Highly efficient visible-light-driven plasmonic photocatalysts based on graphene oxide-hybridized one-dimensional Ag/AgCl heteroarchitectures†

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In this paper, we report that one-dimensional (1D) Ag/AgCl nanostructures could be facilely fabricated by means of an oxidation-chloridization process, wherein prefabricated 1D Ag nanowires are employed as a template. Graphene oxide (GO)-hybridized 1D Ag/AgCl nanocomposites, Ag/AgCl/GO, could also be easily formulated when GO nanosheets are involved during the oxidation-chloridization procedure. We find that compared with the parent plain 1D Ag nanowires, commercially available P25-TiO2, and spherical Ag/AgCl nanospecies, the as-produced 1D Ag/AgCl nanostructures could be used as high-performance visible-light-driven plasmonic photocatalysts for the photodegradation of organic pollutants. Moreover, the 1D Ag/AgCl/GO nanocomposites exhibit enhanced photocatalytic activity compared with the corresponding 1D Ag/AgCl nanostructures. Our experimental facts indicate that the cooperative or synergistic effects between the intrinsic morphological features of the 1D nanostructures, which facilitates an efficient directional electron transport and suppresses the scattering of the free electrons, and the advantages brought out by GO nanosheets, which favors a nice adsorption of methyl orange (MO) molecules and an efficient charge separation, conjointly contribute to the enhanced photocatalytic performance of the 1D Ag/AgCl/GO nanocomposites. This work might initiate new and more varied opportunities for the development of visible-light-driven high-performance plasmonic photocatalysts for the photodegradation of organic pollutants.

1. Introduction

Nanostructured architectures with various dimensions, including zero-, one-, two-, and three-dimensional (0D, 1D, 2D, and 3D) nanomaterials, have received broad interest both in the scientific and technological communities, owing to their unique size- and/or shape-dependent physicochemical properties, as well summarized by recent review articles.1–8 Among these nanostructures, 1D nanospecies such as nanowires, nanorods, etc., have become the focus of intensive research aimed at developing various materials with unique advanced functions. This is essentially due to their bright possibilities for application in nanoelectronics, photonics, catalysis, and others more.9–17 Among these sophisticated applications, 1D nanostructure-based catalysts have received particular attention, since they might initiate new opportunities for the development of high-performance catalytic species.15–20 This is due to their intrinsic large aspect ratio, which favors a directional charge transport with a reduced grain boundary. This endows them with superior charge transport properties, which generally play an important role for the enhancement of photocatalytic performances.15–20

In the frontier area of catalysis, the investigation of the development of efficient photocatalysts for the degradation of organic pollutants has currently been considered to be an issue of paramount importance, since the overwhelming environmental problem calls for more varied and alternative opportunities for pollutant degradation.21–23 From this point of view, 1D nanomaterial-based photocatalysts might match the high requirements of future environmental problems.18–20,24–30

With respect to photocatalysts for the organic pollutants degradation, numerous UV-light-driven photocatalytic species have been developed.21–23 However, considering energy utilization and saving, investigation focusing on the development of visible-light-energized photocatalysts is a significant issue to be explored intensively and extensively.23 Visible-light-driven photocatalysts have become one of the hottest topics in the field of organic pollutant photodegradation, wherein those based on the plasmonic absorptions aroused by metallic nanospecies have gained much interest.15–38 This is owing to their highly efficient catalytic activity, distinct stability, and ease of synthesis and characterization. It has
been demonstrated that silver/silver chloride-based (Ag/AgCl) plasmonic photocatalysts display distinguished photocatalytic performance for the photodegradation of organic pollutants under visible-light irradiation. Their intrinsic responses to visible-light could be attributed to the existence of metallic Ag nanoparticles, which could give rise to distinct plasmon resonance absorptions in the visible region. At the same time, the Ag-nanospecies could also favor efficient charge separation/transfer, resulting in a boosted photocatalytic performance.

