Metal Oxide Nanoparticle Mediated Enhanced Raman Scattering and Its Use in Direct Monitoring of Interfacial Chemical Reactions

Li Li,† Tanya Hutter,‡ Alexander S. Finnemore,† Fu Min Huang,† Jeremy J. Baumberg,† Stephen R. Elliott,‡ Ullrich Steiner,† and Sumeet Mahajan*,†

†Department of Physics, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, U.K.
‡Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

Supporting Information

ABSTRACT: Metal oxide nanoparticles (MONPs) have widespread usage across many disciplines, but monitoring molecular processes at their surfaces in situ has not been possible. Here we demonstrate that MONPs give highly enhanced (x10⁴) Raman scattering signals from molecules at the interface permitting direct monitoring of their reactions, when placed on top of flat metallic surfaces. Experiments with different metal oxide materials and molecules indicate that the enhancement is generic and operates at the single nanoparticle level. Simulations confirm that the amplification is principally electromagnetic and is a result of optical modulation of the underlying plasmonic metallic surface by MONPs, which act as scattering antennae and couple light into the confined region sandwiched by the underlying surface. Because of additional functionalities of metal oxides as magnetic, photoelectrochemical and catalytic materials, enhanced Raman scattering mediated by MONPs opens up significant opportunities in fundamental science, allowing direct tracking and understanding of application-specific transformations at such interfaces. We show a first example by monitoring the MONP-assisted photocatalytic decomposition reaction of an organic dye by individual nanoparticles.

KEYWORDS: Metal oxide, plasmons, surface-enhanced Raman scattering, photocatalysis, interface

Transition-metal oxides, due to the strong correlations of their d electrons, give rise to a wide variety of phenomena such as magnetism, ionic conduction, metal–insulator transitions, multiferroicity, and superconductivity. As a result, they have an extensive range of applications that include fuel cells, batteries, catalysts, sensors, and microelectronics. Despite the resulting importance of molecular bonding and surface reactivity, their utilization in plasmonic applications has been prevented by the tuning of their localized surface plasmon resonance (LSPR) into the infrared. Surface-enhanced Raman scattering (SERS) is a popular plasmonic application utilizing ultraviolet (UV), visible (VIS), or near-infrared (NIR) excitation, which overcomes the extremely small scattering cross section (~10⁻⁵⁰ cm² per molecule) in conventional Raman scattering to yield a technique that offers noninvasive and nondestructive fingerprint characterization with extensive applications in chemical and biological sensing. The amplification in SERS stems primarily from the electromagnetic (EM) enhancement (up to 10¹⁴) obtained by excitation of SPR. This is accompanied by typically smaller and system-dependent chemical enhancement as a result of formation of charge-transfer complexes, limiting its widespread application to interfaces.

In this work, we demonstrate that Raman scattering can be greatly amplified just by placing metal oxide nanoparticles (MONPs) on flat metallic surfaces. In order to differentiate this approach from the various metallic NP (or NP array) based SERS strategies, we christen it metal oxide nanoparticle-enhanced Raman scattering (MONERS). Although its construction is analogous, it is unlike systems where the enhancements are due to coupling between the LSPR of the metallic NP and the propagating surface plasmon polaritons of the underlying metallic substrate or the modification of LSPR modes of the plasmonic NP by a dielectric substrate. In this case the MONPs are nonplasmonic and do not have a LSPR in the wavelength range studied. Further, our method is generic and applicable to a variety of MONPs fabricated from materials such as Fe₂O₄, TiO₂, WO₃, and ZnO. Advantages of using MONPs in comparison to metallic NPs are that they are abundant, less expensive, easily modified, biologically compatible, and most importantly bring additional functionalities to the system. For example, Fe₂O₃ NPs have been widely used in magnetically assisted bioseparations, controlled drug delivery, and magnetic resonance imaging, while TiO₂ NPs are widely used in nanoformulations such as sun creams and are of great utility in photocatalysis.

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interest for applications in dye-sensitized solar cells, catalysis, and biosensors. Probing enhanced Raman scattering signals by utilizing MONERS therefore opens up significant opportunities in a variety of fields involving metal oxide materials and their interfaces. We demonstrate this by directly monitoring an interfacial chemical reaction and show an exemplar application utilizing the advantages of a MONERS system by tracking the photocatalytic decomposition of an organic dye mediated by TiO₂ NPs.

