Ultrasmall Plasmonic Nanoparticles Decorated Hierarchical Mesoporous TiO₂ as an Efficient Photocatalyst for Photocatalytic Degradation of Textile Dyes

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ABSTRACT: Hierarchical mesoporous TiO₂ was synthesized via a solvothermal technique. The sonochemical method was adopted to decorate plasmonic nanoparticles (NPs) (Ag, Au) on the pores of mesoporous TiO₂. The crystallinity, structure, and morphology were determined to understand the physicochemical nature of the nanocomposites. The catalytic efficiency of the plasmonic nanocatalysts was tested for the azo dyes (congo red, methyl orange, acid orange 10, and remazol red) under solar and visible light irradiations. The generation of hydroxyl radicals was also studied using terephthalic acid as a probe molecule. An attempt was made to understand the influence of size, work function and Fermi level of the metal NPs toward the efficiency of the photocatalyst. The efficiency of the nanocomposites was found to be in the order of P25 < mesoporous TiO₂ < mesoporous Ag−TiO₂ < mesoporous Au−TiO₂ nanospheres under both direct solar light and visible light irradiation. The results indicated that the adsorption of dye, anatase phase, and surface plasmon resonance of NPs favored the effective degradation of dyes in aqueous solution. Further, the efficiency of the catalyst was also tested for xanthene (rose bengal), rhodamine (rhodamine B, rhodamine 6G), and thiazine (methylene blue) dyes. Both TiO₂ and NPs (Ag & Au) possess a huge potential as an eco-friendly photocatalyst for wastewater treatment.

INTRODUCTION

The removal of toxic pollutants from industrial effluents is a great concern to environment and ecosystem. The synthetic origin and aromatic nature of azo dyes make them stable, nonbiodegradable, and potential carcinogenic agents. Discharge of these dyes even in microquantities leads to acute problems to aquatic life thereby causing major health hazards to humans via the food chain. Semiconductor-based photocatalytic materials have attracted immense attention for cleaning up the textile effluents as wastewater treatment is cost-effective and eco-friendly. Several semiconductor materials are tested under ideal conditions to diminish the toxicity of industrial effluents, of which TiO₂ has been found to be a most active photocatalyst because of its band gap (3.2 eV), redox potential, photocatalytic stability, nontoxicity, and chemical and biological inertness. Recently, size- and shape-controlled TiO₂ nanomaterials show better catalytic efficiency compared with their bulk counterparts. In addition, in the nanoscale regime, the probability of photogenerated electron–hole pair recombination will drastically reduce owing to their fast arrival at the surface of the reaction sites. Because the surface of the photocatalyst plays a vital role in the case of photocatalytic reaction; these TiO₂ nanostructures made of small nanoparticles (NPs) arranged in a hierarchical nanostructured fashion possess a mesoporous structure in nature, thus higher surface area is highly sought. However, wide band gap energy forbidden their photo absorptivity of visible light in our solar spectrum and moreover rapid recombination of the photo excitons limits their photocatalytic efficiency. Hence, to enhance the photocatalytic efficiency of...
TiO$_2$, the evolution of hybrid nanostructures made up of noble metal NPs decorated TiO$_2$ is a promising choice. The noble metal NPs present on the surface of TiO$_2$ acts as the electron scavenging centers to increase the electron−hole pair separation thereby paving way for visible light absorption through their surface plasmon resonance (SPR), consequently enhancing the photocatalytic efficiency toward the degradation of the textile effluent. Noble-metal NPs, especially, Ag and Au show strong and broad SPR absorption in the visible region of the solar spectrum and the frequency of the SPR band directly proportional to their size and shape. Further, the size of the metal NPs plays a major role in the photocatalytic degradation of environmental pollutants. When the metal NP is less than 5 nm, the Fermi level energy of TiO$_2$ shifts to the more negative direction and the resultant potential difference between the conduction band of TiO$_2$ and the Fermi level of the metal NPs is reduced. As a result, number of excitons accumulates on the surface of the deposited metal NPs; hence, the apparent Fermi level of metal NPs will come close to the bottom of the conduction band of TiO$_2$. As a result, the Fermi level equilibrium takes place quickly and rapid electron transfer from TiO$_2$ to metal NPs occurs for improved photo-oxidation reaction by the photoexcited hole. In addition, the surface modification of TiO$_2$ with size- and shape-controlled Au and/or Ag NPs will make them an efficient visible-light-driven plasmonic photocatalyst. Recently, uniformly dispersed 2−5 nm sized Au NPs were successfully synthesized through the sonochemical method with effects generated by acoustic cavitation. In this context, it is essential to develop new plasmonic photocatalysts with the high specific surface area, low charge recombination, and good stability with superior photocatalytic activity. In this work, an architectural design was implemented to study the possible effects of the small size of Au and Ag NPs decorated on mesoporous TiO$_2$ nanospheres (NSPs). The photocatalytic performance was studied toward the degradations of azo dyes; congo red (CR), methyl orange (MO), remazol red (RR), and acid orange 10 (AO10) in water under the illumination of direct solar light. Efforts were made to quantify the HO$^-$ radical generation during the photocatalytic degradation. The photocatalytic efficiency was also tested for other classes of dyes such as xanthene [rose bengal (RB)], rhodamine [Rh B, rhodamine 6G (Rh 6G)], and thiazine [methylene blue (MB)] dyes.

