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Two-Tiered Designer Architecture for Matrix-Free LDI-TOF MS of a Self-Assembled Monolayer

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Introduction

•In the recent past lot of interest over self assembled monolayer (SAM) because of its various application like chemical reactivity and functionality of organic and biological molecules.

•SAMs are a versatile class of chemical structures on the order of 1–3 nm, which present a well-defined interface for both nanosystem and biochemical applications.

•Recent advances introduce electrostatic layer-by-layer (LBL) strategy for the fabrication of SAM and it leads to the construction of several elegant functional porous systems.

•Nanocomposite films with both the stability and surface chemistry of gold and nanoporosity and surface area of an organic–inorganic hybrid has its own advantage.

•In this report the utilization of a two-tiered nanostructure, comprising an underlying porous film of a polyelectrolyte/SiO_2 NP and a top layer of gold NP, for the successful characterization of a SAM with matrix-free LDI-TOF MS.

Why matrix free?

Matrix-assisted LDI-TOF MS (MALDI-TOF MS) analysis of SAMs has allowed one to gain insight into chemical reactivity and functionality of organic and biological molecules.

The quality of SAM characterization (e.g., variation of signal intensity from spot to spot) on flat gold substrates could be compromised by the inhomogeneous, complicated crystallization process of typically adopted organic matrixes. In addition, the inclusion of a matrix in the sample preparation could lead to lower spatial resolution, reduced sensitivity, and interference in the analysis of small molecules.

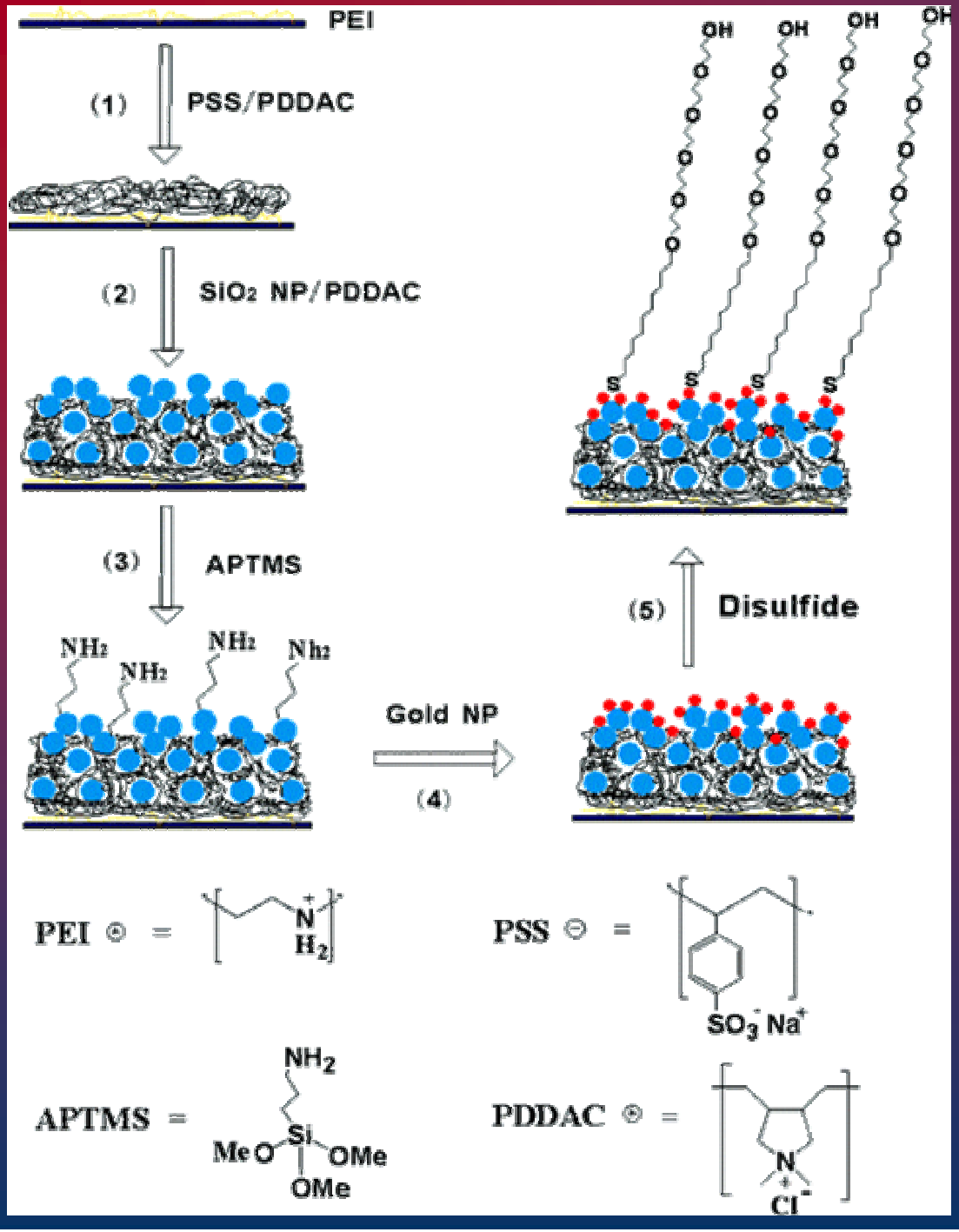
The goal of the current study is to develop a matrix-free LDI-TOF MS platform for potential application in the chemical and biological sample.

