Recent Developments in Plasmonic Sensors of Phenol and Its Derivatives

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Abstract: Many scientists are increasingly interested in on-site detection methods of phenol and its derivatives because these substances have been universally used as a significant raw material in the industrial manufacturing of various chemicals of antimicrobials, anti-inflammatory drugs, antioxidants, and so on. The contamination of phenolic compounds in the natural environment is a toxic response that induces harsh impacts on plants, animals, and human health. This mini-review updates recent developments and trends of novel plasmonic resonance nanomaterials, which are assisted by various optical sensors, including colorimetric, fluorescence, localized surface plasmon resonance (LSPR), and plasmon-enhanced Raman spectroscopy. These advanced and powerful analytical tools exhibit potential application for ultrahigh sensitivity, selectivity, and rapid detection of phenol and its derivatives. In this report, we mainly emphasize the recent progress and novel trends in the optical sensors of phenolic compounds. The applications of Raman technologies based on pure noble metals, hybrid nanomaterials, and metal–organic frameworks (MOFs) are presented, in which the remaining establishments and challenges are discussed and summarized to inspire the future improvement of scientific optical sensors into easy-to-operate effective platforms for the rapid and trace detection of phenol and its derivatives.

Keywords: phenolic compounds; plasmonic resonance; Raman spectroscopy; noble metal nanostructures; environmental detection

1. Introduction

Plasmonic resonance-based optical sensor technology has been considered to be an efficient method applied for sensing techniques of either indoor or outdoor carbon dioxide molecules [1], various gases [2], inorganic arsenic compounds [3], and pesticides [4]. Optical sensors have been known as simple analytical techniques to demonstrate numerous advantages such as facile design and effective detection, leading to promising potential applications in environmental metal ion monitoring [5]. Recently, plasmonic nanomaterials [6] and 2D materials [7] have rapidly emerged as unique sensing platforms for varieties of engineering applications thanks to their specific features such as enhanced electrical, optical, and electrochemical signals.

Among various optical sensor materials, scientists are increasingly interested in pure noble metals and combined structures of hybrids and MOFs to utilize their plasmonic resonance. For example, some scientific reports have been published, such as an SPR sensor of Hg²⁺ [8], Au-modified-tyrosinase enzyme-based graphene oxide used for phenol detection [9], dopamine-inspired Au-assisted Raman monitoring of Cd²⁺ and polycyclic aromatic hydrocarbons [10], Au@Ag nanorod dimer-introduced dopamine detection [11], Ag nanocube-assisted Raman detection of protein [12] and thiram [13], and Ag-coated Au nanostar-supported Raman sensing of microplastic pollutants in water [14].
Phenol—also called benzenol, or mono-hydroxybenzene—has been known as the simplest compound of the aromatic alcohol group. Its main structure includes a benzene ring and a hydroxyl group (—OH) binding directly to one C atom of the aromatic ring. Although phenol can be toxic and its solutions with high concentration induce burned skin, it has been widely used as either primal raw materials or significant intermediates for the modern industrial manufacturing of many household products. For example, phenol with a suitable concentration has been used as one of the important ingredients in a mouth rinse thanks to its efficient bactericidal features. In industrial products, phenol has been widely adapted to use as an indispensable material to manufacture synthetic textiles, phenolic resins, plastics, dyes, and aspirin. Besides the benefits, phenols also caused serious chemical accidents through leakage [15], attracting many concerns of environmental scientists and governments owing to its negative risk impact on humans and the environment. For example, some researchers have recently investigated the ecotoxicity of phenol on four marine microalgae [16], the toxicological effects of phenol and cresols on aquatic organisms [17], and deriving hazardous concentrations of phenol in soil ecosystems [18].

Recently, various optical sensor techniques have been developed, such as colorimetric [19,20], fluorescence [21,22], LSPR phenomenon [23,24], and plasmon-enhanced surface enhanced Raman scattering (SERS) [25–27]. Among these techniques, the SERS method based on plasmonic resonance nanomaterials is promising because of its high specific, selective, and sensitive detection capability. Combining nanostructured materials, as an effective plasmonic resonance phenomenon, with Raman spectroscopy is becoming a potential analytic tool for trace detection of analyte molecules with many advantages such as easy-to-use, low-cost, specific targets, and on-site detection. Specific studies on the development of several novel nanomaterials have been reported to assist effective Raman platforms including nanogold film-based Raman detection of rhodamine 6G and p-nitrophenol [28], Raman detection of multiple analytes based on Ag nanoparticle-modified SiO₂ nanofibrous [29], Ag nanostructure-assisted Raman sensing for monofluoroacetic acid [30], Ag nanoparticle-introduced Raman detection of carbofuran [31], on-site Raman detection of 1,2,3-benzotriazole on colloidal lignin particles [32], Ag-capped silicon nanopillar-based Raman detection of ochratoxin A [33], nano-shell composite array-based Raman sensor for antioxidant [34], and bimetallic plasmonic nanoparticle-assisted Raman detection of hazardous contamination [35]. Moreover, a series of scientific reports on several special metal–organic framework (MOF) structures has been investigated, leading to successful fabrication of novel Raman substrates applied in trace detection of phenol red [36], phenol-soluble modulin [37], and engine oil [38].

