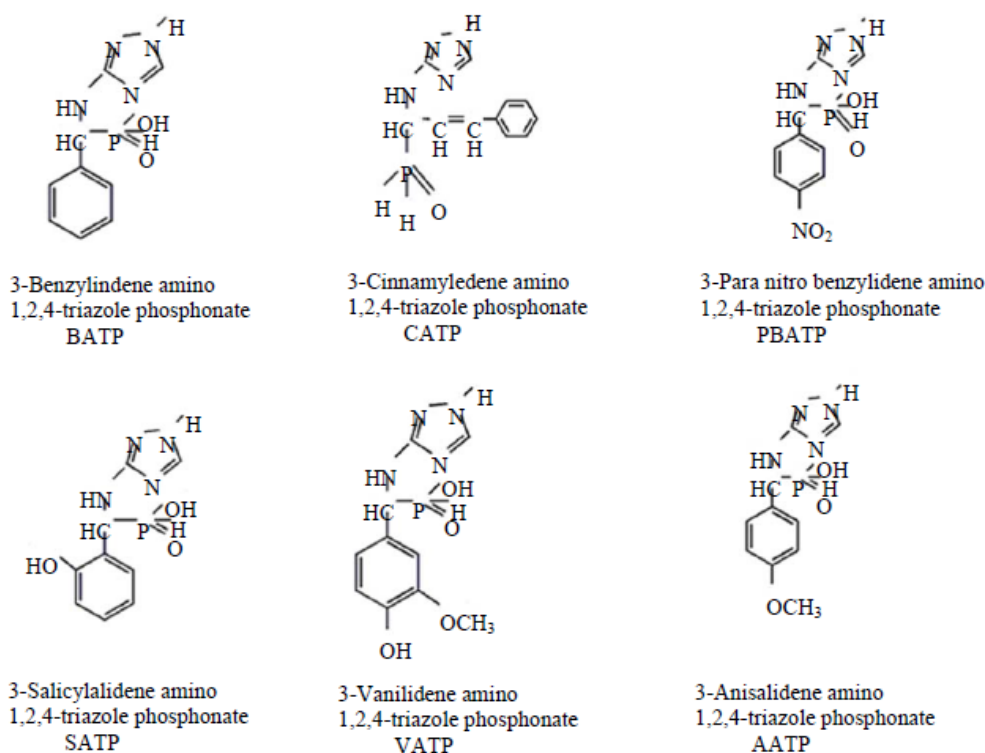


is a thermodynamically inert metal, having a positive ratio of hydrogen to hydrogen in an electric sequence, and has no tendency to corrode in water and non-oxidizing acids that do not contain dissolved oxygen. However, complex ions can be formed in oxidizing acids or in airborne, as well as in copper (e.g.  $\text{CN}^-$ ,  $\text{NH}_4^+$ ) is vulnerable to corrosion damage and dissolution. Biological pollution can reduce its conduction effect and lead to local corrosion dissolution.

Organic phosphoric acid molecules bond with copper coordination, forming an insoluble stable film on its surface, and forming a solid "corrosion barrier" between the metal and the environment. Triazole phosphoric acid can modify the surface of copper and form complexes on the surface of copper to provide long-term protection.

