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Gold Nanoparticle-loaded Filter paper: A Recyclable "Dip-Catalyst" for Real-Time Reaction Monitoring by Surface Enhanced Raman Scattering

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We report a robust and recyclable "dip-catalyst" based on a gold nanoparticle (Au NP)–loaded filter paper composite, prepared by a simple dip-coating process using concentrated Au NP suspensions in toluene. While acting as catalysts, the composites display excellent surface enhanced Raman scattering (SERS) efficiency, allowing the real-time monitoring of chemical reactions.

Research on metal nanoparticle-based catalysis by multiple industrial applications, as well as by the need of fundamental understanding of nanoscopic behaviour for efficient catalysis.[1-4] Noble metal nanoparticles (NPs) such as gold, palladium and platinum of various morphologies have been extensively investigated for a number of chemical reactions due to their high catalytic activity. Unlike Pd and Pt, gold NPs additionally exhibit rich optical properties in the visible and near infrared regions due to the so-called localized surface plasmon resonances (LSPRs), which arise from the coherent oscillation of conduction band electrons.[5,6] Additionally, the resulting spatial confinement and field enhancement render these NPs suitable for LSPR based optical sensing[7] or surface enhanced Raman scattering (SERS).[8-10] Therefore, LSPRs in Au NPs can be utilized as an additional tool to study catalyzed reactions by monitoring the time-dependent SERS signals of reactants and/or products, while employing the same NPs as catalysts. Colloidal suspensions of Au NPs with different morphologies have recently been investigated in this context.[11-14] However, the use of NPs in solution is usually limited by the need to maintain their colloidal stability, as well as reusability, under typically harsh reaction conditions. One general approach that is often applied to overcome this limitation comprises the integration of NPs within various kinds of solid supports, leading to nanocomposites with greater stability and recyclability.[15-19] Recently, we and other research groups have introduced ordinary filter paper as a suitable support material for NPs as it offers several advantages apart from particles stability, such as low-cost, biodegradability, flexibility and availability.[8, 20-24] Most reports dealing with Au NP-loaded paper substrates were mainly focused on their application as SERS substrates for sensing.[8, 20-24] Most of these approaches involve the attachment of NPs from aqueous dispersions, which limits the NP concentration and therefore requires longer dipping times (typically 48-48 hours) to obtain a sufficiently high loading.[22, 25] Additionally, since the nanoparticle-paper interaction is mainly driven by electrostatics, surface charge further hinders high surface loadings and therefore prevents the nanoparticle self-assembly. These limitations could be overcome if the doping process is promoted from non-aqueous NP dispersions.

We report a fast strategy that can easily be extended to large scale fabrication of robust and recyclable "dip-catalysts" with the ability to exhibit strong SERS activity. The approach is based on simple dip-coating of filter paper in a concentrated Au NP dispersion in toluene. The proposed strategy relies on the capability of filter paper to wick fluids (especially volatile solvents, such as toluene), combined with the strong Van der Waals and hydrophobic interactions between metal particles and cellulose fibers and the spontaneous self-assembly of oleylamine stabilized nanoparticles upon drying.[26] The catalytic activity and recyclability of such a dip catalyst was tested for the conversion of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP), which indicated that the rate constants remained practically constant for up to 20 reaction cycles. Additionally, such