## RESULTS AND DISCUSSION

### Characterization of Photocatalysts.

Ultrasonic wave with high frequency plays a vital role in the synthesis of ultrasmall noble-metal NPs decorated mesoporous TiO$_2$. The ultrasonic waves interact with the water molecules to generate the acoustic cavitation. Because acoustic cavitation makes high temperature ($\sim$5000 K) and pressure ($\sim$500 atm) during...
the bubble collapse, it helps the reduction of Au\(^{3+}\) and Ag\(^{+}\) to ultrasmall Au\(^{0}\) and Ag\(^{0}\) NPs with the assistance of NaBH\(_4\) to deposit over the surface of mesoporous TiO\(_2\).\(^{13a,b,14}\) Moreover, during sonication, both the mesoporous TiO\(_2\) network and metal NPs underwent configuration changes in association with crystallization and particle coarsening.\(^5\) The two phases were confined with each other, leading to the formation of well-dispersed ultra-small metal NPs within the titania network, with spherical morphology and narrow pore size distribution, preserving the mesoporous structure.\(^{14}\) The size and shape of the ultrasmall metal (Au and Ag) NPs were identified through their SPR. In general, SPR is a key factor to identify the shape, size, and dielectric constants of both the metal NPs and the surrounding material.\(^{10c,e,11a,13a,b,14}\) Figure 1A shows the characteristic SPR bands maxima at 510 and 408 nm for Au and Ag NPs, respectively.\(^{5,11d,4,}\) This is the primary confirmation for the presence of ultrasmall Au and Ag NPs deposited over the mesoporous TiO\(_2\). Furthermore, the band gap of the photocatalyst was calculated using the Tauc plot (Figure 1A inset). The band gap of metal-decorated mesoporous TiO\(_2\) (\(E_g \text{Au–TiO}_2 = 2.99 \text{ eV}, E_g \text{Ag–TiO}_2 = 3.05 \text{ eV}\)) is found to be lower than the band gap of the bare TiO\(_2\) (\(E_g \text{TiO}_2 = 3.16 \text{ eV}\)) from the view of the spectra, it is clearly evident that the presence of anatase phase in the prepared mesoporous TiO\(_2\) (Figure 1C inset). These observed shifts might be due to the effect of metal (Au and Ag) NPs.\(^{7,18}\) When metals are deposited on TiO\(_2\), two effects may occur on the vibrational properties of the TiO\(_2\). First, the volume contraction might occur within TiO\(_2\) NPs because of the addition of metal (Au and Ag) NPs. The specific interaction that occurs on the surface of TiO\(_2\) while adding metal NPs causes size-induced radial pressure and disrupts the interatomic distances within TiO\(_2\) NPs which lead to increase of force constant.\(^{13b}\) As in vibrational transitions, the wavenumber varies approximately in proportion to \(k^{1/2}\), where \(k\) is the force constant. As a result, the Raman bands shift toward a higher wavenumber because of the increasing force constants while adding metal NPs incorporated within the pores of TiO\(_2\) NPs.\(^{17,18}\) Second, the contraction effect induces a decrease in the vibrational amplitude of the nearest neighbor bonds because of the increase of the mean square relative displacement, which can be interpreted as a measure of the static disorder and thermal vibrational disorder of the material. This decrease in vibrational amplitude with the addition of metal NPs affects the intensity of the Raman bands. Hence, the variation in the Raman spectra of mesoporous TiO\(_2\) NPs after the addition of metal NPs is due to the force constants and vibrational amplitudes of the nearest neighbor.\(^{17,18}\) N\(_2\) adsorption–desorption isotherm (Figure 1D) for the mesoporous TiO\(_2\) displayed a typical type-IV isotherm curve with H4 hysteresis loop (according to IUPAC classification), the characteristic of mesoporous solids, in the range of 0.6–0.85 P/P\(_0\) indicates the presence of mesoporosity suggesting that the adsorption is due to the mesopore channels and not by the interstitial voids between aggregates among the assembled NPs.\(^{14}\) Brunauer–Emmett–Teller (BET) measurement for TiO\(_2\) showed the specific surface area as 173 m\(^2\)/g. The Barrett–Joyner–Halenda method analysis revealed the pore size and pore volume of TiO\(_2\) as 3.3 nm and 0.30 cm\(^3\)/g, respectively. Interestingly, the pore size distribution shows that the formed pores are very narrow in size (10–30 Å). This further confirms the existence of well-ordered nature of the mesoporous.\(^{35,40}\) The physicochemical properties of the mesoporous plasmonic TiO\(_2\) catalysts are tabulated in Table 1. The surface area, pore