On another front, due to high optical transmittance, high chemical and thermal stability, large specific surface area, nice locally conjugated aromatic system, nice dispersibility in aqueous systems, and unique electronic properties, graphene oxide (GO) nanosheets have been recognized to be one of the most ideal candidates as catalyst carrier or promoter. In this regard, great efforts have been paid on the hybridization of GO and non-1D nanostructures, while those focusing on 1D nanomaterials are relatively fewer. As a matter of fact, by taking advantage of the above-mentioned merits of 1D nanostructures and GO, it is strongly desired that highly efficient photocatalysts are realized by hybridization of these two components. Consequently, considering the general and broad interest in 1D nanostructures, visible-light-driven Ag/AgCl-based plasmonic photocatalysts, GO-involved catalysts, and the importance of environmental problems as well, an investigation on the development of GO-hybridized 1D Ag/AgCl plasmonic photocatalysts for the photodegradation of organic pollutants might provide more and new opportunities for pollutant elimination, which is an issue of paramount importance.

On the basis of the above-described background, we herein report the fabrication of high-performance plasmonic photocatalysts in terms of a hybridization of GO nanosheets and 1D Ag/AgCl nanostructures. By means of an in situ oxidation and chloridization of the prefabricated 1D Ag nanowires, wherein H$_2$O$_2$ and HCl are used as oxidizing and chloridizing agents, respectively, we show that 1D Ag/AgCl nanoarchitectures could be easily synthesized under ambient conditions. It is disclosed that, compared with the parent plain 1D Ag nanowires, thus-fabricated 1D Ag/AgCl nanostructures could exhibit distinct photocatalytic performance for the photodegradation of methyl orange (MO) and 4-chlorophenol (4-CP) pollutants under visible-light irradiation. The catalytic performance of our 1D Ag/AgCl could be further distinctly enhanced upon the hybridization of GO nanosheets (Ag/AgCl/GO). At the same time, we demonstrate that, compared with the previously synthesized spherical Ag/AgCl and Ag/AgCl/GO nanospecies, the corresponding 1D Ag/AgCl and Ag/AgCl/GO nanostructures display much higher photocatalytic activity, indicating the advantage of our present 1D plasmonic photocatalysts. Our work might open up new possibilities for the development of highly efficient visible-light-driven plasmonic photocatalysts for the degradation of organic pollutants.

2. Experimental section

2.1. Materials

Silver nitrate (AgNO$_3$, Sigma-Aldrich, >99%), hydrogen peroxide (H$_2$O$_2$, 30%, Beijing Chemical Works, A.R.), concentrated hydrochloride (HCl, 36–38%, Beijing Chemical Works, A.R.), anhydrous ethylene glycol (EG, TCI, >99.5%), poly(vinylpyrrolidone) (PVP, TCI, $M_w$: 40 000), and graphite powder (Alfa Aesar, 325mesh, 99.999%) were used as received without further treatments. P25-TiO$_2$ (ca. 80% anatase and 20% rutile) nanospheres were purchased from Degussa, and were used as the reference catalyst for comparison.

2.2. Synthesis of graphene oxide (GO) nanosheets

GO nanosheets were synthesized through a chemical exfoliation of graphite powder by using a modified Hummers’ method. The synthesis procedure was carried out according to the methods described previously.

2.3. Synthesis of Ag nanowires

The 1D Ag nanowires were prepared by means of a polyol process described elsewhere. In a typical procedure, 5 mL of anhydrous EG was stirred with a magnetic bar and heated to 160 °C in a three-necked round-bottomed flask. Then, solutions of PVP (0.1275 M) and AgNO$_3$ (0.085 M) dispersed in anhydrous EG (each 3 mL) were drop-wise injected simultaneously into the hot PVP solution by a syringe at a rate of approximately 0.3 mL min$^{-1}$. After all of the solutions were added, the heating and stirring were continued for another 60 min until the solution turned gray. When the reaction was finished, the mixture was cooled to room temperature, and was then diluted with ethanol and centrifuged (2000 rpm, 15 min). The supernatant was taken out in order to remove the excess PVP and unconverted salts. This process was repeated at least six times.