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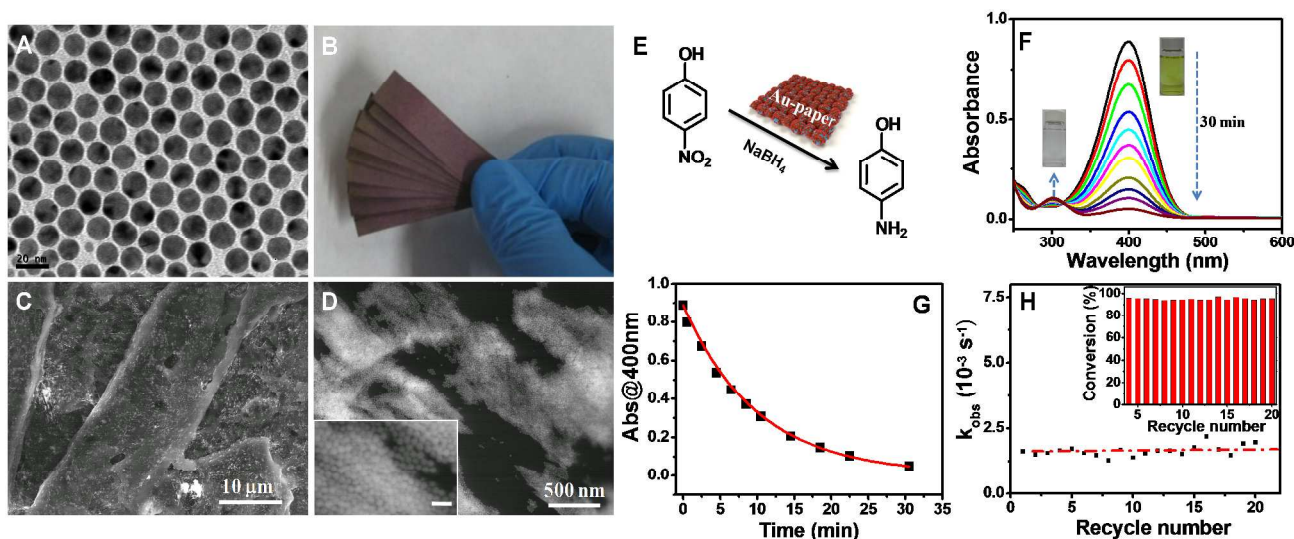*c* Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

Fig.1(A) TEM image of oleylamine-capped Au NPs. (B) Photograph of Au nanoparticle-doped filter papers. (C&D) SEM images of Au NPs on filter paper(inset in D shows the Au NP packing at higher magnification, scale bar represents 50nm).. (E) Reaction scheme for the conversion of 4-NP to 4-AP in the presence of NaBH$_4$ and Au-NPs filter paper. (F) Time evolution of the UV-visible absorption spectra, showing the gradual decrease of 4-nitrophenolate ions (peak at 400 nm) and the gradual production of 4-AP (peak at 300 nm). The yellow colour of solution becomes colourless after complete reaction of 4-NP. (G) Kinetic trace of the absorbance at 400 nm during the reaction of 4-NPand the best fit of a first order equation to the experimental data (red line). (H) Observed first-order rate constants, k$_{obs}$, for 20 consecutive reaction cycles using the same Au NP loaded paper. The inset shows their corresponding catalytic conversion efficiency.

"dip-catalysts" can be used to probe the progress of the reaction on the catalytic surface by monitoring the fingerprint signals of reactants and products through SERS.

In this approach, the first step comprises the preparation of Au NPs in volatile organic solvents in high concentrations. Monodisperse oleylamine-capped Au NPs were prepared in toluene by means of a previously reported method,[27] followed by washing with ethanol and redispersion in 10 mL of toluene. A representative TEM image of the prepared Au NPs is shown in Fig.1A, from which the average particle size was found to be 12 nm (±1 nm). The corresponding UV-visible spectrum of the Au NPs colloid exhibits an extinction maximum at 522 nm (Fig.S1, ESI†). The Au NPs were then impregnated into filter paper by simply dipping the paper into a concentrated colloid in toluene, followed by drying using hair-drier. This process was repeated for 5 times in order to achieve a close packed Au NP assembly. This paper based dip-catalyst is flexible, and its size and shape can be adjusted depending on the requirement. The loading of Au NPs into filter paper is clearly visible to the naked eye through a purple colour, as shown Fig.1B, which originates from the collective LSPR absorption of close-packed Au NPs upon adsorption and assembly on the cellulose fibers of filter paper. It is important to note that the particles do not desorb upon immersion in various solvents, indicating strong adsorption via van der Waals forces and hydrophobic interactions between the particles and the cellulose fibers. The Au NPs impregnated paper was characterized by SEM (Fig.1C and 1D), which reveals assembly of the NPs into small domains (~500 nm to 1 μm, magnified SEM images are shown in Fig.S2, ESI†). The as-prepared Au NP-loaded papers were washed with concentrated

NaBH$_4$ solution to remove oleylamine from the surface of particles and facilitate access of the reactant molecules to the metal surface.[28] SEM images taken before and after washing confirm that the particle morphology and their organization on the filter paper were not affected (Fig.S3, ESI†).