Table 1. BET Surface Area, Pore Volume, and Pore Size of the Photocatalysts

| photo catalyst       | surface area (m\(^2\)/g\(^{-1}\)) | pore volume (cm\(^3\)/g\(^{-1}\)) | pore size (nm) |
|----------------------|-----------------------------------|----------------------------------|----------------|
| TiO\(_2\) NSPs       | 173                               | 0.30                             | 3.3            |
| Ag–TiO\(_2\) NSPs    | 160                               | 0.25                             | 3.0            |
| Au–TiO\(_2\) NSPs    | 153                               | 0.24                             | 3.0            |

DOI: 10.1021/acsomega.8b01322
ACS Omega 2018, 3, 9834–9845
volume, and pore size of the photocatalyst slightly decreased after the addition of noble metal NPs which further confirms the metal deposited on the pore void of the TiO₂ NSPs. Even though, the small reduction of the surface area due to the presence of Au or Ag NPs is more beneficial for the photocatalytic reactions as they facilitate good interfacial charge transfer between target organic pollutant and TiO₂ NPs.

The morphology of the as-synthesized mesoporous TiO₂ is analyzed using SEM. It is evident from the micrograph that ~5–6 nm sized TiO₂ NPs aggregates as clusters resulting in the formation of mesoporous spherical shape (Supporting Information Figure S1 inset). The high-resolution transmission electron microscopy (HRTEM) analysis further examined the morphology, particle size and shape of the synthesized mesoporous TiO₂ and metal (Au and Ag) NPs decorated mesoporous TiO₂. Figure 2A shows that relatively rough surfaces with the ~250 nm sized hierarchical NSPs were formed by the aggregation of the TiO₂ NPs and the average size of the primary particles is found to be around ~5 nm which is in good agreement with the XRD analysis. The HRTEM (Figure 2A inset) clearly shows the crystalline anatase phase of the particle is evident from the clear lattice fringes with an inter-planar spacing of d = 0.35 nm which is observed at higher magnifications. The selected area electron diffraction (SAED) pattern (Figure 2B) shows a sequence of broad diffraction rings, that matches well with the (101), (004), (200), and (211) reflections of the anatase phase. The observed diffractions along with the uniform intensity of the rings support explicitly a random orientation of highly crystalline mesoporous TiO₂. The chemical composition is confirmed by energy dispersive X-ray analysis (EDAX) analysis as shown in Figure S1. The HRTEM images show that the dark spherical spots clearly indicate that the uniform size and shaped ultrasmall Ag (~3 nm) (Figure 2C) and Au (~2 nm) (Figure 2E) NPs are highly dispersed on mesoporous TiO₂ matrix. The 2D lattice fringe of the HRTEM images (Figure 2C,E insets) is found to be 0.24 and 0.20 nm for Ag and Au NPs, respectively. Corresponding SAED patterns (Figure 2D,F) obtained by directing the incident electron beam perpendicular to one of the square facets of the cube shows that the square spot array is indexed to four clear diffraction rings that are assignable to planes of the fcc pattern of metals.

The presence of metals is further confirmed by EDAX analysis (Figure S2). The highly crystalline, ultrasmall metal NPs decorated anatase phase TiO₂ with mesoporous structure is expected to enhance the efficiency of the photocatalyst for the degradation of textile dyes.