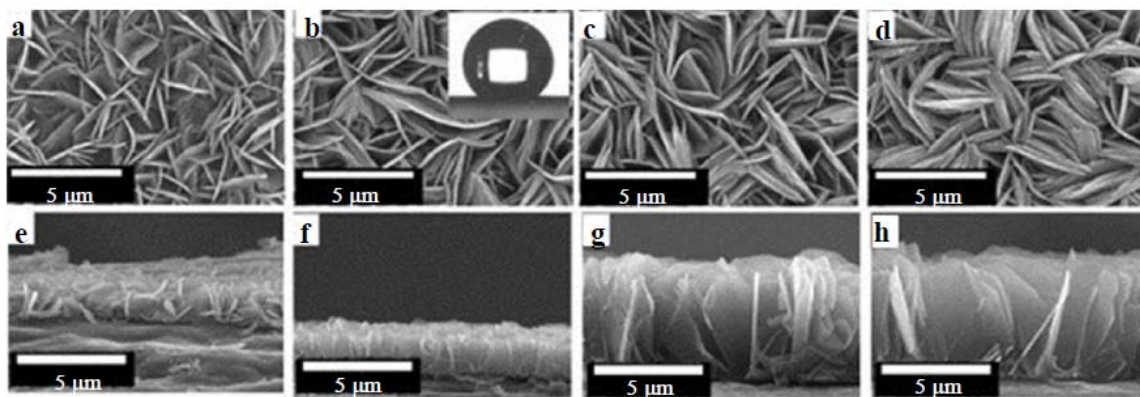
Ramesh etc research shows that the SATP VATP, AATP molecular structure (see figure 1) with hydroxyl, methoxy push electronic effect makes the benzene ring activation and has good corrosion effect. PBATP (see figure 1) molecular structure on the nitro benzene ring and coplanar gives the largest electronic absorption effect, make the benzene ring passivation effect the worst. This series of compounds with  $\text{MoO}_4^{2-}$  synergistic effect is produced, and corrosion protection performance is increased. Hexadecyl trimethyl ammonium bromide (CTAB), cationic surfactant (pesticide) - molybdate - ternary coordination system of phosphoric acid composition of copper in the lake has better corrosion effect. It is worth mentioning first add CTAB in the lake, then add salt molybdate - triazole phosphoric acid to produce synergistic effect is superior to join at the same time [14-15].

CuNi (55%Cu/45%Ni) alloys are widely used in industrial pipelines, civil water pipes and Marine vessels, but have corrosion problems on their surfaces. Kristen etc impregnation CuNi alloying oxides to form a self-assembled membrane (SAM): N-octadecyl phosphate (ODPA) and 16-phosphonohexadecanoic acid (COOH-PA) monolayer. These single-layer films are orderly and have a strong chemical bond with the surface. Seawater washing or ultrasonic cleaning remains stable. In addition, the formation of SAM monolayer film can effectively limit the oxidation of CuNi alloy surface and inhibit corrosion, which has great development prospects in marine transportation and related fields [16].



**Figure 1.** Structures of triazole derivatives [14-15]

Studies have shown that the in-situ hydrothermal synthesis method generates super hydrophobic phenyl phosphonate zirconium (ZrPP) thin films on the surface of copper. The hexagonal crystal orientation grows perpendicular to the copper base, and the static contact angle on the surface reaches 150 degrees. The super hydrophobicity remains stable within the pH (2, 12) range. Electrochemical tests showed that the corrosion current decreased by 2 orders of magnitude [17].



**Figure 2.** Top and cross-section views of SEM images of the ZrPP films crystallized at 100°C for different times: (a, e) 0.5 h, (b, f) 1 h, (c, g) 6 h, and (d, h) 24 h [17]

### 3. Surface modification of steel

As a metal widely used in industry, iron and steel are easily oxidized in harsh atmosphere and harsh marine environment. The corrosion and dissolution phenomenon is quite serious. The use of organic phosphonic acid to modify the surface of steel can effectively prevent the corrosion and oxidation of steel.