2.4. Synthesis of 1D Ag/AgCl and Ag/AgCl/GO nanostructures

In a typical process, a 250 µL aqueous solution of GO nanosheets (1 mg mL$^{-1}$) was added dropwise into a 5 mL aqueous solution of H$_2$O$_2$ (0.15 mol L$^{-1}$) under vigorous magnetic stirring. Subsequently, a 500 µL solution of 1D Ag nanowires, which contained ca. 1 mg Ag nanostructures, was added into the system. After that, a 250 µL aqueous solution of HCl (0.1 mol L$^{-1}$) was also dropped into the above aqueous solution within 3 minutes under vigorous magnetic stirring. The stirring was maintained for another 20 min, after which a dispersion containing 1D Ag/AgCl/GO hybrid nanocomposite was obtained. The resultant solids were collected by centrifugation (10 000 rpm, 10 min). When only 1D Ag nanowires but no GO nanosheets were involved during the synthesis procedure, the corresponding bare 1D Ag/AgCl heterostructures could also be synthesized via a parallel process.

2.5. Photocatalytic performance

For the photocatalytic experiments, photocatalysts typically involving 1 mg Ag/AgCl or Ag/AgCl/GO nanospecies were dispersed in a 4 mL aqueous solution of methyl orange (MO, 10 mg L$^{-1}$), with a quartz cuvette used as the reactor. A 500 W xenon arc lamp installed in a laboratory lamp housing system (CHF-XM35-500 W, Beijing Trusttech Co. Ltd., China) was employed as the light source. The light passed through a 10 cm
water filter and a UV cutoff filter (>400 nm) before entering the reactor. The reaction system was kept for 30 min in a dark room to achieve an equilibrium adsorption state before visible-light irradiation. An aliquot of the dispersion (0.25 mL) was taken from the reaction system for real-time sampling. For the evaluation of the photocatalytic activities, \( C \) is the concentration of MO dye at a real-time \( t \), and \( C_0 \) is that in the MO solution immediately before it was kept in a dark room. For comparison, we also investigated the photocatalytic performance of the commercially available P25-TiO\(_2\), and the spherical Ag/AgCl and Ag/AgCl/GO nanospecies previously synthesized via a water/oil emulsion method.\(^{36}\) In these cases, ca. 1 mg of the above-referenced photocatalysts were employed. The photocatalytic performance of our samples was also investigated in terms of the photodegradation of 4-chlorophenol (4-CP) pollutant, which had no absorption in visible region, under visible-light irradiation. In this case, the photodegradation was monitored by means of measuring the absorbance of 4-CP at a wavelength of 280 nm. The reaction conditions were similar to those employed for MO, except that the concentration of 4-CP was 16 mg L\(^{-1}\).

### 2.6. Apparatus and measurements

Scanning electron microscopy (SEM) measurements were carried out by using a Hitachi S-4800 system. Energy dispersive X-ray spectroscopy (EDX) was measured with a Horiba EMAX X-act energy dispersive spectroscope that was attached to the Hitachi S-4800 system. X-ray diffraction (XRD) measurements were performed on a PANalytical X’Pert PRO instrument with Cu K\(\alpha\) radiation. JASCO UV-550 and JASCO IR-660 spectrometer were employed for the UV-vis and FT-IR spectral measurements, respectively. The photodegradation of the MO dye was monitored by measuring the real-time UV-vis absorption of MO at 463 nm using a JASCO UV-550 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K\(\alpha\) radiation. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The Raman spectra were recorded on a Renishaw inVia plus Raman microscopy using a 532 nm excitation laser. The low-resolution transmission electron microscopy (LRTEM) and high-resolution transmission electron microscopy (HRTEM) of the nanostructures were obtained with a FEI Tecnai G\(^2\) F20 U-TWIN, which was operated with an accelerating voltage of 200 kV. All the measurements were carried out at room temperature.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of 1D Ag/AgCl and GO-hybridized 1D Ag/AgCl nanospecies