Phenolic compounds—such as catechol, p-nitrophenol, 2,4-dichlorophenol, 2,6-dichlorophenol (2,6-DCP), cresol, 4-tert-butylphenol, 4-tert-octylphenol, alpha-napthol, dopamine, and so on—have been listed as hazardous substances by the United States Environmental Protection Agency owing to their toxicity [39]. Besides their significant potential application in industrial manufacturing, these compounds still faced some issues including environmental pollution and harmful effects on human health, in their included chemical products such as antioxidants, antimicrobials, and anti-inflammatory reagents that have been widely used in the daily activities of people [40,41].

In addition, 2,6-DCP—one of the most significant chlorophenol compounds—has been widely applied in industrial manufacturing for several chemicals, medical compounds, and other products, despite being potentially carcinogenic [42]. Recently, organic compounds with high toxicity such as p-nitrophenol have been found to cause increasingly serious pollution in environmental water [28]. As bisphenol substances have been considered as having a serious impact on the environment and human health risks, the early monitoring of these compounds is not only significant, but also still has many challenges.

Recently, there have been a large number of scientific reviews promising not only therapeutic applications of phenolic acids [43,44], but also phenolic compound’s effects on the environment and human health risk [25,45]. Furthermore, several authors have investigated varieties of analytical technologies using trace detection of phenolic sub-
stances such as electrochemical [39,46–49], liquid chromatography with diode array and mass spectrometry [50], high performance liquid chromatography [51,52], conductometric biosensor [53], photoelectrochemical reduction [54], voltammetric detection [55,56], biosensor electrode [57], and nanomaterial-based sensing [58]. However, these methodologies often require additional procedures for separation of analytes in sample preparation, leading to time-consuming and toxic organic solvents, as well as adverse effects on the environment. Detection of phenols still needs more consideration, focusing on the novel detection methods such as plasmonic resonance-based optical sensors.

Plasmonic resonance phenomenon-based Raman sensing has emerged as a scientific tool for detecting analytes using molecular vibrations on nanomaterial surfaces [59]. Raman technology has related to LSPR in terms of introducing nanogap-enhanced plasmonic behaviors on noble metal surfaces [60]. Raman scattering as a supplementary application in which LSPR plays a significant role, has been introduced to pollutant monitoring [61]. Although there have been several reports on surface plasmon-based Raman sensors for detecting phenolic substances [59–61], there is no literature review, despite their universal application. We evaluate and discuss the recent development and trends in designing unique structured materials that aid in plasmonic sensor platforms used for efficient detection of phenolic substances that affect the human health risk in this review to understand the correlations between the Raman technique and plasmonic resonance phenomena (Figure 1). The main content used for on-site detection of phenolic compounds using plasmonic resonance-based optical sensors can be divided into four parts: (1) colorimetric, (2) fluorescence, (3) localized SPR, and (4) Raman detection based on sensing platforms of pure noble metals, hybrid nanomaterials, and MOF structures.

Figure 1. Applications of plasmonic resonance-based optical sensor for on-site detection of phenolic compounds that impact the human health risk. Adapted from [2,31,43,44] with permission.
2. Plasmonic Resonance-Based Colorimetric Sensor for Phenolic Compounds

The colorimetric sensor is a simple method that has been widely used in the selective detection of analytes using color changes in probes under unique conditions. This method can be widely applied in environmental gas sensing [62] and trace detection of tetracyclines in foods [63] thanks to its convenient performance. For example, a paper-based bioassay has been developed by assembling alginate and chitosan layer-by-layer. A tyrosinase enzyme has been used to bind these layers, leading to successful bioassay-based colorimetric sensing of not only phenol, but also bisphenol A, catechol, and cresols. The detection limit of these phenolic substances has been estimated at 0.86 (±0.1) µg/L for each of the analytes [64]. A colorimetric sensor, based on plasmonic resonance nanomaterials, is one of the best analytical techniques for the efficient detection of various phenolic compounds by observing the color change of nanomaterials with either UV/Vis or the naked eye [39].

The basic principle of colorimetric technology is based on the specific interaction between the analytes with either pristine or probe-modified nanomaterials. For illustration, single-stranded DNA-regulated gold nanoparticle (GNP)-based colorimetric sensors have been demonstrated as an effective indicator for the sensitive detection of phenols [65]. As shown in Figure 2A, colorimetric detection of phenol has been successfully performed using Fenton reaction with a mixture of single-stranded DNA and initial GNPs. The authors have found that single-stranded DNA assisted in making initial GNPs more stabilized owing to electrostatic repulsion, leading to the prevention of GNP aggregation under the NaCl-introduced condition. However, these single-stranded DNAs have been destroyed by the Fenton reagents (OH free-radical) generating small fragments as mono- or oligonucleotide, resulting in the disruption of AuNP stability. In the presence of the phenolic substances, a reduction–oxidation between Fenton reagents and phenolic compounds will firstly occur to avoid the destruction of single-stranded DNA to assist the stability of GNPs from NaCl-induced aggregation.

Meanwhile, Figure 2B illustrates that OH free-radical generated from Fenton reagents could attack catechol, leading to a reduction in phenolic compounds. Either with the naked eye or using UV/Vis spectroscopy, a GNP-assisted sensor exhibits rapid micromolar detection of catechol and hydroquinone.