A slight shift was observed while comparing the Ti 2p3/2, and Ti 2p1/2 peaks (Figure 3A) of Au–TiO₂ NSPs (458.82 and 464.71 eV) and Ag–TiO₂ NSPs (458.88 and 464.59 eV) with that of TiO₂ NSPs (458.50 and 464.21 eV) and this suggests that Au NPs or Ag NPs strongly interacted with Ti atom.8h,10b The observed spin–orbit splitting value of ~5.7 eV in all samples suggests that Ti exists in the IV oxidation state (Ti⁴⁺)8h,10a,b. The wide and asymmetric O 1s spectra (Figure 3B) were observed along with a higher binding energy shift in the case of Au–TiO₂ NSPs and Ag–TiO₂ NSPs when compared with bare TiO₂ NSPs. This confirmed the presence of more than one component and the strong binding of Au or Ag NPs on the surface of TiO₂. The Au 4f7/2 and Au 4f5/2 peaks were centered at 82.46 and 86.06 eV in the high-resolution Au 4f X-ray photoelectron spectroscopy (XPS) spectra (Figure 3C).10a,c,11c,d This demonstrates the characteristic of the Au cubic crystal with the spin–orbit splitting value of 3.6 eV. The Ag 3d5/2 and Ag 3d3/2 peaks were located at 367.95 and 373.95 eV which show a spin–orbit splitting value is 6.0 eV and this confirms the metallic silver.10a All these results obtained from the XPS concluded that the metallic state of Au and Ag are present in Au–TiO₂ NSPs and Ag–TiO₂ NSPs, respectively, and the same observation was observed in the XRD and Raman spectra. The charge recombination behavior and the migration efficiency of the as-synthesized samples were determined using the photoluminescence (PL) measurements. The PL spectrum of pure TiO₂ NSPs excited at a wavelength of 325 nm (Figure 3D) exhibits broad bands with high intensity in the 350–600 nm peak region which corresponds to the radiative recombination of self-trapped excitons.19 The drastic decrease in the emission of the broad bands was observed in the PL spectra of Au–TiO₂ and Ag–TiO₂ NSPs. In particular, the emission intensity of Au–TiO₂ NSPs was quenched completely because the presence of Au NSPs effectively trapped the excited electrons and promote into the surface recombination, thus increasing the lifetime of the excitons. These fluorescence behaviors suggest the better photocatalytic activity of Au–TiO₂ NSPs toward the degradation of azo dyes under direct sunlight irradiation.8f

Photocatalytic Degradation Studies. The photocatalytic activity of mesoporous TiO₂ and metal (Au and Ag) decorated mesoporous TiO₂ and Degussa P25 were evaluated for the degradation of textile dyes. Initially, the control experiment (dye + solar light; dye + catalyst) shows no change in the initial absorption intensity of dyes. However, a slight
reduction in the initial absorption was observed due to the adsorption of the dye molecules on the photocatalyst surface. Once the photocatalyst was added in the presence of solar light, the absorption intensity was decreased with respect to time, suggesting that the dyes are gradually degraded in the presence of a photocatalyst under direct solar light irradiation as shown in Figure 4A–D. The photocatalytic degradation of azo dyes ($5 \times 10^{-5}$ M) in the presence of various photocatalysts (0.5 g L$^{-1}$) and the variation of normalized $-\ln C/C_0$ of dye concentration as a function of solar irradiation time gives a straight line (Figure 5A–D). The rate constant ($k'$) for the degradation reaction is calculated
from the slopes of linearized straight lines obtained from the plot of $-\ln \frac{C_t}{C_0}$ versus time is shown in Table 2. The results clearly denoted that the photocatalytic degradation reaction is found to follow “pseudo-first-order kinetics”.$^{3a,b,d,8d-11a,14}$

Further, the percentage of degradation of dye was calculated from the following expression, and their results are given in the Figure S3.

\[
\text{Percentage degradation} = \left(1 - \frac{C_t}{C_0}\right) \times 100
\]