An ideal catalyst should exhibit high catalytic activity, excellent stability, recyclability, operation simplicity and ability to generate fingerprint signals of reactants, products and intermediates to monitor the reaction progress.[29] The catalytic activity and recyclability of Au NP-loaded filter paper was tested as "dip-catalyst" for the conversion of 4-nitrophenol (4-NP)into 4-aminophenol (4-AP) (Fig.1E**)**. This reaction can be typically monitored by UV-visible spectroscopy, since nitrophenolate ions and 4-AP display absorption bands centred at 400 nm and 300 nm, respectively (Fig.1F). Immersion of the dip-catalyst into the reaction medium leads to a gradual decrease of the nitrophenolate ions band along with the gradual increase of the intensity of the 4-AP band, which indicates the catalytic conversion of 4-NP to 4-AP (Fig.1F).Complete conversion was achieved within 30 min, as reflected by the loss of colour in the solution. The large excess of NaBH$_4$with respect to 4-NP allows us to treat the kinetics of the catalytic process as a pseudo-first order reaction. Fig.1G shows the reaction kinetics through a plot of the absorption intensity at 400 nm *vs.* reaction time, as well as a fit with a first order rate equation that yields a calculated rate constant of 1.7×10^{-3}s^{-1}. In order to check the reusability of the "dip-catalyst", the same catalytic substrate was used for 20 consecutive reactions and it was found that the rate constant and catalytic efficiency did not vary throughout all 20 reaction cycles, indicating excellent stability and recyclability (Fig.1H).
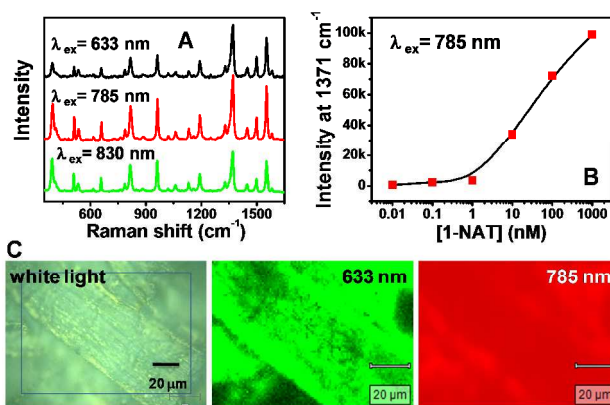
Fig.2(A)SERS spectra of 1-NAT on Au NP-loaded paper at three different excitation wavelengths (633, 785, 830 nm). (B) Plot of concentration of 1-NAT*vs*SERS intensity of the 1371 cm⁻¹ band. (C) Optical microscopy image of paper fiber at which the Raman mapping was performed and Raman intensity maps at 1371 cm⁻¹ with excitation laser wavelengths of 633 and 785nm.

In addition to the catalytic properties of Au NP-loaded paper, we have further explored its performance in SERS, which we intended to use for monitoring chemical reactions taking place on their surface. We used 1-napthalenethiol (1-NAT) as a standard Raman active probe molecule. Fig. 2A shows the SERS spectra of 1-NAT obtained with three excitation laser wavelengths, 633, 785 and 830 nm, which show the typical vibrational pattern of 1-NAT,including peaks for C–S stretching (392 cm-1), C–H bending (1195 cm-1), ring stretching (1371, 1500, and 1553 cm⁻¹), ring breathing (818 and 964 cm⁻¹), and ring deformation (514, 536, 660, and 792 cm⁻¹). Interestingly, the Au NP-loaded substrates exhibit good SERS activity with all three excitation wavelengths, which is probably due to extensive surface plasmon coupling between densely packed Au NPs on the paper substrate.[8, 9, 20] A detection limit of 0.1 nM was determined for the 785 nm excitation laser line. (Fig.S4, ESI†). The plot of concentration vs. Raman scattering intensity shows a monotonic increase of SERS signals with concentration of 1-NAT, as shown in Fig. 2B. Additionally, SERS mapping was performed over an extended area (~100 μm x 100 μm, step size of 1 μm) for two laser lines (633 and 785 nm). The optical image and the SERS maps (for the peak at 1371 cm⁻¹) in Fig. 2C show a nearly uniform SERS intensity on the fiber surface, with a slightly higher intensity at the edges, likely due to the addition of signals from bottom fibers. Overall, the SERS results clearly indicate that the Au NP-loaded paper substrate exhibits SERS activity with a wide range of excitation lasers and homogeneous signals, rendering it an excellent SERS substrate for practical applications. As compared with recent reports of highly efficient SERS substrates prepared by dipping paper in aqueous solutions of NPs for 24-40 hours,[21, 25]the present substrate can be prepared in large areas within short time by a simple dipping process.