![Figure 2](image-url)

**Figure 2.** (A) AuNP-based colorimetric sensor for phenols’ detection by means of Fenton reaction. (B) Schematic diagram of the mechanism of catechol oxidation owing to OH free-radicals generated from Fenton reagents. Adapted from [65].
Colorimetric detection of bisphenol A has been successfully performed using specific aptamer-based and cationic polymer-assisted GNP aggregation with a limited detection as low as 1.50 nM [66]. In contrast, an aptasensor-based and GNP-assisted colorimetric technique has been developed for ultra-sensitive detection of bisphenol A. In this study, the authors have reported that GNPs have been modified with the two types of specific aptamers as truncated 38-mer and 12-mer, leading to the limits of bisphenol A detection of 7.60 pM and 14.41 pM, respectively [67]. On the other hand, elliptical or sphere shapes of Fe$_3$O$_4$ nanoparticles with an average size of 7 nm indicate successful colorimetric detection of phenol in a range of 1–200 mM concentration [19]. Among various plasmon resonance nanomaterials, spherical Au nanostructures are well-known as the best colorimetric sensing units. Recently, special MOF structures have emerged as a novel material construction successfully applied in colorimetric detection. Numerous MOF structures with tunable colorimetric characteristics have been well designed and synthesized, aiming to be applied for sensing various analytes, including organic compounds and gaseous pollutants [68].

Furthermore, some specific studies on smart MOF nanomaterials can effectively detect contaminants of phenolic compounds in the environment, which are extremely significant for human health protection. For example, the dual-functional Co-MOF-74-based Co$_3$O$_4$ nanoparticle-decorated cellulose derivative membrane has been well-synthesized for colorimetric detection of phenol [69]. Moreover, Zr-based MOFs capped with polyvinylpyrrolidone have been reported to successfully contribute to the application of colorimetric detection of phenol [70]. However, relying on the self-assembly of copper ions and DNA, the authors have successfully fabricated a novel copper hybrid nanoflower, which induces a new paper-based microfluidic device. This device has displayed effective application for the colorimetric detection of catechol, dopamine, and hydroquinone [20]. In addition, UV/Vis detection of 2,4-dichlorophenol has been successfully performed using an enzyme mimic that has been well-synthesized by Cu ion and adenosine monophosphate [71].

Through a solvothermal route, a new core–shell nanostructured metal of Au and Ni (Au@Ni) with a size < 8 nm on reduced graphene oxides (rGOs) was designed to obtain a novel nanomaterial composite as Au@Ni/rGO (Figure 3A). Subsequently, the peroxidase mimetic feature of this nanocomposite was checked by analyzing the process oxidation of 3,3',5,5'-tetramethylbenzidine in H$_2$O$_2$. As shown in Figure 3B, the examined results indicated that this nanocomposite exhibited excellent peroxidase mimetic activity, which has been successfully applied in colorimetric detection of phenol, relying on its oxidative reaction with 4-aminantipyrine, thereby inducing a change from colorless to pink of the quinoid dye in the presence of H$_2$O$_2$. The detection limit and range of this method have been estimated for phenol concentrations as low as 1.68 µM and 1–300 µM, respectively. In addition, under natural irradiated sunlight, these Au@Ni/rGO nanostructures exhibit an excellent photocatalytic reaction, thereby degrading over 87% of phenol and phenolic substances as 2-chlorophenol and 2-nitrophenol [72]. However, reduced graphene-based magnetic MOF nanocomposites exhibited an excellent enzyme-like feature. Phenol can be identified based on this property using a visual colorimetric method in water solution by oxidization of 4-aminantipyrine in the presence of H$_2$O$_2$. Simultaneously, these nanocomposites have also been exposed to a specific feature as a Fenton-like catalyst, which shows a high ability to degrade phenol effectively [73].
3. Plasmonic Resonance-Based Fluorescence Sensor for Phenolic Compounds

As a normal type of optical sensor, fluorescence techniques have been extensively applied in many fields, such as fast detection of phenolic substances [22], bioimaging [74], detection of aniline [75], determination of peroxynitrite products [76], analysis of total phenolic substances in teas [21], quantification of bisphenol A and its derivatives [77], determination of phenolics [78], and aptamer-labeled fluorescent detection of bisphenol A [79]. Plasmonic resonance-based fluorescence method has been used predominantly, because of its excellent plasmonic resonance mechanism. Various scientific studies have reported the successful fabrication of novel plasmonic resonance nanomaterials that exhibit uniform geometries and enhanced plasmon, aiming to assist fluorescence technology. Great efforts have been made on new nanomaterials with high plasmon resonance, such as AgNP-based fluorescence sensors for trace detection of dopamine [80], bimetallic Au-Ag nanocluster-assisted fluorescent biosensing of dicofol [81], polyethyleneimine-modified ovalbumin-stabilized gold nanoclusters (AuNCs) used for fluorescence sensor of tetracyclines [82], and MOF-based fluorescence detection of bisphenol substances [40]. A fluorescent sensor of 2,6-dimethyl phenol in seawater has been successfully performed relying on Eu$^{3+}$-2-aminoterephthalate immobilized on mesoporous silica nanoparticles [83].