Fig. 1A shows a typical SEM image of the pre-fabricated 1D Ag nanowires. It can be seen that nanowires with an average diameter of ca. 100 nm and with a smooth surface could be obtained. No secondary nanostructures could be observed from the surface of these nanoarchitectures. Experimentally, our Ag/AgCl heterostructures could be facilely manufactured via an oxidation-precipitation method, where the prefabricated 1D Ag nanowires were employed as the template. The corresponding GO-hybridized nanocomposites (Ag/AgCl/GO) could also be produced when an aqueous solution of GO nanosheets was added to the synthesis system prior to the addition of 1D Ag nanowires and HCl aqueous solution. In this process, metallic Ag was oxidized to Ag\(^{+}\) by H\(_2\)O\(_2\), which subsequently combined with chloride ions to form AgCl nanospecies. As shown in Fig. 1B, after the in situ oxidation-chloridization, the obtained nanospecies basically maintain their 1D morphological features. The surface of these 1D nanostructures, however, is no longer smooth but decorated with numerous nanoparticles, suggesting the possible formation of 1D Ag/AgCl nanospecies. On the other hand, when GO nanosheets are involved during the synthesis procedure, the formed nanostructures are enveloped with silk-like nanospecies, as shown in Fig. 1C. The LRTEM and HRTEM images of the as-fabricated nanostructures were also investigated, as shown in Fig. S1. It can be seen that sphere-like nanoparticles with an average diameter of 20–50 nm are loaded on the Ag nanowires. The determined lattice spacing of 2.7 Å of the nanoparticles is in good agreement with the (200) phase of cubic AgCl (JCPDS 31-1238). These results preliminarily suggest the possible formation of GO-hybridized Ag/AgCl nanocomposites, Ag/AgCl/GO.

To validate the generation of Ag/AgCl and Ag/AgCl/GO nanospecies, the components of the obtained 1D nanostructures were investigated by EDX analysis. As shown in Fig. 1D, only silver could be detected from the parent 1D nanowires. After the in situ oxidation-chloridization, besides the signals ascribed to Ag element, those attributed to chlorine, could also be detected (Fig. 1E), suggesting the formation of Ag/AgCl species. In the case of the GO-hybridized nanostructures, besides chlorine and silver elements, carbon and oxygen elements could also be detected distinctly, as shown in Fig. 1F. This result confirms the existence of GO nanospecies in the samples. Moreover, quantitative analysis shows that the atomic ratio between Cl and Ag are both ca. 1 : 5 for Ag/AgCl and Ag/AgCl/GO. This result indicates that ca. 20% metallic Ag species in the parent 1D Ag nanowires are transferred to form AgCl nanoparticles during the oxidation-chloridization process, and thus resulting in the formation of Ag/AgCl heterostructures or Ag/AgCl/GO nanostructures.