So far we have demonstrated that Au NP-loaded filter paper exhibits excellent SERS activity together with efficient catalytic activity and recyclability, so the next step is to analyze
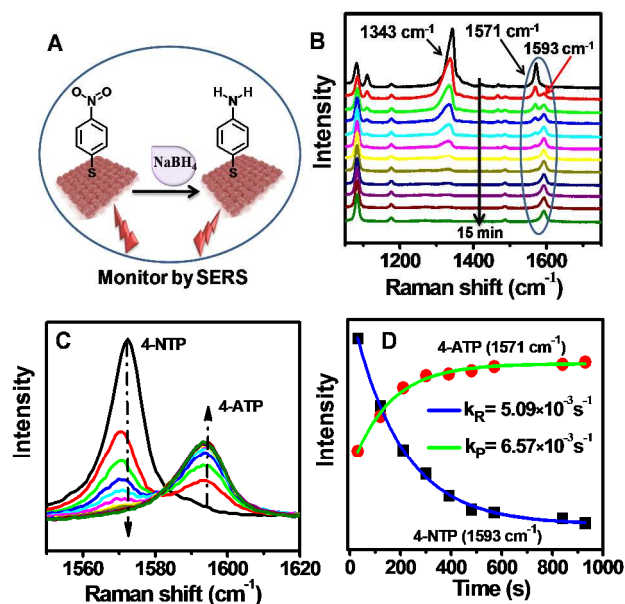

Fig.3 (A) Schematic illustration of 4-NTP conversion to 4-ATP on the Au NPs-loaded paper surface and probing the progress by SERS. (B&C) Time dependent SERSspectra of 4-NTP conversion. (D) Kinetic trace of the SERS intensities at 1571 cm⁻¹ (4-NTP)and at 1590 cm⁻¹ (4-ATP). The lines represent the best fit of a first order equation to the experimental data.

if these substrates could be used as catalytic SERS platform for real-time monitoring of chemical reactions that take place on the catalytic surface. To facilitate the study, the conversion of 4-nitrothiophenol (4-NTP) into 4-aminothiophenol (4-ATP) was selected as a model reaction in which the thiol groups in the molecule drive the chemisorption of the molecule on the surface of Au NPs that are adsorbed on the filter paper (see Fig. 3A). First, Au NP-loaded filter paper was soaked in a 4-NTPsolution and the adsorption was characterized by SERS (Fig.S5, ESI†). A detection sensitivity for 4-NTPwas found to be 1 nM (for the 785 nm excitation laser line) and the substrate exhibited excellent homogeneity with 10-15% intensity variation over large areas (Fig.S5, ESI†). Finally, the reduction of 4-NTP into 4-ATP was followed by SERS. Fig.3B displays the time dependent SERS spectra of4- NTP functionalized substrate that was recorded continuously for 15 min after adding a NaBH₄ solution(0.1 M). The SERS spectra of 4-NTP exhibit three main characteristic peaks at 1080, 1343 and1571 cm⁻¹, attributed to C–S stretching, O–N=O symmetric stretching and phenyl ring stretching modes, respectively. As the reaction progresses, the peak intensities at 1343 and 1571 cm⁻¹ were observed to gradually decrease while a new peak shows up at 1593 cm⁻¹, corresponding to the phenyl ring of 4-ATP. Fig. 3C clearly shows that the conversion of 4-NTP into 4-ATP was completed within 15 min, as indicated by the complete disappearance of the peak at 1343 cm⁻¹ and the emergence of the peak at 1593 cm⁻¹.