To demonstrate MONERS, we coated a monolayer of 4,4’-diaminobenzenesulfonic acid (dithiol) on flat Au substrates, and the respective NPs were then allowed to adsorb onto the monolayer, as illustrated schematically in Figure 1a. At the outset, we investigated Fe₃O₄ NPs (single Fe₃O₄ NPs; average diameter 254 ± 71 nm). The MONERS effect is generated at the single-particle level; to show this, the concentration of suspensions and the adsorption time were controlled such that the Fe₃O₄ NPs were well separated from each other (Figure 1c). Figures 1d and 1e show respectively an SEM image and a MONERS image of a single Fe₃O₄ NP on a dithiol-functionalized Au surface obtained by excitation with a 532 nm laser. The MONERS image is reconstructed by using the integrated intensities of the 1581 and 1628 cm⁻¹ peaks of the dithiol molecule.

Table 1. Average Experimental EFs for Various NP–Dithiol–Au Systems

<table>
<thead>
<tr>
<th>NPs</th>
<th>EF × 10⁵ (532 nm)</th>
<th>EF × 10⁵ (633 nm)</th>
<th>n (633 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₄ (520 nm)</td>
<td>7.3 ± 2.7</td>
<td>17 ± 14</td>
<td>2.35±1</td>
</tr>
<tr>
<td>Fe₂O₄ (22 nm)</td>
<td>3.9 ± 2.7</td>
<td>9.7 ± 7.6</td>
<td>2.35±1</td>
</tr>
<tr>
<td>TiO₂–rutile</td>
<td>4.2 ± 3.2</td>
<td>23 ± 15</td>
<td>2.49±2</td>
</tr>
<tr>
<td>WO₃</td>
<td>7.7 ± 5.9</td>
<td>4.5 ± 5.2</td>
<td>2.10±3</td>
</tr>
<tr>
<td>ZnO</td>
<td>4.3 ± 5.3</td>
<td>2.5 ± 3.6</td>
<td>1.99±4</td>
</tr>
<tr>
<td>100 nm AuNP</td>
<td>150 ± 160</td>
<td>6400 ± 5200</td>
<td></td>
</tr>
</tbody>
</table>

Data were collected from 30–50 different NP spots. The 8b band (1581 cm⁻¹) of the dithiol is used for calculating the EF values. The refractive indices have been taken from the literature. Standard deviation is indicated in brackets.

Figure 1. (a) Schematic of a MONP on a functionalized Au surface and (b) schematic of a functionalized MONP brought onto a bare Au surface. (c) A representative SEM image of well-separated Fe₃O₄ NPs. (d) An SEM image of an Fe₃O₄ NP and (e) a MONERS image of an Fe₃O₄ NP on a dithiol-functionalized Au surface obtained by excitation with a 532 nm laser. The MONERS image is reconstructed by using the integrated intensities of the 1581 and 1628 cm⁻¹ peaks of the dithiol molecule.

To explore the universality of the MONERS effect, we carried out experiments with a variety of MONPs (Table 1) in addition to the single Fe₂O₄ (sFe₂O₄) NPs mentioned above, each possessing a different crystalline structure (Figure S3), band gap, and refractive index (Table S1). MONERS spectra collected from different MONPs with the dithiol molecules on the surface are shown in Figure 2 (obtained with 532 nm laser excitation) and Figure S4 (obtained with 633 nm laser excitation), respectively. It is evident that all of these display different EFs. This was again surprising because some of these MONPs were irregularly shaped, and a few of them formed agglomerates (typically 100–400 nm; see Figure S5). In the case of cFe₂O₄, WO₃, and ZnO even though the particles used were clusters composed of small NPs, remarkably large MONERS signals were still observed from molecules on the Au surface. Strong MONERS signals were also observed with TiO₂-rutile NPs as well as TiO₂-anatase and the commercially available TiO₂-P25 (Degussa) NPs (data not shown). In all the MONERS spectra shown in Figure 2, four distinct vibrational modes of dithiol are clearly observed, at 1078 cm⁻¹ (ring mode-7a), 1186 cm⁻¹ (ring mode-9a), 1581 cm⁻¹ (ring mode-8b), and 1628 cm⁻¹ (ring mode-103).
and 1628 cm$^{-1}$ ($\nu(C-C)$).$^{26}$ In addition to the vibrational modes of dithiol, some bands are also observed below 900 cm$^{-1}$. These are characteristic of the MONP powders used and are attributed to various phonon modes of the metal oxides, as also confirmed by the bulk Raman spectra collected from the corresponding MONP powders (Figure S6).

The enhancements obtained in the MONERS system were typically 3–4 orders of magnitude compared to corresponding normal Raman measurements (Table 1). These are comparable to or higher than what has been achieved from nanostructured transition metals themselves,$^{27,28}$ for which reported enhancement values range between 10 and 10$^5$. The reported enhancements obtained for the transition metals, Fe ($\times$1942)$^{29}$ and Zn ($\times$221),$^{30}$ are lower than the enhancements with MONERS. This is due to the higher absorption (interband transitions) in the VIS and NIR regions in transition metals compared to the transition-metal oxides investigated here.