The XRD patterns of our nanostructures were also investigated to identify the formation of Ag/AgCl and Ag/AgCl/GO nanoarchitectures. As shown in Fig. 2A, the XRD pattern of the original metallic Ag nanowires displays distinct diffraction peaks (2\(\theta\)) at 38.2°, 44.6°, 64.8°, and 77.9°. These peaks correspond respectively to the (111), (200), (220), and (311) cubic planes of the typical cubic metallic Ag (JCPDS file: 65-2871).\(^{33,36–38}\) When no GO nanosheets are involved during the oxidation-chloridization process, the resultant nanostructures exhibit distinct diffraction peaks (2\(\theta\)) at 38.2°, 44.6°, 64.8°, and 77.9°. These peaks correspond respectively to the (111), (200), (220), and (311) cubic planes of the typical cubic metallic Ag (JCPDS file: 65-2871) and of AgCl (JCPDS 31-1238).\(^{33,36–38}\) On the other hand, when GO nanospecies are involved during the oxidation-precipitation reaction, the obtained nanomaterials display similar XRD patterns. Note that negligible diffraction peaks ascribed to GO nanosheets could be detected in this case. This might be due to the relatively low diffraction intensity of
On the other hand, it might also be a consequence of the existence of the intercalated nanoparticles in the system, which could destroy the regular stack of GO nanosheets. Nevertheless, together with the experimental facts derived from the SEM and EDX analysis (Fig. 1), these results further confirm the formation of 1D Ag/AgCl and Ag/AgCl/GO hybrid nanocomposites.

In order to verify the hybridization of Ag/AgCl and GO in the Ag/AgCl/GO systems, their FT-IR spectra together with that of the bare powdery GO nanosheets were measured, as presented in Fig. 2B. It can be seen that the powdery GO nanospecies display several characteristic bands at 1730, 1630, 1429, and 1222 cm$^{-1}$, which could be ascribed to \( \text{CO} \) carbonyl stretching, vibrations of the adsorbed water molecules and skeletal vibrations of un-oxidized graphitic domains, O–H deformation vibration, and C–OH stretching, respectively. In the case of Ag/AgCl/GO, the \( \text{CO} \) carbonyl stretching band manifests itself at ca. 1708 cm$^{-1}$, which exhibits a ca. 22 cm$^{-1}$ shift to low wavenumber compared with that of the bare powdery GO nanosheets. Generally, the carboxylic acid group itself is monitored for shifts in the carbonyl band to verify the bonding or capping of the nanoparticles.

For visible-light-driven photocatalysts, it is required that they could exhibit absorptions in the visible region. Fig. 3 shows the typical UV-visible spectra of the as-synthesized 1D metallic Ag nanowires, Ag/AgCl heterostructures, and Ag/AgCl/GO nanostructures. It can be seen that all the samples display a broad absorption band around 400–500 nm, corresponding to the transition of Ag nanoparticles.
absorption band maximum around 415 nm, which is accompanied by a tail absorption between 500 and 800 nm. Similar spectra profiles of Ag nanowires were reported by others. The distinct absorption peak around 415 nm is essentially attributed to the existence of metallic Ag species in the systems, which could arouse surface plasmon resonance (SPR) absorptions. These results indicate that our nanostructures might have potential applications as visible-light-energized photocatalysts for the photodegradation of organic pollutants.

3.2. Photocatalytic performance of the 1D nanostructures for the photodegradation of organic pollutants under visible-light irradiation

On the basis of the experimental facts deduced from the SEM images, XRD pattern, EDX analysis and the UV-vis spectra of the samples, it can be seen that metallic Ag and AgCl nanospecies exist in our fabricated 1D nanomaterials. It thus could be proposed that they might be photocatalytically active under visible-light irradiations. To verify this, photocatalytic performance of these 1D nanostructures for the photodegradation of MO pollutants under visible-light irradiations were carried out. Practically, the catalytic performance of the parent plain Ag nanowires, commercially available P25-TiO2, and the spherical Ag/AgCl-based nanostructures previously fabricated via a water/oil microemulsion system were also explored for comparison. Experimentally, a dark adsorption was carried out for 30 min prior to the visible-light irradiations to achieve an equilibrium adsorption state. As shown in Fig. S2, compared with the bare Ag nanowires, commercial P25-TiO2, 1D Ag/AgCl heterostructures, Ag/AgCl nanospheres, the GO-hybridized nanocomposites exhibit a higher adsorptive capacity for MO molecules. This could be attributed to the hybridization of GO species in these systems, since it has been proven that GO could facilitate the adsorption of pollutant molecules, owing to the non-covalent intermolecular π–π interactions between the pollutant molecules and GO nanosheets.