The nitro to amine reduction can be considered as a two step consecutive reaction, either by a direct route via a hydroxylamine intermediate (see Scheme S1) or via a condensation route (through the formation of an azo compound).[30] For instance, it

has been reported that the 4-NTP to 4-ATP conversion could proceed through dimerization and formation of 4,4'-dimercapto-azobenzene (4,4'-DMAB) when the reaction was catalyzed by metal nanoparticles in colloidal solutions.[12-14] In our experiments we did not observe the formation of intermediates such as hydroxylamine or dimercaptoazo benzene as showed in the SERS spectra (Figure 3B), suggesting that in the present case the intermediate reacts very fast and therefore it cannot be detected.

Additionally, the time evolution of the Raman scattering modes of 4-NTP (1343 cm^{-1}) and 4-ATP (1593 cm^{-1}) allowed us to quantify the fraction of reactant (4-NTP) and product (4-ATP)at various reaction times. The reaction kinetics were treated as a pseudo-first order reaction (NaBH$_4$concentration is in large excess with respect to 4-NTP) and we applied the steady-state approximation (since the evidences show that the intermediate reacts very fast).The steady-state approximation requires that the reaction rate of the second step will be larger than the first one, and therefore the formation of the intermediate should be the rate determining step. The fit of the exponential decrease of the 1343 cm^{-1} band to a first order equation resulted in a rate constant for the first step (k_R) of 5.09 10^{-3} s^{-1}. Therefore, the product formation, i.e. the band located at 1593 cm^{-1}, should show an exponential increase with time, also with a first order rate constant (k_P) similar to that for the first step (k_R). The good agreement between both reaction rates (5.09×10^{-3} s^{-1}vs.6.57×10^{-3} s^{-1} for k_R and k_P, respectively) indeed demonstrate the previous assumption.

In conclusion, we report a new type of bifunctional "dip-catalyst" based on Au NPs loaded on filter paper, which can be prepared by simple dip-coating of paper in concentrated Au NPs dispersions in toluene. The catalyst shows excellent recyclability with unchanged catalytic efficiency for more than 20 consecutive cycles. In addition, the catalytic substrate exhibits high SERS efficiencies that allow us to monitor the progress of reactions occurring on catalytic surfaces through the detection of SERS signals of reactants and products. The present work is expected to open new ways of application of multifunctional NP-loaded paper, not only for heterogeneous catalysis but also for monitoring reaction progress by SERS.