Although the enhancements are lower than in an analogous AuNP-on-Au system (Table 1 and Figures S7 and S8),$^{17,18}$ they are sufficiently intense to give high signal-to-noise ratios in MONERS spectra (Figure 2). Signals could be repeatedly recorded from the same NP more than 50 times under conditions below the degradation threshold. Variations in enhancement factors (EFs) across all systems are a manifestation of nanoscale differences in size, shape, and nanoscale geometry. Nevertheless, given the large enhancements, especially compared to transition-metal nanostructures and the multifunctional aspects of metal oxides, MONERS holds enormous potential to study interfacial phenomena.

In order to interpret the observed results in terms of an EM mechanism, finite-element simulations (using the COMSOL Multiphysics software package) were carried out on the Fe$_3$O$_4$ NP on Au system with a gap distance of 1.3 nm, corresponding to the presence of the dithiol molecule.$^{35}$ Because of the weak spectral dependence, we consider enhancements in SERS from the quantity $E^4$, where $E$ denotes $|E_r/E_0|$. Here, $E_r$ refers to the localized scattered field in the $y$-direction midway in the gap between the NP and the Au surface (Figure S9), and $E_0$ refers to the field in the absence of the particle. We used three laser sources ($\lambda_{ex}$) in our experiments at 532, 633, and 785 nm. For a 200 nm Fe$_3$O$_4$ NP, the simulated $|E_r/E_0|^4$ is highest for 633 nm excitation and lowest for 785 nm excitation (Figure S10). This is in good agreement with the observed experimental EFs of the sFe$_3$O$_4$ MONERS system under excitation with different wavelengths (Figure S10). However, the broad MONERS resonance is effective over a much wider wavelength range than traditional plasmonic enhancements.

Figure 3a and Figure S11 display the effect of the NP size on the enhancement over the vis–NIR range in the Fe$_3$O$_4$ NP–Au system under a p-polarized field at angles of incidence of 45° and 0° to the surface normal, respectively. Clearly, the enhancements increase with increasing NP diameter up to 300 nm and then show a slight decrease. This is due to an increase in the scattering cross section with size, which, after a critical size, is radiatively damped due to depolarization effects across the particle.$^{36}$ The simulated scattering cross section at a 45° angle of incidence for 200 nm Fe$_3$O$_4$ NPs is overlaid on the measured dark-field scattering spectra in Figure 3b. There is a good correspondence between them, as the size of the Fe$_3$O$_4$ NPs used here is of the order of 200 nm. The red-shift observed with increasing Fe$_3$O$_4$ NP size is very similar to the well-known size dependence of SPR wavelengths found in all metallic NP systems.$^{17}$

![Figure 3](image)

The simulation results indicate that the observed enhancement in MONERS is indeed due to optical modulation from the local dielectric perturbation by the MONPs. When a Fe$_3$O$_4$ NP is brought very close to the Au surface, the local dielectric constant is altered due to an EM interaction with the continuum of delocalized propagating surface plasmons at the underlying Au surface, leading to a localization of the electric field in the gap formed between the NP and the metal surface. An alternative view considers enhanced scattering by the high-index NP exciting surface plasmons on a flat Au surface, which become confined in the gap, producing a large EM-field enhancement. While coupling to flat metal surfaces is impossible due to the momentum mismatch between the wave vectors of a free-space photon and a plasmon confined to a surface, the high-index NP acts as an antenna coupling light into the gap above the metal surface. Although electric dipoles$^{39}$ and array of dielectric spheres$^{40}$ near a metallic surface as well as the case of a metal NP on a high dielectric substrate$^{19}$ have been predicted to enhance scattering, the coupling and enhancement with a high refractive index MONP on a plasmonic surface are uniquely examined here.

The evidence that indeed excitation of localized surface plasmons of the substrate occurs on bringing MONPs close to the surface is seen in experiments with Pt which is only weakly plasmonic. Only a weak MONERS signal can be detected (data not shown) although thiols form well-organized self-assembled monolayers on Pt similar to Au.$^{41}$ Clearly the size and type of NP material are important in MONERS, but the plasmonic properties of the substrate are significant. A dielectric surface does not give any enhancement; Fe$_3$O$_4$ NPs on glass gave no enhancement and yield an MONERS EF of only $\sim$23 in simulations (Figure S12). Furthermore, by comparing the same vibrational modes of different molecules between Au NP on an Au surface and sFe$_3$O$_4$-based MONERS systems, we find consistent shifts in vibrational frequencies across all bands due to different chemical interactions but little difference in
enhancements for the different peaks (Figure S13). Also, the molecules mixed with MONPs alone do not produce any enhanced Raman signals (Figure S14). Therefore, we rule out a “chemical effect” as a mechanism for the observed enhancements in MONERS.