where $C_0$ is the initial concentration of the dye solution, $C_t$ is the concentration remaining after irradiation at the time. The half-life of dye degradation was calculated using the formula $t_{1/2} = \ln 2 / k$ and their results are given in Table S1. Further, the experiments conducted under the same condition using visible light through cut off the UV portion in the solar light are shown in Figure 6A—D. The above results denote that the photocatalytic activities are in the following order: P25 < mesoporous TiO$_2$ < mesoporous Ag–TiO$_2$ < mesoporous Au–TiO$_2$ NSPs under both direct solar light and visible light irradiation. It clearly indicates that the mesoporous anatase TiO$_2$ NSPs show better photocatalytic activity compared with TiO$_2$ Degussa P25 under both direct solar and visible light irradiation. The anatase phase, a continuous framework made up of small particles and mesoporous nature with the high surface area, provides active sites for the adsorption of dyes which paves way for the enhanced photocatalytic reaction through the dye-sensitized mechanism.$^{5b,11e}$ Further, ultrasmall plasmonic metal (Au and Ag) NP-decorated mesoporous TiO$_2$ NSPs exhibited higher photocatalytic activity than the mesoporous TiO$_2$. Upon solar light irradiation, Fermi levels of the ultrasmall Au or Ag NPs and the TiO$_2$ start to equilibrate this electron flow from the conduction band of TiO$_2$ to Au or Ag surface owing to their electron accepting nature. The Fermi level of ultrasmall (∼2 nm) Au or Ag NPs is greatly shifted to more negative potential (Scheme 1), and the resultant interfacial charge-transfer process is greatly enhanced.$^{3a,8h,9,10,11a,c,d,14}$ Therefore, the electron density in the conduction band of TiO$_2$ is reduced which leads to an increase in active holes in the photocatalytic system. Subsequently, the injected electrons are transferred to the ubiquitously present molecular oxygen to form numbers of powerful oxidative radicals resulting in the effective degradation of dyes.$^{3a,8h,9,10,11a,c,d,14}$

Table 2. Rate Constant ($k'$) for the Dye Degradation Reaction in the Presence of Various Photocatalysts under Direct Solar Light and Visible-Light ($\lambda > 395$ nm) Illumination$^a$

| irradiation | photo catalysts | rate constant ($k'$) × 10$^{-4}$ (s$^{-1}$) |
|-------------|-----------------|---------------------------------|
| solar light  | TiO$_2$ P25     | 1.85   2.98  3.16  2.00        |
|             | TiO$_2$ NSPs    | 2.82   3.67  3.83  2.83        |
|             | Ag–TiO$_2$ NSPs| 4.33   6.33  5.83  4.17        |
|             | Au–TiO$_2$ P25  | 7.83   8.83 10.33  6.33        |
|             | TiO$_2$ P25     | 0.66   1.17  1.33  0.67        |
| visible-light ($\lambda > 395$ nm) | TiO$_2$ NSPs | 0.83   1.67  2.05  1.00        |
|             | Ag–TiO$_2$ NSPs| 2.33   3.33  3.91  2.00        |
|             | Au–TiO$_2$ NSPs| 4.00   4.50  5.50  3.16        |

$^a$The photocatalytic system notations CR, MO, RR, and AO10 are congo red, methyl orange, remazol red, and acid orange 10, respectively. [Catalyst] = 0.5 g L$^{-1}$; [azo dye] = 5 × 10$^{-5}$ M.
mesoporous Ag−TiO₂ NSPs. Because the work function of the Au (5.1 eV) effectively scavenge the excitons than that of Ag NPs (4.77 eV), Au NPs prevent the charge carrier recombination leading to greater activity.