The approach described herein utilizes well-defined, nanometer-scale-controlled assembly process to furnish a SAM-anchoring surface and could therefore provide solution to the difficult problem.

Experimental Section

Reagents

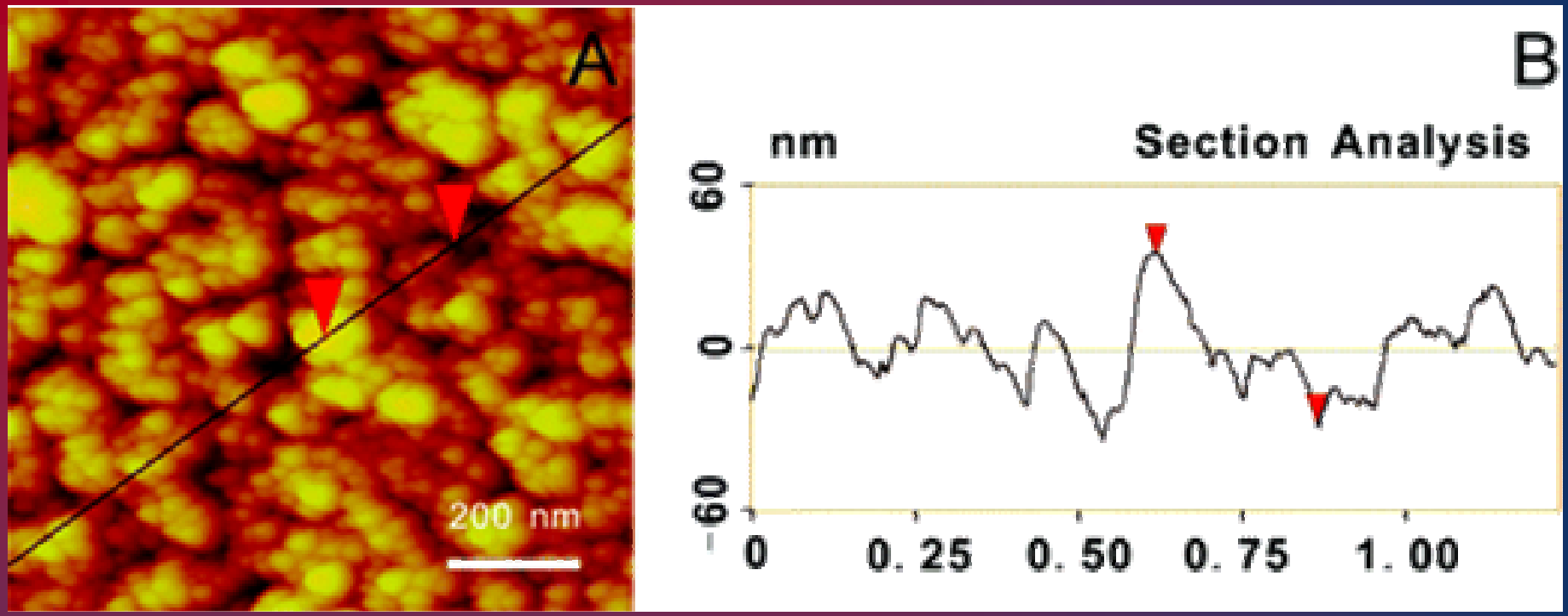
- Penta(ethylene glycol)undecane disulfide
- Aqueous solutions of 0.05 wt% SiO_2 NPs
- Poly(ethylene imine) (PEI)
- Poly(styrene sulfonate) (PSS),
- Poly(diallyldimethylammonium chloride) (PDDAC)
- 3-(aminopropyl)trimethoxysilane (APTMS)
- Au NPs