#### 3.1. Single phosphoric acid system

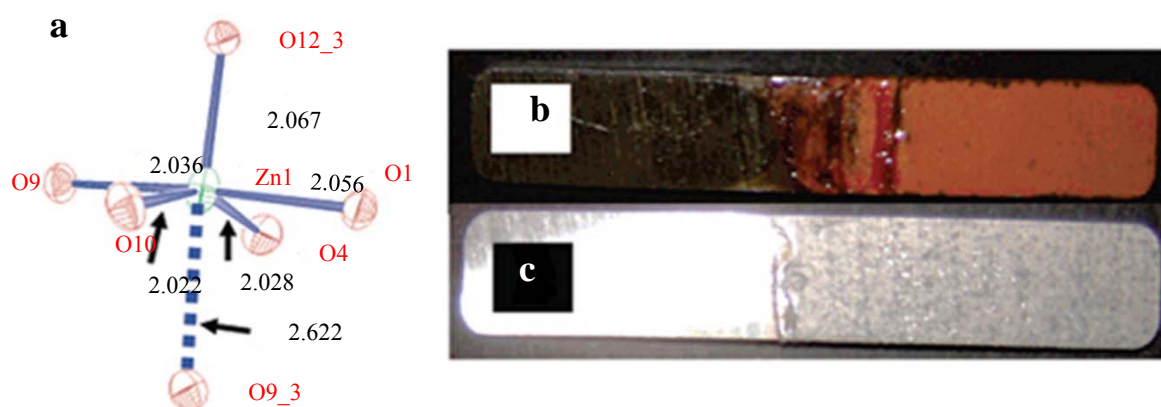
Organic phosphonic acid is an environment-friendly chemical modification reagent on metal surface, which can form an adsorption film on the surface of metal oxides and hydroxides to protect the metal. Steel surfaces can be modified in saturated solution of  $\text{Ca}(\text{OH})_2$  (simulated concrete solution) in NTMP. The results showed that NTMP Langmuir adsorption on steel surface.  $\text{Ca}^{2+}$  Crosslinking with three phosphoric acid groups to form coordination polymer coating in the cathode region of steel inhibit the cathode reaction. In the anode area, NTMP and  $\text{Ca}^{2+}$  adsorption of iron oxide on the surface of steel and high concentration of NTMP (greater than  $2.5 \times 10^{-2} \text{ Mol/L}$ ) dissolved with iron oxide reduce the corrosion inhibition efficiency of the anodic reaction [18]. Experiments have shown that the chemical composition of adsorbed films is affected by pH. Fe is completely immersed in cement filtrate containing a small amount of calcium ions ( $\text{pH} = 13$ ) and N-dimethyl phosphonate N-tetra alkyl amine solution ( $7 \leq \text{pH} \leq 13$ ) contain  $\text{Fe}_2\text{O}_3$  on the surface of low-carbon steel, which is covered with a thin film of  $\text{FeOOH}$ . The outer layer of  $\text{FeOOH}$  is formed by the oxide surface reacting with an aqueous solution. When  $1.3 \leq \text{pH} \leq 7.55$ , phosphoric acid deprotons and  $\text{FeOOH}$  gets protons, phosphoric acid forms  $\text{FeOOH}_2^+ \dots \text{P}^-$  with  $\text{FeOOH}$ , the bond is stable and the  $\text{Ca}^{2+}$  exits. There is calcium phosphonate and a small amount of  $\text{Ca}(\text{OH})$  on the surface of steel at  $\text{pH} > 7.55$ . The  $\text{Ca}^{2+}$ 's going to be a bridge bond for OH from  $\text{FeOOH}$  and  $\text{O-P}$  from phosphoric acid to cross-linked to form bonds [19]. PBTC (1, 2, 4-tricarboxylic acid-2-butylphosphonic acid), EDTMP (ethylene diamine tetramethylenephosphonic acid), PMPP (phosphonyln-methylphosphonic acid-polycaprolactam derivative) not only have protective effect on low carbon steel, but also inhibit  $\text{CaCO}_3$  crystallization in water. PMPP in neutral water to low carbon steel protection effect is the best [20]. PPA and PPPA (piper zine dimethylenephosphonic acid), the corrosion inhibition efficiency of industrial pure iron in 3%NaCl solution increases with the concentration of phosphoric acid, the corrosion potential moves negatively, the dissolution rate of iron decreases, and the corrosion inhibition efficiency increases with the concentration of phosphoric acid at

$5 \times 10^{-3}$  Mol /L up to the maximum: PPA corrosion inhibition efficiency of 76.7%, PPPA corrosion inhibition efficiency of 91.9%. As the temperature increases, the corrosion inhibition efficiency decreases. The adsorption of PPA and PPPA compounds followed Langmuir adsorption isothermal adsorption on iron surface, which acted as a corrosion barrier to inhibit the anodic dissolution reaction and cathode oxygen consumption reaction [21]. Trim ethyl-phosphonate amine and triatic acid amine have a very good inhibition effect on the scale of barium sulfate to the surface of stainless steel electrode. Phosphonic acid is stronger than carboxylic acid, and phosphoric acid modified the surface of stainless steel to form a large charge transfer impedance which produces better protection, while carboxylic acid accelerates the dissolution of steel [22]. Thiomoline-4-methylene phosphoric acid (TMPA) and morpholine-4-methylenephosphonic acid (MPA) modified the surface of carbon steel to produce iron organic phosphonic acid complexes. The dissolution rate of carbon steel in neutral seawater was reduced from  $5 \text{ mm a}^{-1}$  to  $0.1 \text{ mm a}^{-1}$  [23].