The photocatalytic degradation reaction highly depends on the formation of oxidative radicals during the photocatalytic reaction. The photocatalytically generated hydroxyl radicals were identified through the PL technique using terephthalic acid (TA) as a probe molecule. The TA reacts with the formed hydroxyl radical to form 2-hydroxy TA.8e,f,20 The PL intensity of TA changes with respect to the formation of 2-hydroxy TA.20 The control experiments (TA + catalyst; TA + solar light) does not alter the PL intensity of TA. However, the intensity of TA is increased with respect to time in the presence of both catalyst and solar light irradiation because the photocatalytically generated hydroxyl radicals react with TA to form hydroxyl TA. As shown in Figure 7A, the generation of hydroxyl radicals increased incrementally in the presence of mesoporous Au−TiO₂ NSPs under direct solar light irradiation, evidencing for its higher photocatalytic degradation efficiency. Further, the photocatalytically formed 2-hydroxy TA profile of mesoporous TiO₂, Ag−TiO₂, Au−TiO₂ NSPs, and TiO₂ degussa P25 under identical condition are shown in Figure 7B. The concentration of 2-hydroxy TA increased in the following order: mesoporous Au−TiO₂ > Ag−TiO₂ > mesoporous TiO₂ > TiO₂−Degussa P25 which clearly evidence the correlation between the hydroxyl radical generation and photocatalytic degradation of azo dyes. Further, the similar experiments were carried out under visible light irradiation, and the results denoted that the concentration of 2-
hydroxy TA is very low in the case of mesoporous TiO2 and TiO2 Degussa P25 (Figure 7B), owing to their wide band gap which limits the visible light absorption. However, the concentration of 2-hydroxy TA is reasonably high in the presence of mesoporous Au−TiO2 NSPs and comparatively mesoporous Au−TiO2 NSPs show higher PL intensity of 2-hydroxy TA than mesoporous Ag−TiO2 NSPs. The above study indicated that the uniformly distributed ultrasmall plasmonic Au and Ag NPs on the mesoporous TiO2 NSPs increase the visible light absorption as a result, enhancing incident photo-conversion efficiency. The formation of Schottky barriers between the ultrasmall plasmonic metal NPs and mesoporous TiO2 upon irradiation which facilitate to shift of Fermi level to more negative potential leads to increase the lifetime of charge carriers. Therefore, this energy barrier will suppress the recombination reaction between the photogenerated electrons and holes. Thus, the effective transfers of photogenerated electrons occur and participate with surface-adsorbed oxygen to form more numbers of active oxidative species. These active oxidative species are reasonable.
for the effective degradation of dyes. Further, the concentration of 2-hydroxy TA is estimated by using a predetermined calibration curve (Figure 7C and inset), and the results are shown in Figure 7D. The obtained results evidently correlate the amount of photocatalytically generated hydroxyl radicals in the presence of various photocatalysts and their amount of dye degradation. The amount of dye degradation increases with respect to the photocatalytically generated HO•. However, the amount of dye degradation is higher than that of the formed HO• which could be equilibrated with the surface-trapped holes. These results concluded that the surface deposited ultrasmall Au and Ag NPs are responsible for the generation of more numbers of HO• which might be equilibrated with the surface-trapped holes. These two powerful oxidative species are synergistically involved in the photocatalytic degradation of azo dyes.

The degradation of the azo dyes is easy to monitor through their optical intensity as shown in Figure 4A–D. The main characteristic band responsible for the chromophoric group of azo dyes CR, MO, AO10, and remazol red (RR) appear at visible region 497, 487, 484, and 521 nm, respectively. During the degradation process, the characteristic absorbance bands decrease rapidly because of the fragmentation of azo links in the case of azo dyes and aromatic rings. As the time of irradiation extended, the absorbance bands of the dyes get reduced. These results indicate that the first step must be an oxidative process that leads to the cleavage of chromophoric N=N bonds responsible for the decoloration of the azo compounds and further "benzene-like" intermediate are also deconstructed to a certain extent during the photocatalytic reaction. The above discussion was confirmed through total organic carbon (TOC) analysis Figure 8A, which indicates that in the presence of a catalyst, the rate of mineralization of dyes was low when compared with the rate of photocatalytic degradation observed through spectrophotometrically. Generally, complete mineralization of dyes requires an extended irradiation, owing to the fact that its mineralization mandates completion of two different stages: the ring cleavage of dye molecules in the initial photocatalytic degradation stage and subsequent oxidation of the fragments in the latter stage. The mesoporous Au–TiO2 NSPs exhibited above 85% TOC removal within 7 h for all azo dyes under solar light irradiation because of its higher photocatalytic efficiency. The reusability of the TiO2 nanocomposites is depicted in Figure 8B. In all seven cycles, the catalyst showed the equal photocatalytic efficiency. It is henceforth considered as an indirect evidence for the porous structural stability. The reason for the excellent stability is due to the confinement of metal NPs within the pores of TiO2. Eventually, in the eighth cycle, the catalyst activity is dropped nearly to 5% where the structural or morphological changes are assumed to occur. The efficiency of the photocatalysts was also tested for other classes of dyes such as RB, MB, Rh B, and Rh 6G and their degradation kinetics is shown in Figure S4. It has been found that the Au–TiO2 NSP photocatalyst effectively degrades thiazine, xanthenes, and rhodamine moieties. Further, to find out the influence of the tap water on the photocatalytic degradation of azo dyes, similar experiments were done at identical conditions as mention above. Figure S5 shows the % degradation of the dyes in tap water and Milli-Q water in the presence of mesoporous Au–TiO2 NSPs. The results denoted that the percentage of dye degradation in tap water was slightly reduced (~8%) compared with dyes at Milli-Q water, owing to the very small amount of organics, inorganics, and metallic ion species present in tap water which acts as competing species against the dye molecules for the catalytic active sites or for oxidation by the radical species present in solution. Moreover, the position and shape of the characteristic absorption maxima (λmax) of the tested dyes are unaltered during the degradation process; also, ~85% of mineralization was achieved within a 7 h irradiation period. This might be both dyes and its degradation intermediates are decomposed unselectively without generating any long-lived toxic compound. For identification of the toxicity of photocatalytic degradation intermediate products, the eco-toxicological experiment was conducted for the dyes and its degradation intermediates against the luminescent bacteria Vibrio fischeri through a standard protocol. The dyes exhibited moderate toxicity against V. fischeri which was observed from the ~30% inhibition in the luminous of the bacteria; additionally, the % luminescence inhibition increased almost 10–15% of all dyes at 1 h irradiation because of the formation of degradation intermediates of both azo and non-azo dyes. However, % luminescence inhibition are gradually reduced and finally reached to <3 at after 7 h of light irradiation (Figure S6). These results suggest that the formed intermediates are removed with respective irradiation time and these results are support to the above discussion in the mineralization part. Hence, synthesized TiO2 NSPs and modified ultrasmall Au and Ag NPs are found to exhibit efficient photocatalytic activity over textile dyes.