As shown in Figure 4, although dopamine has been known as one of the most significant neurotransmitters in the human body, its specific monitoring remains many chal-
Using a one-pot process, the authors successfully fabricated bimetallic Au-Ag nanoclusters using a protein template as bovine serum albumin. These initial Au-Ag hybrid nanoclusters have been found to exhibit a weak level of fluorescent intensity. However, dopamine has been introduced to enhance the extremely strong fluorescent intensity of nanoclusters, simultaneously causing a red shift in the spectrum. Using electrochemical spectroscopy, dopamine has contributed to reducing Au-Ag hybrid nanoclusters, enhancing their fluorescence, which has been adopted for trace and sensitive detection of dopamine. This facile and efficient method provided a limit of detection of dopamine at 6.9 nM [84].

Figure 4. (A) Schematic diagram of bimetal Au-Ag nanocluster-based fluorescence detection of dopamine. (B) (a) Fluorescence intensity-correlated different concentrations of dopamine samples at 0, 0.01, 0.08, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 µM labeled from “a” to “m”. (b) A linear curve of fluorescence intensities correlated with the concentrations of dopamine at pH 8.5 Tris-HCl buffer. Fluorescence measurements under 370 nm excitation after 15 min incubations. Adapted from [84].

Figure 5 shows a dual-emissive AuNC-based sensor technique used for detecting 4-NP by means of fluorescence quenching. Herein, the first AuNCs were synthesized and stabilized by BSA to form the AuNCs@BSA complex. Subsequently, the inner filter effect (IFE), indicated that 4-NP selectively induced fluorescence quenching at 410 nm (F_{410}) of residual di-tyrosine (diTyr) more effectively than that at 630 nm (F_{630}) of AuNCs. Within 1 min, this sensor was successfully employed for trace detection of 4-NP by measuring the ratio of fluorescence intensity of F_{410}/F_{630}. Based on the 4-NP concentration-correlated ratio of F_{410}/F_{630}, its limit of detection was estimated at 13.8 nM (1.9 ng/mL). Furthermore, this technique shows highly sensitive and selective detection of 4-NP, despite the presence of eight other common phenol derivatives. Thus, this method was practically applied for an efficient analysis of trace 4-NP in actual river water samples [85].
Other authors have successfully developed a novel Zn porphyrin MOF-based fluorescence sensor of bisphenol A detection using luminescence quenching. The experimental fluorescence data indicated that these MOF structures exhibited excellent monitoring of bisphenol A thanks to their electrostatic interaction, causing high sensitivity and selectivity in fluorescence quenching. In contrast, there was no significant quenching when the MOFs encountered the other phenolic substances, including p-cinnamyl phenol nonylphenol, octylphenol, 4-tert-butylphenol, 2,4-ditert-butylphenol, and diphenyl carbonate [86].

4. Localized Surface Plasmon Resonance Phenomenon-Based Optical Sensor for Phenolic Compounds

LSPR has been responsible for an enhanced electromagnetic field, inducing surface-enhanced spectroscopic technologies [87]. Several scientists are increasingly interested in plasmon resonance-based optical sensors, especially noble metal nanostructured materials such as Pt, Au, and Ag nanoparticles with various shapes and sizes, exhibiting plasmonic features that have been successfully used as a powerful analytic technique [6,88]. Here, these plasmonic nanostructures were practically employed as efficient transducers that convert changes in the spectral location of refractive index, thereby shifting the LSPR peak upon binding of analytes to either the surface of bare plasmonic nanostructures or specific receptor-conjugated nanomaterials. By coating unique probe molecules on the surface of plasmonic nanomaterials, LSPR-shift assay-based sensor techniques were introduced for specific analytics, considering a change in the signal localization of refractive index around their surfaces [89]. In addition, graphene oxide-based nanostructured hybrids have been successfully used as a novel material for enhanced SPR sensors thanks to their significant features, including strong adsorbed molecules, amplified signals, high electronic bridge, and simple fabrication. Moreover, regarding amplification of signals obtained by plasmonic materials, graphene-based nanostructure composites can significantly increase the sensitive detection of analytes up to fM [90]. Owing to their sensitivity and the selectivity of the spectral location of the refractive index, SPR-based optical sensors have been widely...
investigated in sensing applications such as mercury ion detection \[8,91\], CO\(_2\) detection \[1\], and gas sensors \[2\]. Some special emphasis on plasmonic nanostructures has been developed for the fabrication of novel surfaces, exposing high SPR-based optical sensors for phenolic compounds, such as GNP impregnation in TiO\(_2\) structure-assisted hydroquinone detection \[24\], Au- and tyrosinase-modified graphene oxide film-introduced detection of phenol \[9\], and polymeric film-based phenol determination \[92\].

As shown in Figure 6A, an SPR-based optical sensor method was successfully implemented for dopamine detection based on a sensing layer of chitosan and graphene quantum dots, which were fabricated on Au thin film. The system of the SPR angle shift-based optical sensor showed a detection limit of 1.0 fM of dopamine \[93\]. In contrast, Figure 6B shows an innovative polyaniline/Pt-coated fiber optic-based SPR sensor used for ultra-sensitive detection of 4-nitrophenol, with a limit of detection of 0.34 pM \[23\].