Fig. A shows the photocatalytic activities of our photocatalysts under visible-light irradiation. It can be seen that when the parent bare 1D Ag nanowires and the commercially available P25-TiO2 are used as the referenced photocatalysts, no more than 6% and 8% MO molecules, respectively, are decomposed within 40 min. This indicates that these two materials have less efficient photocatalytic activity. In contrast, when our present 1D Ag/AgCl nanostructures are employed as photocatalyst, ca. 70% MO molecules are photodecomposed under similar experimental conditions. Importantly, when the 1D Ag/AgCl/GO heterostructures are used as the photocatalysts, about 92% MO pollutants are decomposed within 40 min. It thus can be seen that the photocatalytic performance of our 1D Ag/AgCl nanomaterials could be further enhanced by ca. 22% via the hybridization of GO nanosheets. At the same time, as shown in Fig. 4A, respectively 64% and 88% MO molecules are photodecomposed under similar experimental conditions when the previously fabricated spherical Ag/AgCl and Ag/AgCl/GO nanostructures are used as the catalysts. These data are distinctly smaller than those of corresponding 1D Ag/AgCl and 1D Ag/AgCl/GO nanostructures, indicating that our present 1D Ag/AgCl-based GO-hybridized nanostructures could be used as efficient visible-light-driven plasmonic photocatalysts for the photodegradation of MO pollutant.

As plotted in Fig. 4B, there is a nice linear correlation between ln(C/C0) and the reaction time (t). This indicates that the decomposition reaction of MO molecules photocatalyzed by our Ag/AgCl-based catalysts follows the first-order kinetics:

\[
-\frac{dC}{dt} = kC
\]

where C is concentration of the MO molecules, t is reaction time, and k is the rate constant. It can be seen that the rate constants of the 1D Ag/AgCl and Ag/AgCl/GO heterostructures are determined to be 0.029 min\(^{-1}\) and 0.046 min\(^{-1}\), respectively, which are distinctly higher than those of the corresponding spherical Ag/AgCl (0.026 min\(^{-1}\)) and Ag/AgCl/GO (0.037 min\(^{-1}\)) nanospecies. These results further confirm that compared with their spherical counterparts, our present 1D Ag/AgCl-based nanoarchitectures are high-performance visible-light-active plasmonic photocatalysts for the elimination of MO.

The photocatalytic performance of our 1D nanostructures was also studied by photodegradation of 4-CP under similar experimental conditions. As shown in Fig. S3, the Ag/AgCl/GO exhibits distinctly enhanced catalytic activity compared with the corresponding Ag/AgCl. This fact further suggests that upon the hybridization of GO, the photocatalytic activity of our Ag/AgCl could indeed be improved.

3.3. An interpretation of the enhanced photocatalytic performance of the 1D Ag/AgCl/GO heterostructures

It is well known that an efficient charge separation/transfer is one of the most crucial factors that affect the photocatalytic performances of a photocatalyst. On one hand, the unique morphological feature of 1D nanomaterials favors directional charge transport and suppresses scattering of the free electrons with a reduced grain boundary, leading to their superior charge transport properties. On the other hand, graphene-based materials could promote electron transfer occurring in the photocatalysts. Consequently, it is reasonable to propose that a reinforced charge separation/transfer might be achieved in our 1D Ag/AgCl/GO heterostructures.

To verify this proposal, XPS and Raman spectra of our samples were examined. As shown in Fig. 5, for the 1D Ag/AgCl
and Ag/AgCl/GO nanostructures, the XPS spectra of the Cl species display a binding energy of Cl 2p3 and Cl 2p1 at about 198.0 and 199.5 eV, respectively. The surface content of Cl is calculated to be ca. 25 mol%. These results further verify the existence of Cl species in our samples after the oxidation-chloridization of the parent 1D Ag nanowires, as suggested by the EDX (Fig. 1) and XRD (Fig. 2) spectra described in the above paragraphs.