CONCLUSIONS

Solventthermally prepared mesoporous TiO2 NSPs were modified with ultrasmall Au (2 nm) and Ag (4 nm) plasmonic NPs by the sonochemical method. The anatase phase of mesoporous TiO2 NSPs in the size of ~250 nm which is composed of ~5–6 nm sized TiO2 NPs was observed. The band gap of TiO2 was 0.13 and 0.08 eV red-shifted in the case of Au–TiO2 NSPs and Ag–TiO2 NSPs, respectively, which suggested their visible light absorption ability. Drastic reduction in the PL intensity of the Au–TiO2 NSPs and Ag–TiO2 NSPs was the primary confirmation for their reduction in the rate of charge carrier recombination. The photocatalytic results were denoting that the photocatalytic activity toward the degradation of azo dyes indicated the following order: P2S < mesoporous TiO2 < mesoporous Ag–TiO2 < mesoporous Au–TiO2 NSPs under both direct solar light and visible light irradiation. It was clearly indicated that the mesoporous anatase TiO2 NSPs showed better photocatalytic efficiency when compared with TiO2 Degussa P25 under both direct solar and visible light irradiation. The mesoporous Au–TiO2 NSPs showed ~twofold higher catalytic activity compared with mesoporous Ag–TiO2 NSPs. The study about the formation of HO• radical clearly supported the above photocatalytic activity of all of the catalysts. The mesoporous Au–TiO2 NSPs exhibited above 85% of TOC removal within 7 h for all azo dyes under solar light irradiation because of their higher photocatalytic efficiency. Thus, mesoporous Au–TiO2 NSPs is a good choice for quick cleaning of the large volume of industrial wastewater just by exploiting the sunlight.
**EXPERIMENTAL DETAILS**

**Materials.** Titanium isopropoxide (Sigma-Aldrich, USA) was used as a precursor for the preparation of mesoporous NSPs, and titanium dioxide (Degussa P25, Germany, specific surface area of 57 m² g⁻¹) was used as a reference photocatalyst. Silver nitrate and chloroaucoric acid were purchased from Sigma-Aldrich, USA. Sodium borohydride (Loba Chemie), absolute ethanol (Merck, >99.9%), and analytical grade of CR, MO, AO10, RR, RB, MB, Rh B, and Rh 6G were purchased from Sigma-Aldrich, USA, and used as such without further purification. Water purified in a Milli-Q system (Millipore, Bedford, MA, USA) was used for the preparation of solutions.

**Synthesis of Mesoporous TiO₂ NSPs.** Mesoporous TiO₂ was prepared by the simple solvothermal method.¹⁵ A typical synthesis involves dropwise addition of titanium isopropoxide (20 mL) into ultrapure ethanol (100 mL) under constant stirring, 5 mL of double-distilled water was then added drop-by-drop to the suspension and stirred for 30 min under continuous stirring at ambient conditions, and the whole suspension was transferred to a Teflon beaker and kept closed in a stainless steel autoclave and heated at 120 °C for 12 h. The obtained white slurry was washed several times with distilled water, dried at 100 °C for 12 h and calcined at 400 °C for 3 h in a muffle furnace at a ramp rate of 5 °C/min where nanocrystalline mesoporous TiO₂ NSPs were stored for further use.