![Figure 6A](image1.png)

**Figure 6.** (A) Schematic diagram of dopamine detection using composites of chitosan/graphene quantum dots/Au thin film by means of SPR spectroscopy. Reproduced with permission from \[93\]. (B) Schematic diagram of 4-nitrophenol detection using innovative polyaniline/Pt-coated fiber optic-based SPR sensing substrate. Adapted from \[23\].
Recently, SPR-based sensor systems have also been introduced for application in photoelectrochemistry. Many scientists have investigated the optimized fabrication of new plasmonic nanomaterials, demonstrating unique features such as high and excellent plasmon enhancement as well as assistance for photoelectrochemical technologies. For example, there are several reports on Au-decorated La$_2$Ti$_2$O$_7$/rGO-based plasmon enhancement-assisted photoelectrochemical monitoring of bisphenol A [94], SPR of GNP-activated g-C$_3$N$_4$ nanosheet-based photoelectrochemical determination of bisphenol A [95], and LSPR using carbon dot-functionalized GNPs for sensing of dopamine [96].

5. Plasmonic Resonance-Based Raman Sensors for Detection of Phenolic Compounds

Raman spectroscopic technologies—including micro-Raman mapping, imaging, and SERS spectroscopy—have been widely adopted in many fields such as food safety [97], the monitoring of contaminants [98], and the diagnosis of disease biomarkers [99]. Raman substrates may be divided by several kinds of pure noble metal nanostructured materials, hybrid nanomaterials, and MOF structures.

5.1. Pure Noble Metal Nanomaterial-Based Raman Sensors

Plasmonic nanostructured materials have been well known as one of the most significant keys leading to the success of sensing technologies thanks to their effective Raman-active substrates. Among various nanomaterials, Au and Ag as noble metals have been adapted as a potential platform, which has contributed to the sensitive Raman detection [5,100]. Furthermore, the unique shape and size of noble metals induce highly dense plasmonic hotspots to increase the sensitivity of the Raman method. Many scientists have discovered more novel structures of noble metals that aim to maximize the generation of a high density of plasmonic hotspots, inducing enhanced electromagnetic fields and amplified Raman signals. Besides the preparation of new structures, the modification of the surface of nanostructures were performed by specific probes for the sensitivity and selectivity of Raman sensing. For example, great efforts have been made toward this goal. AgNP-assisted Raman detection for bisphenol A determination [101] and GNP-induced Raman platforms for methyl parathion detection [102] have been considered.

Interestingly, Figure 7A shows SEM images of unique nanostructures of Ag nanorod bundles. Herein, Ag nanorods were well aligned as vertical bundles distributed on an Au/Cu template. This uniformity of Ag nanorod bundles demonstrates a potential application as a Raman-active platform used for trace detection of phenolic pollutants, including 4-chlorobiphenyl, methyl parathion, 2,4-dichlorophenoxyacetic acid (2,4-D), and two pesticides mixtures in water environments. Vertical bundles of Ag nanorod were well designed by combining porous anodic aluminum oxide membranes and spherical polystyrene templates. Based on the well-controlled ~65 nm diameter of AAO pores, the diameter of the Ag nanorods was also well achieved, such as the size of AAO pores. Figure 7A(a,b) show that vertical bundles of Ag-nanorod were well arranged with a P6mm hexagonal symmetry. Each vertical bundle was surrounded by three other bundles and comprised an ~800 nm length size of 30–45 nanorods with a ~65 nm diameter (Figure 7A(c,d)). This unique structure exhibits a small gap (2 nm), leading to highly dense hot spots, inducing an enhanced Raman signal up to $10^8$. As shown in Figure 7B, to further illustrate the practical application of this Raman platform, vertical bundle arrays of Ag nanorods were used to detect phenolic pollutants of methyl parathion and 2,4-D in the environment using Raman spectroscopy, whose limits of detection were estimated as $21.5 \times 10^{-9}$ M and $61.9 \times 10^{-9}$ M, respectively [103].
Figure 7. (A) SEM images of vertical bundles of Ag nanorods including top views with different scale bars of (a) 1 μm and (b) 2 μm, (c) side view of vertical bundle arrays of Ag nanorods, and (d) top view of one unique bundle of Ag-nanorods. (B) Vertical bundle arrays of Ag nanorod-based Raman detection of phenolic pollutants of (a) methyl parathion (0.3 × 10^{-6} M). (b) Linear curve of logarithmic concentration of methyl parathion-correlated Raman intensities (1260 cm^{-1}). (c) Raman spectra of 2,4-D (2 × 10^{-6} M). (d) Linear curve of logarithmic concentration of 2,4-D-correlated Raman intensities (1177 cm^{-1}). Adapted from [103].
An easy and rapid detection of bisphenol A detection has been successfully developed using Raman spectroscopy and a matrix of molecularly imprinted polymers (MIPs), where silver nanoparticles (AgNPs) were fabricated in situ inside this matrix. AgNPs have been well distributed in the matrix, leading to highly dense hotspots. Therefore, these Raman nanosensors of MIPs@AgNPs exhibit not only highly selective detection of bisphenol A in the presence of various similar molecules such as bisphenol AF and diethylstilbestrol, with an excellent detection limit as low as $5 \times 10^{-8}$ M. Raman nanosensors exhibit the potential for practical applications with many benefits of easy fabrication, reusability, selectivity, and sensitive recognition [101].