Schematic representation of the process used to obtain the organic monolayer on a two-tiered hybrid nanostructure that was prepared by LBL assembly (structures not drawn to scale)

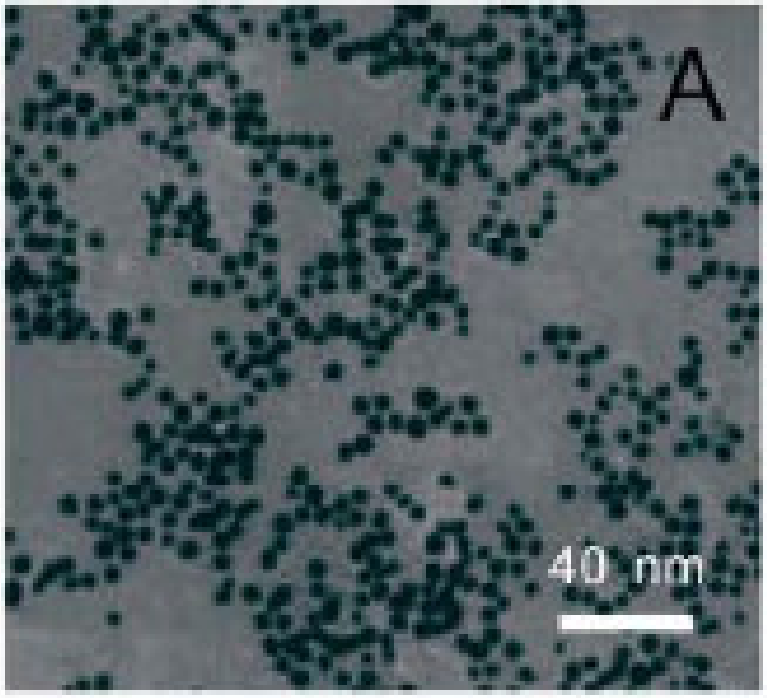
Characterization

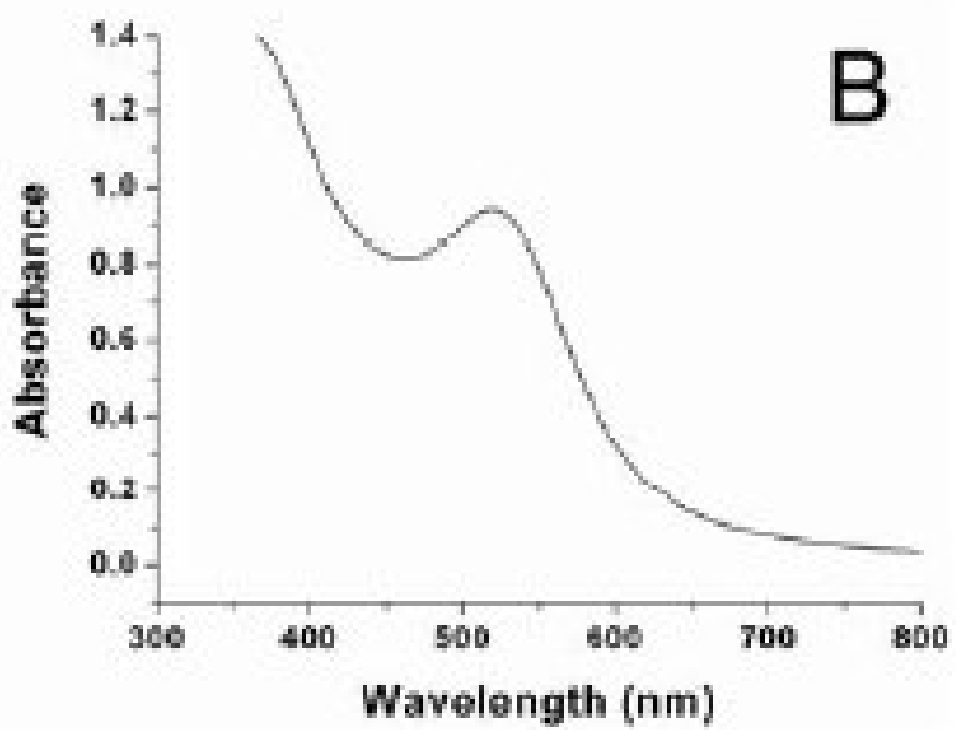
- Atomic force microscopy (AFM)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- X-ray photoelectron energy spectrometry (XPS)
- Inductively coupled plasma atomic emission spectrometer (ICP-AES)
- Mass spectrometry (MS)



(A) Tapping-mode AFM image of a polyelectrolyte/SiO_2 NP film on a Si wafer.