Alkyl phosphoric acid has good adhesion with steel matrix. Sam's films formed by 1-alkyl phosphoric acid derivatives on the surface of steel are compact and continuous, which can effectively prevent the active dissolution of steel matrix [24]. 1-Octyl phosphoric acid on iron surface  $20 \text{ M}\Omega \text{ cm}^2$ . The "barrier effect" of the charge transfer impedance on the dissolution of iron shows a strong protective performance [25]. Alkyl bisphosphonic acid can also form SAMs on the surface of steel, Felhosi etc found that alpha, omega-3 alkyl bisphosphonic acid [ $\text{H}_2\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3\text{H}_2$   $n = 5-10$ ] is an anodic corrosion inhibitor, which self-assemble a layer of self-repairing, protective and dense film on the surface of iron to separate the metal from the environment. The formation of the film is time-dependent. Interestingly, bisphosphonic acid with an odd number of methylene groups provides better protection than alkyl carbon chains with an even number of carbon atoms, and 1, 7-heptane diphosphate provides the best corrosion inhibition [26-27].

### 3.2. Synergistic effect system

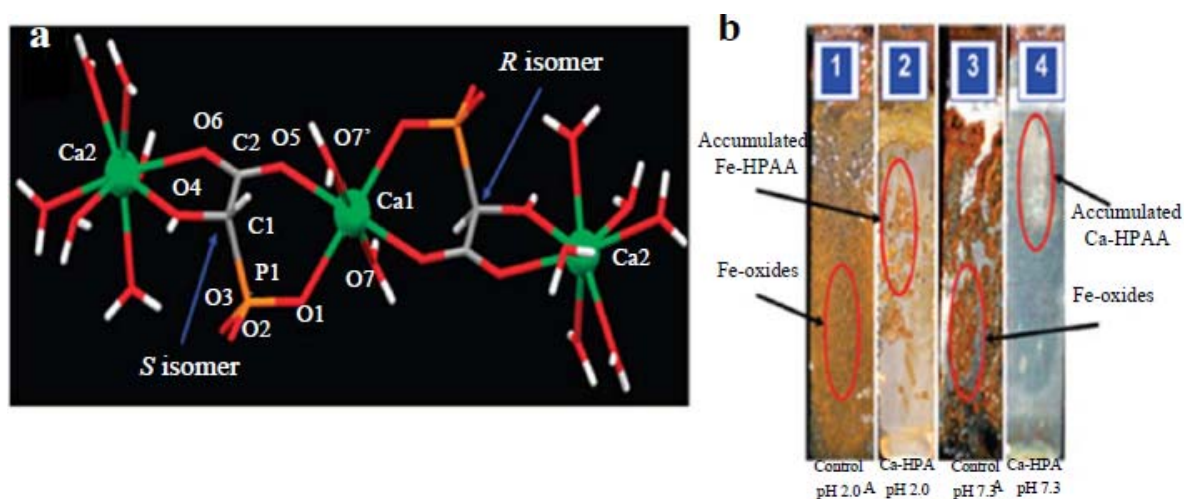
In short, the synergy is  $1+1 > 2$ .  $\text{Zn}^{2+}$  and AMP (amino phosphonic acid) at 1:1 molar ratio to form Zn-AMP system has stronger corrosion inhibition performance than a single  $\text{Zn}^{2+}$  and AMP [28-30]. H. Amar [31] etc studied the corrosion inhibition system constructed by modifying industrial pure iron. The corrosion inhibition efficiency was 77% based on the tafel polarization curve, while it is 90% with the binary system PPA- $\text{Zn}^{2+}$ . The following reaction occurs:  $\text{Zn}^{2+} - \text{PPA} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} - \text{PPA} + \text{Zn}^{2+}$ ,  $\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2$ . Zn-HDTMP coordination compound was generated by 1:1 molar ratio reaction of HDTMP and  $\text{Zn}^{2+}$ , where  $\text{Zn}^{2+}$  six ligands exist in the distorted octahedral ligand environment of phosphonate oxygen (see figure 3). The Zn-HDTMP cooperative system modified the surface of carbon steel to reduce the corrosion rate from  $7.28 \text{ mm/a}$  to  $2.11 \text{ mm/a}$  [32].