The highest field enhancement is localized in the gap between the Fe₃O₄ NP and the Au substrate (Figure 3c and Figure S9). As expected, the enhancement effect in MONERS is highly sensitive to the size of the gap (Figures 3d,e). The distribution of E² becomes tighter and rapidly increases as the gap distance is decreased, due to higher field confinement and scales as (d/R)^−1/2. Indeed, higher MONERS enhancements of (1.6 ± 1.7) × 10⁵ were obtained with 4-mercaptobenzoic acid (MBA), where the MBA molecule is approximately half the length of the diethanol molecule. The intense enhancement obtained from MBA, along with many other dyes and molecules (Figure S15), also proves that the enhancements demonstrated here show no selectivity toward probe molecules, unlike the charge-transfer enhancement observed for semiconductor NPs by other researchers.²⁻¹⁴

Significantly, no MONERS signals were obtained with dielectric particles, such as SiO₂ and polystyrene, under our experimental conditions. Simulations reveal that such SiO₂ NP-based MONERS system should indeed give 2 orders of magnitude lower enhancements (Figure S16). This difference between Fe₃O₄ NP and SiO₂ NP systems indicates that the field enhancement is influenced by the refractive index of the NP. The correlation between refractive indices and EFs at 633 nm is evident since the observed MONERS EFs of ZnO and WO₃ are indeed lower than those of TiO₂-rutile and Fe₃O₄ (Table 1). This is consistent with our explanation that a higher refractive index lead to more efficient scattering with better confinement of the scattered field in the gap.

A key property of Fe₃O₄ NPs is that they are ferromagnetic and hence, are used in bioseparations. They assemble into linear chains under the influence of an external magnetic field (Figure 4a). These chains are formed by single layers of Fe₃O₄ NPs. As clearly seen from Raman map images (Figure 4b), the intense signals are localized only to the assembled chains of NPs. Spectra obtained from MONERS chains under excitation from both 532 and 633 nm pump light (Figures 4c,d) show signals from molecules under the chains. This confirms the field enhancement is maximized in the gap between the particles and the surface, rather than between the particles themselves. This is further confirmed in simulations of a dimer on the surface (Figure 4e and Figure S17), which shows that field enhancements between the particles are very small compared to those in the gap between the particle and the substrate. In this case there is a very weak interaction between the MONPs themselves unlike metallic NPs which are plasmon active. Thus, the ferromagnetic property in tandem with the MONERS approach could be used to separate and detect biomolecules in situ in solutions in real time.

Furthermore, MONPs can not only assist in monitoring the molecular transformation at an interface but also actively catalyze it. We monitored the photocatalytic decomposition of methylene blue (MB) by TiO₂ NPs (P25, Degussa) by MONERS (Figure 5). The spectra in Figure 5b clearly show that with increased exposure to UV radiation the characteristic Raman peaks of MB decrease in intensity. However, comparing the different Raman modes in the spectra the molecular mechanism can be elucidated. The 448, 500, 1510, and 1624 cm⁻¹ peaks are assigned to C=N=C, C=S=C, −NH₂ deformation, and C=C ring stretching modes, respectively. Figure 5c shows that the C=N=C bond is cleaved in preference to the C=S=C bond leading to a decrease in the ratio of the corresponding peaks. The simultaneous increase in the peak ratio of the −NH₂ deformation to the benzene ring mode agrees with the above and confirms predominant scission of the central ring vis-a-vis the adjacent benzene moieties, providing direct evidence of the degradation mechanism proposed for MB on TiO₂.⁴³ This clearly demonstrates that MONERS allows direct molecular observation and understanding of chemical processes at a metal oxide interface.

In conclusion, the straightforward origin of the MONERS effect demonstrated here gives enhanced Raman scattering mediated by MONPs which has never been previously attempted. Although the construction is analogous to the
metallic (Au or Ag) NP-on-substrate systems, it is fundamentally different since MONPs are nonplasmonic and the mechanism of coupling light into metallic surfaces is through optical effects induced by the high-index particle. This system can be similarly extended to other NPs with high refractive index, such as silicon and carbon NPs; further experiments are currently in progress. More importantly, this work opens up a significant area for the fundamental and applied study of chemically active surfaces not possible with the all metallic systems. We have shown initial proof-of-concept experiments to exemplify these distinct advantages, using MONPs to directly monitor and elucidate the mechanism of photocatalytic decomposition of MB. MONERS will thus aid understanding many types of interfacial phenomena, including those in catalysis and energy transfer in photovoltaics and photoelectrochemical systems, besides adding novel functionalities to traditional methods of detection and biosensing.

■ ASSOCIATED CONTENT

Supporting Information
Experimental details; Figures S1–S17. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: sm735@cam.ac.uk.

Notes
The authors declare no competing financial interest.

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