**Synthesis of Mesoporous Au (or) Ag−TiO₂ NSPs.** The as-synthesized TiO₂ NSPs were used directly as templates for the nucleation and growth of metal NPs (Ag and Au) over their surface. The sonochemical approach has been utilized to encapsulate Au and Ag NPs in the pore channels of mesoporous TiO₂ NSPs where the air entrapped in the mesoporous matrix was selectively removed by sonication and metal species were driven into the pores. In a typical procedure, mesoporous TiO₂ NSPs (1 g) was dispersed ultrasonically in Milli-Q water (100 mL) for 5 min followed by the addition of a metal precursor (40 mg) under sonication for 30 min (pH = 7). NaBH₄ (0.25 mM) previously dissolved in Milli-Q water (10 mL) was added as a reducing agent and kept in a sonication bath for 30 min. The product obtained was washed several times with Milli-Q water, dried at 100 °C for 12 h, and used for further applications.

**Characterization Studies.** Diffuse reflectance spectra (DRS) of the samples were recorded using a Shimadzu UV−vis spectrophotometer (UV-2550) fitted with ISR-2200 DRS accessory. Solid-state PL spectra were recorded in a Shimadzu RF-5301 spectrofluorophotometer. Material-phase analysis was carried out by a powder XRD technique (Rigaku diffractometer, Cu Kα radiation, λ = 1.5406 Å and step size 0.02°). Surface morphology and grain size of the samples were examined using a Quanta 200 field emission gun scanning electron microscope (SEM) and a JEOL JSM-6480LA SEM. The surface area, pore volume, and pore diameter of the samples were measured with the assistance of surface area analyzer (Micromeritics ASAP 2030) which provides the single-point and multipoint BET surface area measurements. The extent of photocatalytic degradation of the target organic pollutants (dyes) was followed spectrophotometrically.

**Evaluation of Photocatalytic Activity.** The photocatalytic activity of the prepared nanocatalysts was studied by assessing the photocatalytic degradation of dyes in the presence of solar radiation (intensity ≈ 85−95 mW/cm²). For the experiments in the visible light, the UV portion of the irradiated light (λ ≤ 395 nm) was obstructed using a UV filter film (Solaronix-Switzerland). The photocatalytic degradation reactions were conducted in a borosilicate glass vessel of 125 mL capacity. An appropriate amount of catalyst was added into 100 mL of aqueous dye solution of desired concentration. To ensure the adsorption equilibrium, the solution containing the photocatalyst was stirred for 45 min in the dark (prior to light irradiation). The concentration of the dyes was measured at this condition from their characteristic absorption maxima (λ_max) of the dyes CR, MO, AO10, RR, RB, MB, Rh B, and Rh 6G are 497, 487, 484, 514, 540, 663, 553, and 525 nm, respectively, the molecular structure of the dyes are given in Figures S7 and S8 and utilized as the initial concentration (C₀) for further kinetic analysis. Around 5 mL of aliquots were withdrawn from the reaction mixture after a certain period of light irradiation. The catalyst present in the aliquot solutions was removed by filtration (0.2 μm polyvinylidene fluoride syringe filter), and the concentration of the dyes in the filtrate was determined through a UV−vis spectrophotometer. The concentration of the dyes obtained after a certain period of irradiation (t) is denoted as Ct. All photocatalytic experiments were carried out at natural pH of the dye solution. The TOC content was examined using a Shimadzu TOC VCPH model TOC analyzer. TOC₀ is the TOC measured after the equilibrium adsorption and the TOC obtained at a certain irradiation time is denoted as TOCt. Triplicate experiments were conducted at optimized conditions and the mean values of the results are presented along with the standard deviations of triplicate experiments.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01322.

EDAX analysis of mesoporous TiO₂ NSPs, Ag−TiO₂, and Au−TiO₂ NSPs; histograms for the percentage of the degradation of dyes in the presence of various photocatalysts under direct solar light irradiation; structure of model degradation pollutants (azo dyes); half-life of dye degradation; and plot of photocatalytic degradation kinetic of non azo dyes and their molecular structures (PDF).

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Notes

The authors declare no competing financial interest.
The authors B.V. and S.A.A.V. acknowledge the Department of Science and Technology (DST), India, for funding National Centre for Catalysis Research (NCCR), Indian Institute of Technology Madras (IITM). The author N.P. gratefully acknowledge the FONDECYT Post-doctoral project no. 3160134, the Government of Chile, Santiago for the financial assistance. The author R.V.M. acknowledges the project CONICYT PIA/APOYO CCTE AFB170007.

ACKNOWLEDGMENTS

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