In the cases of the parent 1D Ag nanowires and Ag/AgCl nanowires, two bands at ca. 368.2 and 374.2 eV, ascribed to Ag 3d3/2 and Ag 3d5/2 binding energies, respectively, are observed. For the parent 1D Ag nanowires, these two bands are attributed to Ag0 species. However, in the case of Ag/AgCl nanoostructures, these bands could be further deconvoluted into two peaks, respectively, at 367.5, 368.4 eV and 373.5, 374.4 eV. These at 367.5 and 373.5 eV could be attributed to the Ag+ of AgCl, while those at 368.4 and 374.4 eV could be ascribed to the metallic Ag0. The calculated surface mole ratio between the metallic Ag0 and Ag+ is ca. 4 : 1. In the cases of the 1D Ag/AgCl/GO nanocomposites, the Ag 3d3/2 and Ag 3d5/2 peaks shift to higher binding energies to 368.2 and 374.3 eV, respectively. The deconvolution of these two bands gives peaks at 368.2, 369.1 eV and 374.3, 375.1 eV, respectively. Those at 368.2 and 374.3 eV could be assigned to the Ag+ of AgCl, while those at 369.1 and 375.1 eV could be designated to the metallic Ag0 species, all of which display ca. 0.7 eV shift to higher binding energy compared with those of the corresponding Ag/AgCl nanospecies. These results primarily suggest that the 1D Ag/AgCl species in our Ag/AgCl/GO nanocomposites serve as electron-donor upon hybridization with GO nanosheets. Similar to the Ag/AgCl species, the calculated surface mole ratio between the metallic Ag0 and Ag+ in the GO-based hybrid nanocomposites is also ca. 4 : 1.

Generally, it has been demonstrated that the G-band of GO nanosheets in the Raman spectrum is shifted to lower frequencies (softening) when they are hybridized with an electron-donor component, and to higher frequency (stiffening) when they form composites with an electron-acceptor component. To confirm the above-mentioned proposals derived from the XPS investigations, the Raman spectra of our Ag/AgCl/GO hybrid nanostructures together with that of powder GO nanosheets were measured. As shown in Fig. 6, a G-band at ca. 1599 cm−1, which is a typical Raman feature of GO nanosheets, could be observed from the original powdery GO species. In contrast, the G-band shifts by 12 cm−1 to a lower frequency at 1587 cm−1, in the case of the Ag/AgCl/GO nanocomposites. Accompanied by the information deduced from the above-discussed XPS spectra, this present result further verifies the occurrence of charge transfer between Ag/AgCl and GO in our GO-based hybrid nanocomposites, where the 1D Ag/AgCl and GO species work as electron-donor and electron-acceptor components, respectively.

Moreover, it is interesting that the intensity of the Raman spectrum of Ag/AgCl/GO is significantly enhanced by approximately 8.8 times compared with that of the original powdery GO nanosheets. This could be due to the existence of metallic Ag species in the system, which could arouse a surface-enhanced Raman scattering (SERS) effect. The distinct enhancement in the Raman spectra could be ascribed to the surface plasmon resonance field induced by Ag species in Ag/AgCl/GO hybrid nanocomposites. Accompanied by the information deduced from the FT-IR shown in Fig. 2B, this present result further confirms the successful hybridization of Ag/AgCl and GO nanosheets, wherein the Ag species could greatly influence the charge separation in our plasmonic photocatalytic system.