**Figure 3.** Coordination environment of the  $\text{Zn}^{2+}$  center displaying important bond distances (in angstroms) (a), Anticorrosive effect of Zn-HDTMP films on carbon steel (b, control, no inhibitor present; c, Zn-HDTMP synergistic combination)[32]

Studies have found that 2-chloroethyl phosphoric acid associated with  $\text{Zn}^{2+}$  modified low carbon steel contains Cl, it has better protective effect than ethyl phosphoric acid in neutral aqueous solution. This is the strong electron absorption capacity of chlorine atoms and their size lead to the improvement of corrosion resistance [33]. The generation of synergistic effect should satisfy the matching relationship of molecular structure, otherwise it will produce antagonistic effect. Ethyl phosphoric acid- $\text{Zn}^{2+}$ , sodium phenylphosphonate- $\text{Zn}^{2+}$ , polyacrylamide- $\text{Zn}^{2+}$ , phenylphosphonic acid- $\text{Zn}^{2+}$  for low carbon steel containing Cl in the solution of phenylphosphonic acid-Zn, the synergistic effect is very good for steel protection. The addition of polyacrylamide into the system did not reduce the protection to corrosion inhibition effect, but the system composed of polyacrylamide and phenylphosphonic acid showed the resistance effect and the corrosion inhibition effect was reduced [34-36]. Tartrate - 2-hydroxyethyl phosphoric acid (2-cepa) accelerates the dissolution of steel,  $\text{Zn}^{2+}$ -tartrate has a corrosion inhibition effect, and the corrosion inhibition efficiency is 40%, the synergistic effect of the  $\text{Zn}^{2+}$ -tartrate-2-CEPA system is 96% [37]. 1, 2, 4- tricarboxylic acid - 2-phosphonate butane ( $\text{H}_5\text{PBTC}$ ) and  $\text{Ca}^{2+}$  by 1:1 molar formed the coordination polymer  $\text{Ca}(\text{H}_3\text{PBTC}(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O})_n$ , in which  $\text{Ca}^{2+}$  seven coordination.  $\text{H}_5\text{PBTC}$  only takes away two protons because of  $\text{Ca}(\text{H}_3\text{PBTC}(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O})_n$ . It is an acid complex that accelerates the corrosion dissolution of carbon steel and is not a synergistic system with corrosion inhibition [38-40].