Notes and references

1. D. Y. Wu, L. B. Zhao, X. M. Liu, R. Huang, Y. F. Huang, B. Ren and Z. Q. Tian, *Chem Commun*, 2011, 47, 2520-2522.
2. E. M. van Schrojenstein Lantman, T. Deckert-Gaudig, A. J. G. Mank, V. Deckert and B. M. Weckhuysen, *Nat. Nanotech.*, 2012, 7, 583-586.
3. C. Deraedt, L. Salmon, S. Gatard, R. Ciganda, R. Hernandez, J. Ruiz and D. Astruc, *Chem. Commun.*, 2014, 50, 14194-14196.
4. J. Zhang, D. Han, H. Zhang, M. Chaker, Y. Zhao and D. Ma, *Chem. Commun.*, 2012, 48, 11510-11512.
5. L. M. Liz-Marzán, *Langmuir*, 2005, 22, 32-41.
6. K. A. Willets and R. P. Van Duyne, *Annual Review of Physical Chemistry*, 2007, 58, 267-297.
7. B. Sepúlveda, P. C. Angelomé, L. M. Lechuga and L. M. Liz-Marzán, *Nano Today*, 2009, 4, 244-251.
8. L. Polavarapu and L. M. Liz-Marzan, *Phys. Chem. Chem. Phys.*, 2013, 15, 5288-5300.
9. L. Polavarapu, J. Perez-Juste, Q.-H. Xu and L. M. Liz-Marzan, *J. Mater. Chem. C*, 2014, 2, 7460-7476.
10. R. A. Alvarez-Puebla, R. Contreras-Caceres, I. Pastoriza-Santos, J. Perez-Juste and L. M. Liz-Marzan, *Angew. Chem., Int. Ed.*, 2009, 48, 138-143.
11. Z. Y. Bao, D. Y. Lei, R. B. Jiang, X. Liu, J. Y. Dai, J. F. Wang, H. L. W. Chan and Y. H. Tsang, *Nanoscale*, 2014, 6, 9063-9070.
12. W. Xie, B. Walkenfort and S. Schlucker, *J. Am. Chem. Soc.*, 2013, 135, 1657-1660.
13. X. Q. Ren, E. Z. Tan, X. F. Lang, T. T. You, L. Jiang, H. Y. Zhang, P. G. Yin and L. Guo, *Phys. Chem. Chem. Phys.*, 2013, 15, 14196-14201.
14. H. Jing, Q. F. Zhang, N. Large, C. M. Yu, D. A. Blom, P. Nordlander and H. Wang, *Nano Lett.*, 2014, 14, 3674-3682.
15. Z. Jin, M. Xiao, Z. Bao, P. Wang and J. Wang, *Angew. Chem., Int. Ed.*, 2012, 51, 6406-6410.
16. E. Hariprasad and T. P. Radhakrishnan, *Chem. Eur. J.*, 2010, 16, 14378-14384.
17. J. He, W. Ji, L. Yao, Y. Wang, B. Khezri, R. D. Webster and H. Chen, *Adv. Mater.*, 2014, 26, 4151-4155.
18. X. M. Gu, W. Qi, X. Z. Xu, Z. H. Sun, L. Y. Zhang, W. Liu, X. L. Pan and D. S. Su, *Nanoscale*, 2014, 6, 6609-6616.
19. L. Shang, T. Bian, B. Zhang, D. Zhang, L.-Z. Wu, C.-H. Tung, Y. Yin and T. Zhang, *Angew. Chem., Int. Ed.*, 2014, 53, 250-254.
20. L. Polavarapu, A. L. Porta, S. M. Novikov, M. Coronado-Puchau and L. M. Liz-Marzán, *Small*, 2014, 10, 3065-3071.
21. C. H. Lee, L. M. Tian and S. Singamaneni, *ACS Appl. Mater. Interf.*, 2010, 2, 3429-3435.
22. Y. H. Ngo, D. Li, G. P. Simon and G. Garnier, *Langmuir*, 2012, 28, 8782-8790.
23. W. W. Yu and I. M. White, *Analyst*, 2013, 138, 1020-1025.
24. L.-L. Qu, D.-W. Li, J.-Q. Xue, W.-L. Zhai, J. S. Fossey and Y.-T. Long, *Lab on a Chip*, 2012, 12, 876-881.
25. J. A. Webb, J. Aufrecht, C. Hungerford and R. Bardhan, *J. Mater. Chem. C*, 2014, DOI: 10.1039/c4tc01634c.
26. A. Sánchez-Iglesias, M. Grzelczak, J. Pérez-Juste and L. M. Liz-Marzán, *Angew. Chem., Int. Ed.*, 2010, 49, 9985-9989.
27. H. Hiramatsu and F. E. Osterloh, *Chem. Mater.*, 2004, 16, 2509-2511.
28. S. M. Ansar, F. S. Ameer, W. Hu, S. Zou, C. U. Pittman and D. Zhang, *Nano Lett.*, 2013, 13, 1226-1229.
29. K. N. Heck, B. G. Janesko, G. E. Scuseria, N. J. Halas and M. S. Wong, *ACS Catal.*, 2013, 3, 2430-2435.
30. H.-U. Blaser, *Science*, 2006, 313, 312-313.

TOC graphic

While acting as catalysts, Au NP-loaded paper composites display excellent surface enhanced Raman scattering (SERS) efficiency, allowing the real-time monitoring of chemical reactions.