On basis of the above-described experimental facts and analysis, and by considering referenced data reported by others, we could propose an interpretation to account for the observed enhanced photocatalytic performance of the 1D Ag/AgCl/GO heterostructures, as illustrated in Scheme 1. Upon illumination by visible-light, the incident photons could be efficiently absorbed by the 1D Ag/AgCl nanowires in terms of their SPR excitation. The absorbed photon would subsequently be separated into an electron and a hole such that the electron is transferred to the surface of the Ag species and then to the GO nanosheets farthest away from the Ag/AgCl interface. It is mostly like that the electrons are transferred from Ag to GO, this could be due to the existence of an energy band offset between Ag and GO. At the same time, the photogenerated hole is transferred to the surface of the AgCl nanoparticles, which are located on the surface of the 1D Ag nanowires. On one hand, these photogenerated electrons could be trapped by the oxygen dissolved in the reaction system to form superoxide anions (∙O2−) and other reactive oxygen species. On the other hand, the hole would be transferred to the AgCl surface, arousing the oxidation of Cl− ions and accordingly producing Cl2 atoms, which mainly work as reactive radical species for the oxidation of organic pollutant molecules, after which the Cl− ions are formed again.
Due to their reduced grain boundary, nanoarchitectures featuring a 1D morphological character could intrinsically suppress the scattering of free electrons, and thus provide a directional pathway for the transport of photogenerated electrons. This facilitates the separation of charges, resulting in improved catalytic activity.\textsuperscript{15–20} On the other hand, as suggested by our XPS spectra (Fig. 5) and Raman spectra (Fig. 6), the 1D Ag/AgCl nanostructures and GO nanosheets serve as electron-donor and electron-acceptor, respectively, in the Ag/AgCl/GO hybrid nanocomposites. As a result, the electrons originally photogenerated on the 1D Ag nanowires could migrate into GO nanosheets through a percolation process\textsuperscript{45–48} during the photocatalytic performance. This could further promote the charge separation/transfer, and thus suppress the recombination of electron–hole pairs, additionally enhancing the photocatalytic performance.\textsuperscript{20,48,62}

Accordingly, it can be seen that the cooperative or synergistic effects brought out by the intrinsic morphological feature of the 1D nanostructures and by the advantages of GO nanosheets contribute much to the resultant improved photocatalytic performance of the 1D Ag/AgCl/GO nanocomposites. On the other hand, it can be seen from the dark adsorption experiment (Fig. S2 and S3†) that our GO-hybridized 1D Ag/AgCl displayed a much more adsorptive capacity to MO molecules through non-covalent \( \pi - \pi \) intermolecular interactions.\textsuperscript{48,50,62} This factor might also contribute partially to the enhanced photocatalytic activity of our GO-involved catalysts.

4. Conclusions

In conclusion, we herein have reported that 1D Ag/AgCl nanostructures and the corresponding GO hybridized nanocomposites, Ag/AgCl/GO, could be facilely synthesized via an \textit{in situ} oxidation-chloridization method, where Ag nanowires work as a template. It has been disclosed that the obtained 1D nanospecies could be employed as high-performance visible-light-driven plasmonic photocatalysts for the photodegradation of MO pollutants. Compared with the parent bare 1D Ag nanowires, commercially available P25-TiO\(_2\) and the spherical Ag/AgCl-based nanostructures, our 1D Ag nanowires decorated with AgCl nanoparticles could exhibit much higher photocatalytic performance, wherein it has been found that the photocatalytic activity of our 1D Ag/AgCl nanostructures could be further enhanced upon the hybridization of GO nanosheets. Our experimental facts suggest that the cooperative or synergistic effects between the intrinsic morphological feature of the 1D nanostructures, which facilitates an efficient directional electron transport and suppresses the scattering of free electrons, and the advantages brought out by GO nanosheets, which favors a nice adsorption of organic pollutant molecules and an efficient charge separation, conjointly contribute to the resultant enhanced photocatalytic performance. In terms of the 1D Ag/AgCl/GO nanospecies, our investigation might initiate new and more varied opportunities for the development of visible-light-energized high-performance plasmonic photocatalysts for the degradation of organic pollutants.

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Notes and references