Interestingly, Figure 8 demonstrates an AgNP-based microfluidic Raman biosensor for the highly sensitive detection of dopamine using DNA-assisted fabrication of ortho-nanodimers. Raman probes were modified with dopamine aptamers and 5,5′-dithiobis-(2-nitrobenzoic acid) (DTNB); these aptamers were well designed as unique zipper-like ortho-Ag nanodimers. Owing to the small gap in the specific zipper-like ortho-Ag nanodimers, the microfluidic Raman biosensor exhibited a highly targeted detection of dopamine, with a limit of detection as low as 10 aM [104].

![Figure 8](image)

**Figure 8.** (A) Schematic diagram of Raman detection of dopamine (DA) using DNA-assisted synthesis of ortho-nanodimers (DaSON) of AgNPs. SEM images of Raman platforms with a scale bar of 500 nm (B) before and (C) after the adsorption of Raman probes containing DA aptamers and DTNB. Inserted pictures show an enlarged view of the yellow rectangle. Adapted from [104].

### 5.2. Hybrid Nanomaterial-Based Raman Sensors

As one of the most efficient plasmonic materials, hybrid nanomaterials—either bimetallic nanostructures or nanocomposites—have been widely adapted to prepare Raman substrates used in various fields as biosensors and environments. Recently, a novel Raman method has been developed to detect phenolic acids—vanillic acid, syringic acid, and gallic acid—using three-dimensional nanoprobe of a self-assembled composite of GNPs and SiO$_2$ [34]. In addition, AgNP-embedded poly (diallyl dimethyl-ammonium) chloride has been successfully used as a Raman substrate for biosensors, where this substrate was fabricated by modifying graphene oxide nanosheets. AgNPs have been well designed, yielding highly dense hotspots for enhanced Raman signals [105]. Owing to their excellent electromagnetic mechanism, bimetallic nanostructures have been used predominantly as biosensors, as shown in Figure 9.
Some authors have successfully self-assembled core–shell structured dimers of bimetallic Au@Ag nanorods, which were used as Raman nanosensors, particularly for detecting dopamine—a neurotransmitter—playing a key role in life. Based on aptamers and the electronic field of Ag shell coating outside the Au nanorod dimer, Raman signals have been well enhanced, indicating that the substrates exhibited an ultra-sensitive limit of dopamine detection at 0.006 pM [11]. As shown in Figure 10, Raman detection of chlorophenols was investigated by MIPs based on composites of SiO$_2$, rGO, and Au. Nanocomposite-based Raman have significantly enhanced signals, leading high sensitivity in chlorophenol detection [106]. Despite numerous efforts of Raman sensors based on plasmonic materials as nanostructures of noble metals and hybrids, more scientific studies are required to develop functional plasmonic nanostructured materials used for optical sensors. To understand plasmonic phenomena and interfaces of materials, some authors have discovered various MOF structures and revealed their effective ability for multi-detection of phenolic substances using SERS spectroscopy. In the next section, this review reveals several significant contributions to phenolic compound detection from MOF-assisted SERS sensors, according to some interesting examples.

![Figure 9](image_url)  
**Figure 9.** Schematic diagram of dopamine detection using bimetallic Au@Ag nanorod dimers, Raman reporter of 4-aminothiophenol, and aptamer. Adapted from [11].

![Figure 10](image_url)  
**Figure 10.** (A) Schematic diagram of trace detection of 2,6-DCP using Raman spectroscopy and MIPs based on nanocomposites of SiO$_2$/rGO/Au. (B) TEM images of (a) SiO$_2$/rGO, (b) composites of polyaniline reporter of 4-aminothiophenol, and aptamer. Adapted from [11].

![Figure 11A](image_url)  
**Figure 11A.** A core–shell nanostructure of Cu$_2$O and SiO$_2$ was coated with ZIF-8, AgNPs were uniformly distributed in the structures of Cu$_2$O@SiO$_2$@ZIF-8 templates, exhibited an excellent limit of detection, as low level as 5.76 × 10$^{-12}$ M concentration of phenol red in real samples. These Cu$_2$O@SiO$_2$@ZIF-8@Ag as 3D substrates could be employed for Raman signal enhancement and chemical enhancement mechanisms of these Raman substrates. Firstly, owing to the strong interaction with N and S atoms inside the ZIF-8 structure, thereby effectively preventing AgNP aggregation.