The pH of the system and the concentration of species in the system have an impact on the synergistic effect. The  $\text{Ca}^{2+}$ -HEDP- $\text{SiO}_3^{2-}$  synergistic effect system constructed by the three factors provides better protection for low-carbon steel. Electrochemical test shows that when  $\text{pH} = 7$ , the corrosion inhibition efficiency is 94%. When  $\text{pH} = 11$ , the corrosion inhibition efficiency is 96% [41]. 10 ppm hydroxyethyl bisphosphonate (HEDP) -15 ppm silicate has a synergistic effect and a good protective effect on carbon steel, but 15 ppm hydroxyethyl bisphosphonate (HEDP) - 15 ppm silicate system has an antagonistic effect [42]. The monoclonal crystal Zn-AMP complex was generated at the molar ratio of 1:1 AMP and  $\text{Zn}^{2+}$ , and its corrosion inhibition effect on carbon steel was better at  $\text{pH} = 3.0$  than  $\text{pH} = 1.0$  [43]. The laminated coordination polymer M-HDTMP ( $\text{M} = \text{Sr}, \text{Ba}$ ) was obtained by the  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  reaction with hydroxyphosphonic acetic acid (HPAA) respectively. The corrosion inhibition effect of M-HDTMP on carbon steel reached 100% at  $\text{pH} = 7.3$ , and accelerated corrosion dissolution of carbon steel at  $\text{pH} = 2.0$  [44-45]. M-HDTMP ( $\text{M} = \text{Sr}, \text{Ba}$ ) complexes were generated by 1:1 molar ratio reaction of HDTMP with  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . The coordination environment of a capsid octahedron that exists  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  in octahedron. The protective effect of 0.8mm Ba-HDTMP on carbon steel reaches 90.1% when  $\text{pH} = 7.0$  and 0.8mm Ba-HDTMP is used. When the concentration changes or the pH drops, the corrosion inhibition effect decreases and even accelerates the corrosion dissolution of carbon steel [46]. The linear molecular trimer  $\text{Ca}_3(\text{HPAA})_2(\text{H}_2\text{O})_{14}$  was generated by the molar ratio of 1:1 HPAA and  $\text{Ca}^{2+}$ , the center  $\text{Ca}^{2+}$  is an octahedral environment with six ligands, and two  $\text{Ca}^{2+}$  on the periphery<sup>2+</sup> eight coordination of the two cap triangular prism environment.  $\text{HPAA}^{3-}$  act as three  $\text{Ca}^{2+}$  the bridge ligand. The corrosion weightlessness method showed that  $\text{pH} = 7$ , 1.76 mM Ca.HPAA has the best corrosion inhibition efficiency on carbon steel (94.2%) (See figure 4)[47].



**Figure 4.** Molecule structure of  $\text{Ca}_3(\text{HPAA})_2(\text{H}_2\text{O})_{14}$  trimer (a), anticorrosive effect of Ca-HPAA films on carbon steel(b) [52]

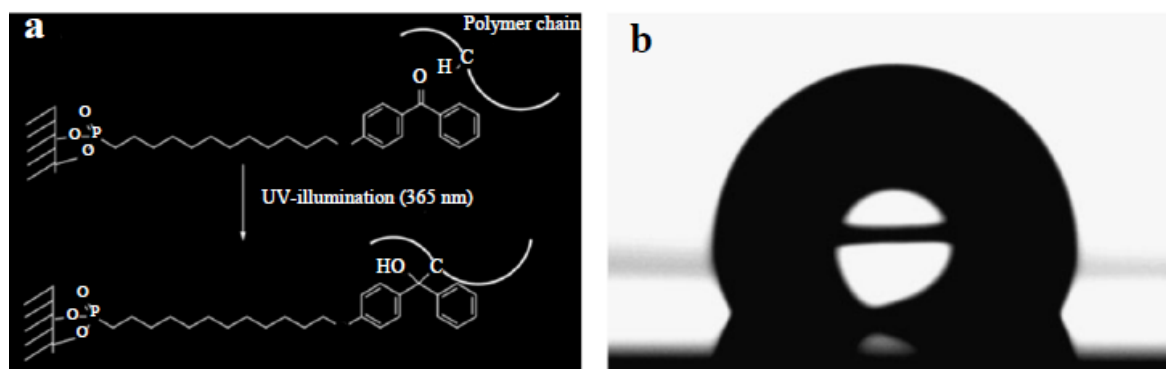
#### 4. Surface modification of aluminium

Aluminum has a wide range of use in automobile, aviation, building facade. Aluminum surface passivation film could form in the atmosphere, but industrial aluminum alloy is prone to local corrosion due to the activation of intermetallic compound particles in aluminum oxide, so it must be coated on the surface of aluminum [48-49].

Using a simple photochemical process at room temperature with phosphoric acid group as the anchor group, polystyrene and plexiglass as film forming substances covalently grafted polymers on the metal surface, modify the polymer film surface generated on the metal aluminium surface, with good hydrophobic properties (contact Angle  $119^\circ$ ), and is stable in harsh environments because polymer chains adhere well to metal surfaces by virtue of strong interactions between phosphonate and alumina (see figure 5).[50].