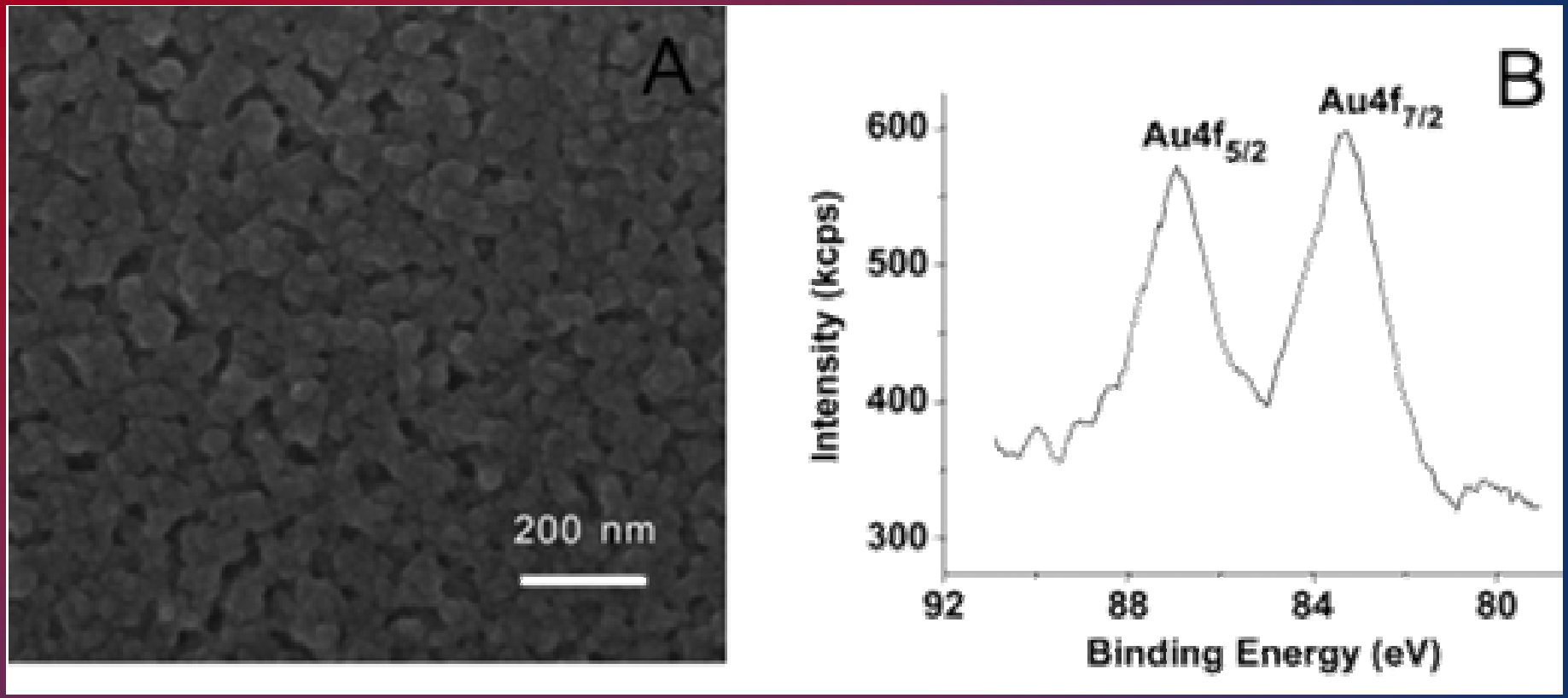
(B) AFM cross section of the line shown in image (A).