![Figure 11B](image_url)  
**Figure 11B.** Subsequently, in situ synthesis of AgNPs with various sizes from 2 nm to 29 nm on the surface of these MOFs was performed, inducing new MOFs and Cu$_2$O@SiO$_2$@ZIF-8@Ag. Owing to the strong interaction with ZIF-8, AgNPs were uniformly distributed in the structures of Cu$_2$O@SiO$_2$@ZIF-8, AgNPs, successfully yielding a novel Cu$_2$O@SiO$_2$@ZIF-8. Subsequently, in situ synthesis of AgNPs with various sizes from 2 nm to 29 nm on the surface of these MOFs was performed, inducing new MOFs and Cu$_2$O@SiO$_2$@ZIF-8@Ag. Owing to the strong interaction with ZIF-8, AgNPs were uniformly distributed in the structures of Cu$_2$O@SiO$_2$@ZIF-8, AgNPs, successfully yielding a novel Cu$_2$O@SiO$_2$@ZIF-8.
of polydopamine modified SiO$_2$/rGO/Au, (c) nanocomposites of SiO$_2$/rGO/Au, and (d) SEM image of SiO$_2$/rGO/Au nanocomposites. (C) Concentration-dependent Raman spectra of 2,6-DCP. (D) Linear curve of 2,6-DCP concentration-correlated Raman intensities at 661 cm$^{-1}$. Adapted from [106].

5.3. Metal–Organic Frameworks Structure-Introduced Raman Sensors

As shown in Figure 11A, a core–shell nanostructure of Cu$_2$O and SiO$_2$ was coated with ~4 nm porous Zn-based MOFs (ZIF-8) using an organic bridge as 5-mercapto-1-methyltetrazole, successfully yielding a novel Cu$_2$O@SiO$_2$@ZIF-8. Subsequently, in situ synthesis of AgNPs with various sizes from 2 nm to 29 nm on the surface of these MOFs was performed, inducing new MOFs and Cu$_2$O@SiO$_2$@ZIF-8@Ag. Owing to the strong interaction with ZIF-8, AgNPs were uniformly distributed in the structures of Cu$_2$O@SiO$_2$@ZIF-8. Interestingly, 4 nm AgNPs, assembled on Cu$_2$O@SiO$_2$@ZIF-8 templates, exhibited an excellent limit of detection, as low as level of 5.76×10$^{-12}$ M concentration of phenol red in real samples. These Cu$_2$O@SiO$_2$@ZIF-8@Ag as 3D substrates could be employed for Raman monitoring of environmental contaminants [36]. Figure 11B shows the electromagnetic and chemical enhancement mechanisms of these Raman substrates. Firstly, owing to the many porous structures in Cu$_2$O@SiO$_2$@ZIF-8, AgNPs can be powerfully adsorbed and well loaded by the strong interaction with N and S atoms inside the ZIF-8 structure, thereby effectively preventing AgNP aggregation.

Second, Cu$_2$O@SiO$_2$@ZIF-8@Ag exhibited a large surface area, assisting in the absorption of many phenol red molecules and strong binding between Ag and S atom via the Ag–S bond. However, owing to the high density of AgNPs on the surface of the MOF template, this SERS substrate generated many hotspots, enhancing Raman signals of phenol red that correspond to the electromagnetic mechanism. In contrast, charge transfer occurs as a result of the chemical enhancement mechanism between MOFs and phenol red molecules. Here, AgNPs provided an SPR phenomenon and encouraged charge transfer in the SERS system, increasing SERS signals. Importantly, a small size ~4 nm of AgNPs provides a maximum SERS signal of an MOF template because of more AgNPs located in porous ZIF-8. Nevertheless, different sizes of AgNPs will not properly match ZIF-8 pores, yielding weak Raman intensities [36].

As shown in Figure 12, the Raman sensor was combined with MIPs, inducing the distribution of a new Raman detection for selectivity of chloro-phenols. The Raman platforms as Ag@MIL-101(Fe)@MIPs were successfully fabricated by in situ synthesis of AgNPs on the surface of MOFs octahedral structures as MIL-101(Fe), subsequently, by polymerized precipitation between a template and a functional monomer as 2,6-DCP and acrylamide, respectively. MOF-based nanocomposite-assisted Raman monitoring of 2,6-
DCP with a limit of detection of 4.5 nmol/L. This method provides a potential Raman template not only for sensing other chlorophenols, but also for real sample analysis using Raman spectroscopy [42].

As summarized in Table 1, based on plasmonic nanomaterials, numerous novel optical sensor technologies have been successfully developed for trace detection of phenol and phenolic compounds, with improvements in aspects such as selectivity and sensitivity as well as economical and reproducible benefits. The following aspects were studied and evaluated on the current spectroscopic and optical sensor methods. There are several perspectives to be addressed in future studies: (i) improving optical sensor methods based on pure, noble metal nanomaterials, and hybrid nanostructured materials; (ii) developing more MOFs that exhibit high target sensor; (iii) exhibiting the ability of multiple detections of similar analytes under various conditions; (iv) developing a dual functional sensing platform used for both Raman spectroscopy and fluorescence detection or both colorimetric and fluorescence; and (v) preparing a new nanomaterial that exhibits the ability of trace detection simultaneously and the removal of phenol and phenolic contaminants.
Table 1. Comparison of plasmonic resonance-based optical sensors for on-site detection of phenolic compounds.