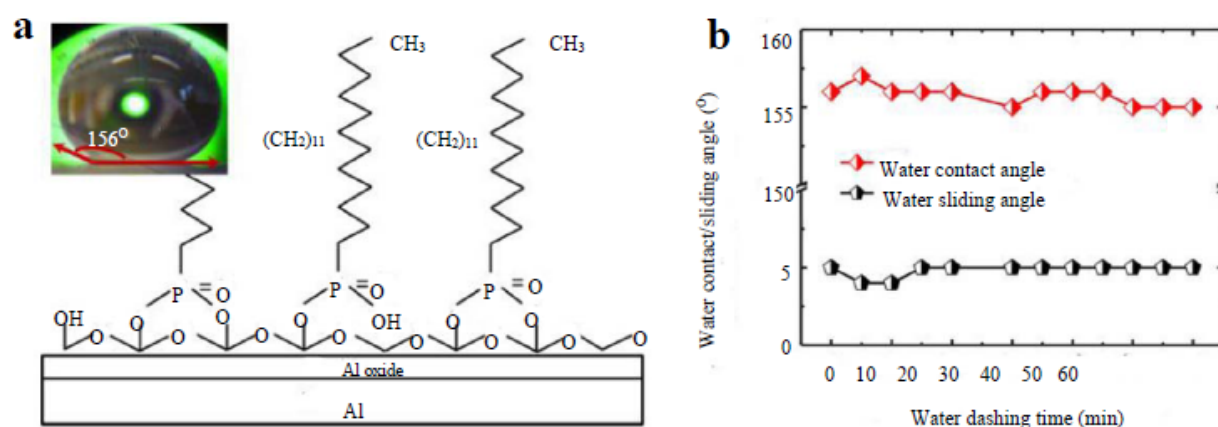
Sol-gel film is the protective layer of metal aluminium. As a result of the  $\pi$ - $\pi$  interaction, phenylphosphonic acid anions can be embedded in phenyltrimethoxysilane-based sol-gel membranes to enhance the membrane's protective properties. The sol-gel method is designed reasonably to protect the metal from corrosion [51]. The adhesion between the coating and the aluminium substrate is extremely important. 3-aminopropane-1-phosphonic acid is a good adhesion agent, which is adsorbed on the surface of aluminium oxide/hydroxide by acid-base reaction to form a double-tooth chelation conformation, greatly reducing the filamentous corrosion rate of aluminium alloy [52].

Ethylene diamine tetramethylenephosphonic acid modified the aluminium surface in sodium tetra borate as the supporting electrolyte solution, and the passivation film formed was uniform and dense, with few pores, stable, and self-repairing [53].



**Figure 5.** Benzophenone phosphoric acid immobilization on aluminium surfaces and the attachment of polymers (a), Optical image of a water droplet on an aluminium surface modified with a polymer film (b) [50]