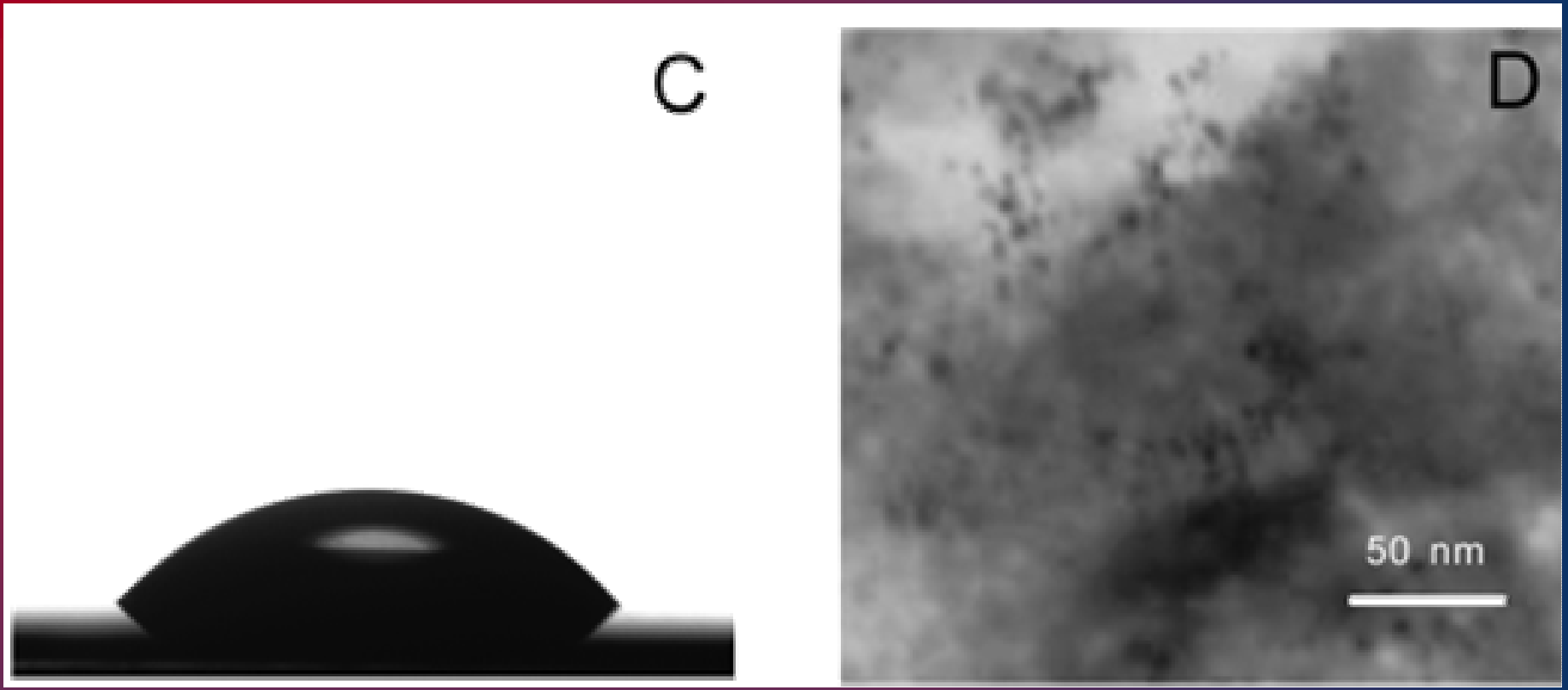
(A)TEM image

(B)UV-vis absorption spectrum of the as-prepared gold NP (~6 nm) solution.