| Plasmonic Structures                          | Detection Methods | Target Compounds | Limit of Detection | Reference |
|-----------------------------------------------|-------------------|------------------|--------------------|-----------|
| Au-modified tyrosinase-based GO thin film     | SPR               | phenol           | 1 µM               | [9]       |
| Au@Ag nanorod dimers                         | Raman             | dopamine         | 0.006 pM           | [11]      |
| DNA–copper hybrid nanoflowers                | colorimetric      | dopamine         | 4.5 µg/mL          | [20]      |
|                                             |                   | catechol         | 3.0 µg/mL          |           |
|                                             |                   | hydroquinone     | 4.5 µg/mL          |           |
| polyaniline/Pt-coated fiber optic            | SPR               | 4-nitrophenol    | 0.34 pM            | [23]      |
| GNP@TiO<sub>2</sub>                          | SPR               | hydroquinone     | 33.8 nM            | [24]      |
| SiO<sub>2</sub>/GPNPs                        | Raman             | vanillyc acid    | 10–250 µM          | [34]      |
|                                              |                   | syringic acid    | 10–110 µM          |           |
| Cu<sub>2</sub>O@SiO<sub>2</sub>@ZIF-8@Ag    | Raman             | phenol red       | 5.76 × 10<sup>−12</sup> M | [36] |
| Ag@MIL-101(Fe)@MIPs                         | Raman             | 2,6-dichlorophenol | 4.5 nmol/L        | [42]      |
| GPNs                                          | colorimetric      | catechol         | 0.11 µM            | [65]      |
|                                              |                   | hydroquinone     | 1.6 µM             |           |
| Co-MOF-74-based Co<sub>3</sub>O<sub>4</sub>/cellulose | colorimetric   | phenol           | 1.02 µM            | [69]      |
| Zr(IV)-based MOFs                           | colorimetric      | phenol           | 1.28 µM            | [70]      |
| Adenosine monophosphate-Cu nanozymes         | UV/Vis            | phenolic compounds | 0.033 µmol/L     | [71]      |
| Au@Ni/rGO nanocomposite                     | colorimetric      | phenol           | 1.68 µM            | [72]      |
| Fe<sub>3</sub>O<sub>4</sub>/rGO/MOF          | colorimetric      | phenol           | 3.33 × 10<sup>−6</sup> M | [73] |
| AgNPs                                        | fluorescence      | dopamine         | 5.3934 × 10<sup>−6</sup> M | [80] |
| Au-Ag nanocluster                           | fluorescence      | dopamine         | 6.9 nM             | [84]      |
| Au nanoclusters                             | fluorescence      | 4-nitrophenol    | 13.8 nM            | [85]      |
| chitosan/graphene quantum dots/Au thin film | SPR               | dopamine         | 1.0 fM             | [93]      |
| carbon dot-functionalized GPNs               | SPR               | dopamine         | 0.23 µM            | [96]      |
| GPNs                                         | Raman             | methyl parathion | 0.011 µg/cm<sup>2</sup> | [102]    |
| Ag-nanorod bundles                          | Raman             | methyl parathion | 21.5 × 10<sup>−9</sup> M | [103]    |
| zipper-like ortho-Ag nanodimers             | Raman             | dopamine         | 10 M               | [104]     |
| AgNPs-graphene based nanosheets             | Raman             | p-cresol         | 10<sup>−5</sup> M  | [105]     |
| SiO<sub>2</sub>/GO/Au                        | Raman             | 2,6-dichlorophenol | 100–1.0 nM        | [106]     |
| Au-ZnO nanoparticle-modified tapered optical fiber | SPR              | p-cresol         | 57.43 µM           | [107]     |
| ZnO/MoS<sub>2</sub>                         | SPR               | p-cresol         | 28 nM              | [108]     |
| cetyltrimethylammonium-bromide-functionalized ZnO/carbon nanotube nanocomposite coated over Ag film | SPR | plasmonic sensor | catechol | 0.1 µM | [109] |
6. Conclusions

This review focused on recent developments in optical sensors, including colorimetric, fluorescence, LSPR, and plasmon-enhanced Raman scattering, used to determine phenol and phenolic compounds. Combined with numerous plasmonic nanomaterials such as noble metals, hybrids, and MOFs, these optical methods have been widely applied in many chemical and biological fields by improving sensing performance. Here, this review mainly discussed numerous novel designs of unique nanostructures, inducing enhanced signals, and selective sensing analytes. Among these optical sensors, colorimetric methods showed many benefits such as facile observation with the naked eyes, whereas the Raman method exhibited more selective molecular fingerprints. While the LSPR method revealed an excellent feature of high sensitivity, fluorescence assays showed an ultra-sensitive detection and limited stability for photo-bleaching. Notably, the development of plasmon resonance-based optical sensors for phenol detection indicates that future work would continue exploring superior nanomaterials for phenol determination with simpler manipulation, faster response, higher sensitivity, and better selectivity. We also believe that the combination of new plasmonic nanomaterials with traditional molecular design can improve sensing performance even further.

Author Contributions: Conceptualization, N.H.L., H.H.K. and S.J.S.; methodology, H.H.K.; resources, H.H.K.; data writing—original draft preparation, N.H.L.; writing—review and editing, S.J.S.; visualization, S.-W.J.; supervision, S.J.S. and S.-W.J. All authors have read and agreed to the published version of the manuscript.

Funding: Korea Ministry of Environment (MOE) as The Chemical Accident Prevention Technology Development Project and Korea Environment Industry and Technology Institute (KEITI) through Technology Development Project for Safety Management of Household Chemical Products Program, funded by the Korea Ministry of Environment (MOE) (2020002970005, 1485017845).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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