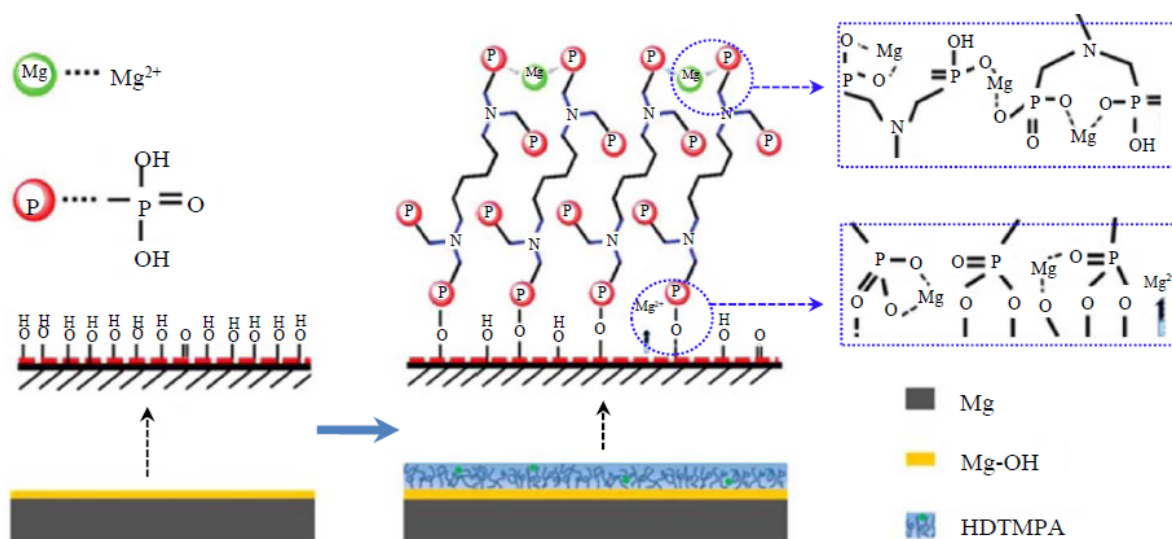
A stable super hydrophobic surface (static contact Angle  $156^\circ$ , rolling Angle  $5^\circ$ ) can be obtained by modifying the aluminium surface with dodecyl phosphoric acid (DDPA) based on the cooperation of phosphoric acid functional groups to form stable P-O-Al chemical bond with aluminium, and it has a strong durability for the circulating water rinsing (static contact Angle and rolling Angle basically do not change after 1 hour of rinsing), as shown in figure 6[54].



**Figure 6.** Schematic illustration of DDPA monolayer derivatisation on Al surfaces, inset shows water droplet on DDPA/Al surface (a), Water contact angle and WSA of prepared Al surfaces after pressure water flushing (b) [54]

## 5. Surface modification of magnesium and alloys

Magnesium and magnesium alloys are the lightest structural materials. Magnesium has a density of only  $1.74\text{g cm}^{-3}$ , which has high specific strength, specific stiffness, electromagnetic shielding, damping performance and other excellent performance. It has a very important application value and broad prospects in the automotive, electronics industry, aviation, and aerospace, military, biomedical, energy industry. With the exhaustion of many metal mineral resources, especially the lightweight structure, miniaturization and sustainable development strategy, the demand for low-carbon life has stimulated the development of magnesium industry to some extent. However, magnesium has a great tendency of anodic dissolution due to its extremely low electrode potential, so physical metallurgy, surface modification and other methods must be used to inhibit its ionization process. To some extent, corrosion is the main bottleneck of the development of magnesium alloy industry.



**Figure 7.** Schematic of the rationale for covalent immobilization and chelating reaction deposition of methylenephosphonic acid-HDTMPA on the magnesium substrate [57]

A. N. Khramov group generated organic-inorganic hybrid films of phosphoric acid functional characteristics by sol-gel method using diethyl phosphoric acid diethyl triethoxy silane - four ethyl silane as precursor on the surface of AZ31B magnesium alloy. Stable P - O - Mg chemical bonds formed by the included phosphoric acid functional groups and magnesium make the film as the inhibiting corrosion barriers of the magnesium alloy. Corrosion inhibition efficiency was 100% [55]. The research of A. Mahapatro group indicates that SAMs can be used as magnesium coating for biomedical applications. Stable phosphoric acid nano-coating can be observed on magnesium surface by optical technology, and N-octadecyl phosphoric acid self-assembled film can be generated on magnesium oxide layer. FTIR, XPS, AFM and other tests show that the self-assembled film has long-term stability [56]. Zhao sheng etc from Southwest Jisotone University modified magnesium surface with HDTMP to form a homogeneous dense coating with good protective effect on magnesium (see figure 7) and good compatibility with bone. In addition, HDTMP has significant biological activity and can improve the proliferation of osteoblasts [57].

## 6. Conclusion and prospect

Metallic organic phosphoric acid compounds have important theoretical significance and potential application value in basic research and industrial application fields due to their structural variability, design ability and predictability of modification function. As organic-inorganic hybrid materials with great potential, they have broad application prospects in the field of metal surface modification. Currently, report on organic phosphoric acid used for metal surface modification in the literature is still very limited and the research on the mechanism of surface modification is almost blank. The relationship between structure and performance is still a long way to go in the future.

## Acknowledgments

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