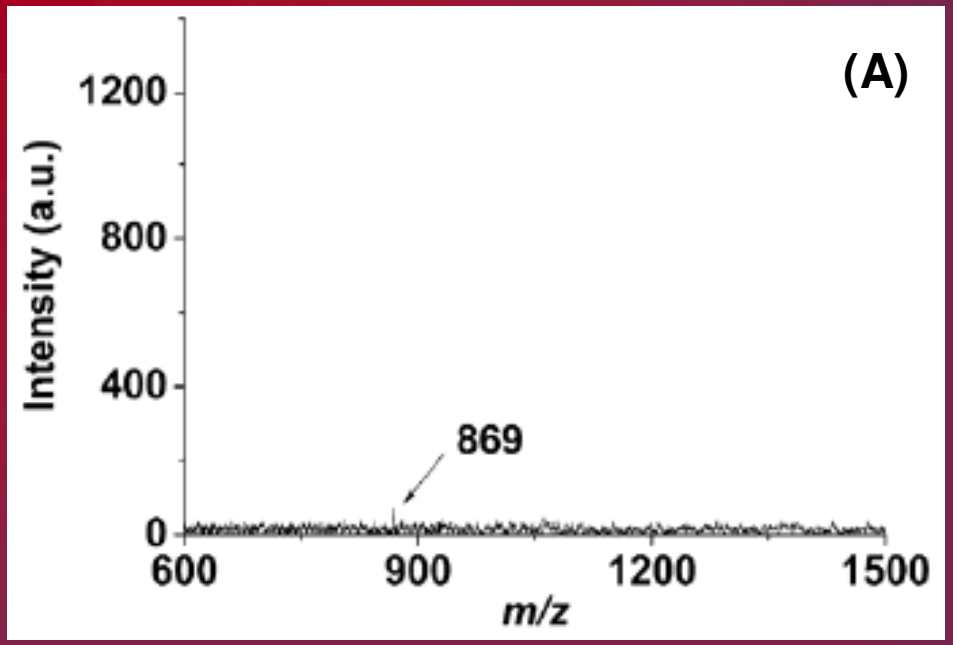
(A) SEM photograph of a two-tiered hybrid nanostructure fabricated by the deposition of one-layer gold NPs on a polyelectrolyte/SiO_2 NP film.

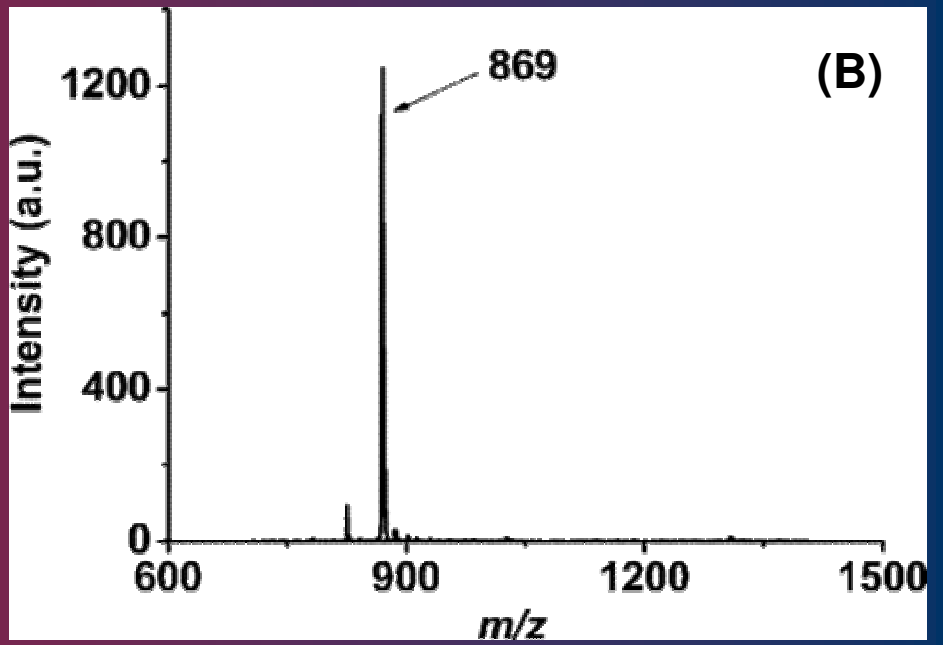
(B) XPS spectrum of a two-tiered hybrid structure.



(C) Shape of the water droplet on the surface of a one-layer gold-NP-coated porous film.

(D) TEM image taken from a flake of a three-layer gold-NP-coated nanocomposite film. The dark-contrasted particles seen at the rim of the flake have a diameter of 4–7 nm.





(A) LDI-TOF mass spectrum of a SAM of molecule **1**, $[HO(CH_2CH_2O)_5(CH_2)_{11}S]_2$, on a porous structure-free gold NP-modified silicon wafer.

(B) LDI-TOF mass spectrum of a SAM of molecule **1**, $[HO(CH_2CH_2O)_5(CH_2)_{11}S]_2$, on a porous structure-free gold NP-modified silicon wafer.

Conclusions

•A two-tiered hybrid nanostructure that combines the unique porous structure offered by a polyelectrolyte/SiO_2 NP multilayer film with gold NPs has been successfully fabricated.

•The hybrid nanostructure has proven useful in the characterization of the SAM structure with LDI-TOF MS in a matrix-free format.

•This platform is widely applicable to a variety of heteroatom-containing molecules, as long as the adsorption of those species on gold NPs results in well-defined monolayer structures.